Equations-of-Motion Method for the Electronic Transitions to Compound (1p-1h)+(2p-2h) States

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The equations-of-motion (EOM) method proposed by Shibuya and McKoy (*Phys. Rev.*, **A2**, 2208 (1970); *J. Chem. Phys.* **58**, 500 (1973)) has been extended to include (2p-2h)-state creation and annihilation operators in the excitation operator $O_\lambda^\dagger$.

The equations-of-motion (EOM) method proposed by Shibuya and McKoy[1)] has been successfully applied to ab initio calculations of the transition energies and oscillator strengths of small molecules like C_2H_4, CO, N_2, C_6H_6, H_2O, and CH_4.[2,3)] The EOM method has the advantage that the equations are set up directly for the electronic transitions, i.e. for the difference between the ground and the excited states, while in the traditional CI method the equation is solved for each of the states separately.

The basic idea of the EOM method is to find an excitation operator $O_\lambda^\dagger$ which creates an excited state $|\lambda\rangle$ by its action on the ground state $|0\rangle$:

$$|\lambda\rangle = O_\lambda^\dagger|0\rangle \qquad (\text{and } O_\lambda|0\rangle = 0). \tag{1}$$

As was shown by Sinanoğlu,[4)] the major part of the closed-shell ground state correlation consists of doubly-excited configurations, i.e. 2p-2h states. Thus, it is natural to construct the $O_\lambda^\dagger$ as a linear combination of 1p-1h creation and annihilation operators. The coefficients of the linear combination are determined in such a way that the excitation operator $O_\lambda^\dagger$ satisfies the equation

$$[H,O_\lambda^\dagger]|0\rangle = \omega_\lambda O_\lambda^\dagger|0\rangle, \tag{2}$$

which takes the same form as the equation of motion for a boson creation operator. In this equation ω_λ is the energy difference between $|0\rangle$ and $|\lambda\rangle$.

The low-lying excited states of molecules are usually well described as the linear combinations of 1p-1h states. However, some of the important valence states of conjugated molecules are essentially of 2p-2h states. The well-known example is the 2^1Ag state of linear polyenes.[5)] For these states, the perturbative treatment proposed earlier[1b)] is not adequate and the whole EOM-Hamiltonian matrix including those elements of 2p-2h states must be diagonalized to give correct solutions of the excitation operator. In the present work, we provide all the matrix elements needed for this type of the EOM calculations. Recently Oddershede and coworkers[6)] have developed the perturbative propagator methods which are essentially equivalent to our perturbative treatment.[1b)] Many references in relation with the propagator methods and the EOM methods are found in a recent review by Oddershede.[7)]

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The EOM for 1p-1h States

In this section, we begin with a summary of the previously developed EOM method for 1p-1h states.[1)] Let us consider the excitation of an electron from the occupied orbital γ to the unoccupied orbital m. The excited electron may take the spin state of α or β. Thus, if the molecule is initially in the closed-shell ground state, its final state may be either singlet (S=0) or triplet (S=1). Therefore, the creation operators of the particle-hole pairs are written[1a)]

$$C_{m\gamma}^\dagger(00) = (2^{-1/2})[c_{m\alpha}^+ c_{\gamma\alpha} + c_{m\beta}^+ c_{\gamma\beta}]$$

$$\left.\begin{aligned} C_{m\gamma}^\dagger(1M) = {} & -c_{m\alpha}^+ c_{\gamma\beta} && (M=+1) \\ & (2^{-1/2})[c_{m\alpha}^+ c_{\gamma\alpha} - c_{m\beta}^+ c_{\gamma\beta}] && (M=0) \\ & c_{m\beta}^+ c_{\gamma\alpha} && (M=-1) \end{aligned}\right\} \tag{3}$$

where $c_{i\alpha}^+$ and $c_{i\alpha}$ are the creation and the annihilation operators of an elcctron in the state of orbital i and spin α, respectively, and they satisfy the anticommutation relations of fermions. Inspecting the structure of the correlated ground state $|0\rangle$ according to Sinanoğlu's many-electron theory,[4)] we have proposed that the excited state $|\lambda\rangle$ of spin-symmetry S, M may be obtained by the action of the excitation operator

$$O^\dagger(\lambda SM) = \sum_{m\gamma} \{Y_{m\gamma}(\lambda S)\, C_{m\gamma}^\dagger(SM) - Z_{m\gamma}(\lambda S)\, C_{m\gamma}(\overline{SM})\} \tag{4}$$

on the ground state $|0\rangle$. In this expression,

$$C_{m\gamma}(\overline{SM}) = (-)^{S+M}\, C_{m\gamma}(S,-M) \tag{5}$$

annihilates the (m, γ) pair and gives a state of spin-symmetry S, M. Note that $C_{m\gamma}(SM)$ is the adjoint operator of $C_{m\gamma}^\dagger(SM)$.

Solutions of Eq. 2 are readily found by solving the variational equation[8)]

$$\langle 0|[\delta O_\lambda, H, O_\lambda^\dagger]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda, O_\lambda^\dagger]|0\rangle, \tag{6}$$

where the double commutator is defined as

$$[a,H,b] = \frac{1}{2}([a,[H,b]] + [[a,H],b]). \tag{7}$$

The problem here is to find the eigenvector (Y,Z) in Eq. 4 and the eigenvalue ω_λ. We have shown[1)] that the substitution of Eq. 4 into 6 leads to the matrix equation

$$\begin{bmatrix} A & B \\ -B & -A \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} \tag{8}$$

where

$$\left.\begin{aligned} A_{m\gamma,n\delta}(S) &= \langle 0|[C_{m\gamma}(SM), H, C_{n\delta}^\dagger(SM)]|0\rangle \\ B_{m\gamma,n\delta}(S) &= -\langle 0|[C_{m\gamma}(SM), H, C_{n\delta}(\overline{SM})]|0\rangle \\ D_{m\gamma,n\delta} &= \langle 0|[C_{m\gamma}(SM), C_{n\delta}^\dagger(SM)]|0\rangle \end{aligned}\right\} \tag{9}$$

Note that A and B are independent of M, and D is independent of S and M. We shall henceforth denote unoccupied orbitals (particle states) by m, n, p, or q, and occupied orbitals (hole states) by γ, δ, μ, or ν. In expanding these elements explicitly, we first let

$$\langle 0|0\rangle = 1. \tag{10}$$

Then, in the level of the 2nd-order perturbation theory of the ground-state correlation, we obtain[1)]

$$\left.\begin{aligned} A_{m\gamma,n\delta}(S) &= A^\circ_{m\gamma,n\delta}(S) \\ &\quad + \delta_{\gamma\delta}[T_{mn} - \tfrac{1}{2}(\varepsilon_m + \varepsilon_n - 2\varepsilon_\gamma)\rho_{mn}] \\ &\quad - \delta_{mn}[T_{\gamma\delta} - \tfrac{1}{2}(2\varepsilon_m - \varepsilon_\gamma - \varepsilon_\delta)\rho_{\gamma\delta}] \\ B_{m\gamma,n\delta}(S) &= B^\circ_{m\gamma,n\delta}(S) + (-1)^S S_{m\gamma,n\delta} \\ D_{m\gamma,n\delta} &= \delta_{mn}\delta_{\gamma\delta} + \delta_{mn}\rho_{\gamma\delta} - \delta_{\gamma\delta}\rho_{mn}, \end{aligned}\right\} \tag{11}$$

where A° and B° are the RPA matrices, i.e.

$$\left.\begin{aligned} A^\circ_{m\gamma,n\delta}(S) &= \delta_{mn}\delta_{\gamma\delta}(\varepsilon_m - \varepsilon_\gamma) - V_{m\delta n\gamma} + (\delta_{S0})\, 2V_{m\delta\gamma n} \\ B^\circ_{m\gamma,n\delta}(S) &= -(-1)^S V_{mn\delta\gamma} + (\delta_{S0})\, 2V_{mn\gamma\delta}. \end{aligned}\right\} \tag{12}$$

ε_k is the HF orbital energy and

$$V_{ijkl} \equiv \langle i(1)j(2)|(r_{12})^{-1}|k(1)l(2)\rangle. \tag{13}$$

T and S are correction terms linear in the ground-state correlation coefficients. ρ is quadratic in the correlation coefficients. They are explicitly written as

$$\left.\begin{aligned} S_{m\gamma,n\delta} &= -\sum_{p\mu}[V_{m\mu\delta p}C_{p\mu,n\gamma}(0) + V_{n\mu\gamma p}C_{p\mu,m\delta}(0)] \\ T_{mn} &= -\frac{1}{2}\sum_{q\mu\nu}[V_{mq\mu\nu}C_{q\nu,n\mu}(0) + V_{\mu\nu nq}C_{m\mu,q\nu}(0)] \\ T_{\gamma\delta} &= \frac{1}{2}\sum_{pq\nu}[V_{pq\gamma\nu}C_{q\nu,p\delta}(0) + V_{\delta\nu pq}C_{p\gamma,q\nu}(0)] \end{aligned}\right\} \tag{14}$$

and

$$\left.\begin{aligned} \rho_{mn} &= \frac{1}{2}\sum_{p\mu\nu}\sum_{S=0,1} C'_{p\mu,m\nu}(S)\, C_{n\nu,p\mu}(S) \\ \rho_{\gamma\delta} &= -\frac{1}{2}\sum_{pq\mu}\sum_{S=0,1} C'_{p\mu,q\gamma}(S)\, C_{q\delta,p\mu}(S), \end{aligned}\right\} \tag{15}$$

where

$$C'(0) = \frac{1}{4}[3C(0) + C(1)];\; C'(1) = \frac{1}{4}[C(0) + 3C(1)]. \tag{16}$$

To the first order in the Rayleigh-Schrödinger perturbation theory the ground-state correlation coefficients are given by

$$C_{m\gamma,n\delta}(S) \cong -B^\circ_{m\gamma,n\delta}(S)/(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta). \tag{17}$$

Finally, in the diagonalization approximation

$$D_{m\gamma,n\delta} \cong \delta_{mn}\delta_{\gamma\delta}(1 + \rho_{\gamma\gamma} - \rho_{mm}) \equiv \delta_{mn}\,\delta_{\gamma\delta}\, g_{m\gamma}^2, \tag{18}$$

Eq. 8 becomes

$$\begin{bmatrix} \mathscr{A} & \mathscr{B} \\ -\mathscr{B} & -\mathscr{A} \end{bmatrix} \begin{bmatrix} \mathscr{Y}(\lambda) \\ \mathscr{Z}(\lambda) \end{bmatrix} = \omega_\lambda \begin{bmatrix} \mathscr{Y}(\lambda) \\ \mathscr{Z}(\lambda) \end{bmatrix}, \tag{19}$$

where

$$\left.\begin{aligned} \mathscr{A}_{m\gamma,n\delta} &\equiv g_{m\gamma}^{-1} A_{m\gamma,n\delta}\, g_{n\delta}^{-1} \\ &= \delta_{mn}\,\delta_{\gamma\delta}(\varepsilon_m - \varepsilon_\gamma) \\ &\quad + \{-[V_{m\delta n\gamma} + \delta_{mn}T_{\gamma\delta} - \delta_{\gamma\delta}T_{mn}] \\ &\quad + (\delta_{S0})\, 2V_{m\delta\gamma n}\}/g_{m\gamma}\, g_{n\delta}) \\ \mathscr{B}_{m\gamma,n\delta} &\equiv g_{m\gamma}^{-1} B_{m\gamma,n\delta}\, g_{n\delta}^{-1} \\ &= \{-(-1)^S[V_{mn\delta\gamma} - S_{m\gamma,n\delta}] \\ &\quad + (\delta_{S0})\, 2V_{mn\gamma\delta}\}/(g_{m\gamma}\, g_{n\gamma}) \\ \mathscr{Y}_{m\gamma} &\equiv g_{m\gamma} Y_{m\gamma};\; \mathscr{Z}_{m\gamma} \equiv g_{m\gamma} Z_{m\gamma}. \end{aligned}\right\} \tag{20}$$

The EOM for (1p-1h)+(2p-2h) States

The excitation operator in Eq. 4 is now extended to include 2p-2h creation and annihilation operators:

$$\begin{aligned} O^\dagger(\lambda SM) &= \sum_{m\gamma}\{Y_{m\gamma}(\lambda S)\, C_{m\gamma}^\dagger(SM) - Z_{m\gamma}(\lambda S)\, C_{m\gamma}(\overline{SM})\} \\ &\quad + \sum_{(m\gamma,n\delta)}\{Y^{(2)}_{(m\gamma,n\delta)}(\lambda S)\, \Gamma^\dagger_{(m\gamma,n\delta)}(SM) \\ &\quad - Z^{(2)}_{(m\gamma,n\delta)}(\lambda S)\, \Gamma_{(m\gamma,n\delta)}(\overline{SM})\}, \end{aligned} \tag{21}$$

where $\Gamma^\dagger_{(m\gamma,n\delta)}(SM)$ are 2p-2h creation operators. The second summation in Eq. 21 runs over all the independent 2p-2h states, not over $m\gamma$ and $n\delta$ separately. In general, $\Gamma^\dagger_{(m\gamma,n\delta)}(SM)$ is a linear combination of $C_{m\gamma}^\dagger(SM)C_{n\delta}^\dagger(00)$, $C_{n\delta}^\dagger(SM)C_{m\gamma}^\dagger(00)$, $C_{m\delta}^\dagger(SM)C_{n\gamma}^\dagger(00)$, and $C_{n\gamma}^\dagger(SM)\, C_{m\delta}^\dagger(00)$.

The substitution of Eq. 21 into Eq. 6 gives

$$\begin{bmatrix} A & B & A^{(1,2)} & B^{(1,2)} \\ -B & -A & -B^{(1,2)} & -A^{(1,2)} \\ A^{(2,1)} & B^{(2,1)} & A^{(2,2)} & B^{(2,2)} \\ -B^{(2,1)} & -A^{(2,1)} & -B^{(2,2)} & -A^{(2,2)} \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \\ Y^{(2)}(\lambda) \\ Z^{(2)}(\lambda) \end{bmatrix}$$

$$= \omega_\lambda \begin{bmatrix} D & 0 & 0 & 0 \\ 0 & D & 0 & 0 \\ 0 & 0 & D^{(2,2)} & 0 \\ 0 & 0 & 0 & D^{(2,2)} \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \\ Y^{(2)}(\lambda) \\ Z^{(2)}(\lambda) \end{bmatrix}, \tag{22}$$

where the matrix elements of A, B, and D are already given above, and the matrix elements of $A^{(1,2)}$, $B^{(1,2)}$, $A^{(2,2)}$, $B^{(2,2)}$, and $D^{(2,2)}$ are defined by

Table 1. The Orthonormal 2p-2h Creation Operators $\Gamma^{\dagger}{}_{(m\gamma,n\delta)}$

$S=M=0$	
$\Gamma^{\dagger}{}_{(m\gamma,m\gamma)}=c_{m\alpha}{}^{+}c_{m\beta}{}^{+}c_{\gamma\beta}c_{\gamma\alpha}=C_{m\gamma}{}^{\dagger}(00)C_{m\gamma}{}^{\dagger}(00)$	
$\Gamma^{\dagger}{}_{(m\gamma,n\gamma)}=(1/\sqrt{2})(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+})c_{\gamma\beta}c_{\gamma\alpha}=\sqrt{2}C_{m\gamma}{}^{\dagger}(00)C_{n\gamma}{}^{\dagger}(00)$	$(m\neq n)$
$\Gamma^{\dagger}{}_{(m\gamma,m\delta)}=(1/\sqrt{2})c_{m\alpha}{}^{+}c_{m\beta}{}^{+}(c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha})=\sqrt{2}C_{m\gamma}{}^{\dagger}(00)C_{m\delta}{}^{\dagger}(00)$	$(\gamma\neq\delta)$
$\Gamma^{\dagger}{}_{(m\gamma,n\delta)_1}=1/2(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+})(c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha})=C_{m\gamma}{}^{\dagger}(00)C_{n\delta}{}^{\dagger}(00)+C_{m\delta}{}^{\dagger}(00)C_{n\gamma}{}^{\dagger}(00)$	$(m\neq n,\gamma\neq\delta)$
$\Gamma^{\dagger}{}_{(m\gamma,n\delta)_2}=(1/\sqrt{3})\{(c_{m\alpha}{}^{+}c_{n\alpha}{}^{+}c_{\delta\alpha}c_{\gamma\alpha}+c_{m\beta}{}^{+}c_{n\beta}{}^{+}c_{\delta\beta}c_{\gamma\beta})$	
$+1/2(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+})(c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha})\}=(1/\sqrt{3})(C_{m\gamma}{}^{\dagger}(00)C_{n\delta}{}^{\dagger}(00)-C_{m\delta}{}^{\dagger}(00)C_{n\gamma}{}^{\dagger}(00))$	$(m\neq n,\gamma\neq\delta)$
$S=1,\ M=0$	
$\Gamma^{\dagger}{}_{(m\gamma,n\gamma)}=(1/\sqrt{2})(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+})c_{\gamma\beta}c_{\gamma\alpha}=(1/\sqrt{2})(C_{m\gamma}{}^{\dagger}(10)C_{n\gamma}{}^{\dagger}(00)-C_{n\gamma}{}^{\dagger}(10)C_{m\gamma}{}^{\dagger}(00))$	$(m\neq n)$
$\Gamma^{\dagger}{}_{(m\gamma,m\delta)}=(1/\sqrt{2})c_{m\alpha}{}^{+}c_{m\beta}{}^{+}(c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha})=(1/\sqrt{2})(C_{m\gamma}{}^{\dagger}(00)C_{m\delta}{}^{\dagger}(10)-C_{m\delta}{}^{\dagger}(10)C_{m\gamma}{}^{\dagger}(00))$	$(\gamma\neq\delta)$
$\Gamma^{\dagger}{}_{(m\gamma,n\delta)_1}=1/2(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}-c_{n\alpha}{}^{+}c_{m\beta}{}^{+})(c_{\delta\beta}c_{\gamma\alpha}+c_{\gamma\beta}c_{\delta\alpha})$	
$=1/2(C_{m\gamma}{}^{\dagger}(10)C_{n\delta}{}^{\dagger}(00)-C_{n\delta}{}^{\dagger}(10)C_{m\gamma}{}^{\dagger}(00)+C_{m\delta}{}^{\dagger}(10)C_{n\gamma}{}^{\dagger}(00)-C_{n\gamma}{}^{\dagger}(10)C_{m\delta}{}^{\dagger}(00))$	$(m\neq n,\gamma\neq\delta)$
$\Gamma^{\dagger}{}_{(m\gamma,n\delta)_2}=1/2(c_{m\alpha}{}^{+}c_{n\beta}{}^{+}+c_{n\alpha}{}^{+}c_{m\beta}{}^{+})(c_{\delta\beta}c_{\gamma\alpha}-c_{\gamma\beta}c_{\delta\alpha})$	
$=1/2(C_{m\gamma}{}^{\dagger}(10)C_{n\delta}{}^{\dagger}(00)-C_{n\delta}{}^{\dagger}(10)C_{m\gamma}{}^{\dagger}(00)-C_{m\delta}{}^{\dagger}(10)C_{n\gamma}{}^{\dagger}(00)+C_{n\gamma}{}^{\dagger}(10)C_{m\delta}{}^{\dagger}(00))$	$(m\neq n,\gamma\neq\delta)$
$\Gamma^{\dagger}{}_{(m\gamma,n\delta)_3}=(1/\sqrt{2})(c_{m\alpha}{}^{+}c_{n\alpha}{}^{+}c_{\delta\alpha}c_{\gamma\alpha}-c_{m\beta}{}^{+}c_{n\beta}{}^{+}c_{\delta\beta}c_{\gamma\beta})=(1/\sqrt{2})(C_{m\gamma}{}^{\dagger}(10)C_{n\delta}{}^{\dagger}(00)+C_{n\delta}{}^{\dagger}(10)C_{m\gamma}{}^{\dagger}(00))$	$(m\neq n,\gamma\neq\delta)$

$$\left.\begin{aligned}
&A^{(1,2)}{}_{m'\gamma';(m\gamma,n\delta)}(S)\\
&\quad=\langle 0|[C_{m'\gamma'}(SM),\ H,\Gamma^{\dagger}{}_{(m\gamma,n\delta)}(SM)]|0\rangle\\
&B^{(1,2)}{}_{m'\gamma';(m\gamma,n\delta)}(S)\\
&\quad=-\langle 0|[C_{m'\gamma'}(SM),\ H,\Gamma_{(m\gamma,n\delta)}(\overline{SM})]|0\rangle\\
&A^{(2,2)}{}_{(m'\gamma',n'\delta');(m\gamma,n\delta)}(S)\\
&\quad=\langle 0|[\Gamma_{(m'\gamma',\,n'\delta')}(SM),\ H,\Gamma^{\dagger}{}_{(m\gamma,n\delta)}(SM)]|0\rangle\\
&B^{(2,2)}{}_{(m'\gamma',n'\delta');(m\gamma,n\delta)}(S)\\
&\quad=-\langle 0|[\Gamma_{(m'\gamma',\,n'\delta')}(SM),\ H,\Gamma_{(m\gamma,n\delta)}(\overline{SM})]|0\rangle\\
&D^{(2,2)}{}_{(m'\gamma',n'\delta');(m\gamma,n\delta)}\\
&\quad=\langle 0|[\Gamma_{(m'\gamma',\,n'\delta')}(SM),\ \Gamma^{\dagger}{}_{(m\gamma,n\delta)}(SM)]|0\rangle
\end{aligned}\right\}\qquad(23)$$

Note that

$$A^{(2,1)}=\tilde{A}^{(1,2)};\ B^{(2,1)}=\tilde{B}^{(1,2)}. \qquad (24)$$

Also note that $A^{(1,2)}$, $B^{(1,2)}$, $A^{(2,2)}$, and $B^{(2,2)}$ are independent of M, and that $D^{(2,2)}$ is independent of S and M.

In the present work, we shall replace the correlated ground state $|0\rangle$ in Eq. 23 by the Hartree-Fock ground state $|HF\rangle$, obtaining $A^{\circ(1,2)}$, $B^{\circ(1,2)}$, $A^{\circ(2,2)}$, $B^{\circ(2,2)}$, and $D^{\circ(2,2)}$, respectively. It is clear that $B^{\circ(1,2)}$ and $B^{\circ(2,2)}$ vanish, for the Hamiltonian H consists of only the pair creation operators $C_{ij}{}^{\dagger}(00)$ and their products $C_{ij}{}^{\dagger}(00)C_{kl}{}^{\dagger}(00)$. The matrix elements of $A^{\circ(1,2)}$ and $A^{\circ(2,2)}$ are obtained from their primitive elements given in the Appendix. The matrix $D^{\circ(2,2)}$ becomes an identity matrix when the basis set of $\Gamma^{\dagger}{}_{(m\gamma,n\delta)}$ is chosen such as given in Table 1. These 2p-2h creation operators were given earlier in Ref. 1b. They are reproduced here for convenience and some typographic errors involved there have been corrected. In this basis set of 2p-2h creation operators, we now have, instead of Eq. 22,

$$\begin{bmatrix} \mathscr{A} & \mathscr{B} & \mathscr{A}^{\circ(1,2)} & 0\\ -\mathscr{B} & -\mathscr{A} & 0 & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & 0 & A^{\circ(2,2)} & 0\\ 0 & -\mathscr{A}^{\circ(2,1)} & 0 & -A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{Y}\\ \mathscr{Z}\\ Y^{(2)}\\ Z^{(2)} \end{bmatrix}=\omega\begin{bmatrix} \mathscr{Y}\\ \mathscr{Z}\\ Y^{(2)}\\ Z^{(2)} \end{bmatrix}, \qquad (25)$$

where $\mathscr{A}$, $\mathscr{B}$, $\mathscr{Y}$, and $\mathscr{Z}$ are already given in the preceding section, and

$$\mathscr{A}^{\circ(1,2)}{}_{m'\gamma';\,(m\gamma,n\delta)}=A^{\circ(1,2)}{}_{m'\gamma';\,(m\gamma,\,n\delta)}/g_{m'\gamma'}. \qquad (26)$$

In order to reduce the matrix size of Eq. 25, we first write it as

$$\begin{bmatrix} \mathscr{A}-\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{Y}-\mathscr{Z}\\ Y^{(2)}-Z^{(2)} \end{bmatrix}=\omega\begin{bmatrix} \mathscr{Y}+\mathscr{Z}\\ Y^{(2)}+Z^{(2)} \end{bmatrix}, \qquad (27a)$$

$$\begin{bmatrix} \mathscr{A}+\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{Y}+\mathscr{Z}\\ Y^{(2)}+Z^{(2)} \end{bmatrix}=\omega\begin{bmatrix} \mathscr{Y}-\mathscr{Z}\\ Y^{(2)}-Z^{(2)} \end{bmatrix}. \qquad (27b)$$

Multiplication of the matrix

$$\begin{bmatrix} \mathscr{A}-\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}$$

from the left on both sides of Eq. 27b gives

$$\begin{bmatrix} \mathscr{A}-\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{A}+\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{Y}+\mathscr{Z}\\ Y^{(2)}+Z^{(2)} \end{bmatrix}=\omega^2\begin{bmatrix} \mathscr{Y}+\mathscr{Z}\\ Y^{(2)}+Z^{(2)} \end{bmatrix}. \qquad (28)$$

Similarly we also have

$$\begin{bmatrix} \mathscr{A}+\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{A}-\mathscr{B} & \mathscr{A}^{\circ(1,2)}\\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix}\begin{bmatrix} \mathscr{Y}-\mathscr{Z}\\ Y^{(2)}-Z^{(2)} \end{bmatrix}=\omega^2\begin{bmatrix} \mathscr{Y}-\mathscr{Z}\\ Y^{(2)}-Z^{(2)} \end{bmatrix}. \qquad (29)$$

Solving either Eq. 28 or 29 may suffices if one is only interested in finding the transition energy ω. For the evaluation of the transition moments, however, both eigenvectors of Eqs. 28 and 29 are needed. In any case, the order of the matrix to be diagonalyzed has been reduced to the half.

The Transition Moment

In deriving the explicit expressions of the matrix elements, we have assumed the normalization condition of Eq. 10 for the $|0\rangle$. For excited states, we let

$$\langle\lambda|\lambda\rangle=1. \tag{30}$$

Then, the transition dipole moment is written

$$\boldsymbol{D}_\lambda=\langle 0|(\boldsymbol{r})_{op}|\lambda\rangle$$
$$=-\sqrt{2}\sum_{ij}\boldsymbol{d}^\circ{}_{ij}\langle 0|[C_{ij}{}^\dagger(00),\ O^\dagger{}_\lambda]|0\rangle, \tag{31}$$

where

$$\boldsymbol{d}^\circ{}_{ij}\equiv\int i(\boldsymbol{r})\,\boldsymbol{r}\,j(\boldsymbol{r})\,\mathrm{d}^3 r. \tag{32}$$

The oscillator strength is given by

$$f_\lambda\equiv(2/3)\,\omega_\lambda|\boldsymbol{D}_\lambda|^2. \tag{33}$$

Employing the diagonalization approximations used in the treatment of D and $D^{(2,2)}$, we can rewrite the normalization condition Eq. 30 as

$$\sum_{m\gamma}\{|\mathscr{Y}_{m\gamma}(\lambda S)|^2-|\mathscr{Z}_{m\gamma}(\lambda S)|^2\}$$
$$+\sum_{(m\gamma,n\delta)}\{|Y^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)|^2-|Z^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)|^2\}=1 \tag{34}$$

Note that the first and the second terms on the left-hand side of this equation are the scalar products of $(\mathscr{Y}+\mathscr{Z},\mathscr{Y}-\mathscr{Z})$ and $(Y^{(2)}+Z^{(2)},\ Y^{(2)}+Z^{(2)})$. These are evaluated by using eigenvectors of Eqs. 28 and 29. With the diagonalization approximation in Eq. 18, Eq. 31 leads to

$$\boldsymbol{D}_\lambda=\delta_{S0}\sqrt{2}\sum_{m\gamma}\{\mathscr{Y}_{m\gamma}(\lambda 0)+\mathscr{Z}_{m\gamma}(\lambda 0)\}\,(g_{m\gamma}\boldsymbol{d}^\circ{}_{m\gamma}). \tag{35}$$

Note that terms of $Y^{(2)}$ and $Z^{(2)}$ vanish in deriving the last expression, for in our approximation,

$$\langle 0|[C_{ij}{}^\dagger(00),\ \Gamma^\dagger{}_{(m\gamma,n\delta)}(00)]|\rangle=0. \tag{36}$$

Thus, $\boldsymbol{D}_\lambda$ is only indirectly affected by $Y^{(2)}$ and $Z^{(2)}$ through the normalization condition Eq. 34. When the second term bccomes large on the left-hand side of Eq. 34, $\boldsymbol{D}_\lambda$ may drastically reduce in comparison with that obtained from the (1p-1h) EOM.

Discussion

With the results obtained above, we are now able to make computations of the EOM at the level of (1p-1h)+(2p-2h). Previously we[9] analyzed the dynamical screening due to sigma-electrons in the $\pi\rightarrow\pi^*$ transition of the ethylene molecule. We showed that the N→T (triplet) transition is almost free from this kind of screenings but the N→V (singlet) transition is significantly affected. More recently we[10] have shown that in the zero-differential overlap (ZDO) approximation between sigma- and pi-orbitals, the triplet $\pi\rightarrow\pi^*$ transitions are generally unaffected by the dynamical screening. Such observations have led us[11] to propose a scheme to parametrize the EOM for $\pi\rightarrow\pi^*$ transitions. In the forthcoming papers, we propose a semi-empirical scheme of the (1p-1h)+(2p-2h) EOM for $\pi\rightarrow\pi^*$ transitions and present numerical results of its application to linear polyenes.

Appendix: The Matrix Elements of $A^{\circ(1,2)}$ and $A^{\circ(2,2)}$

The matrix elements of $A^{\circ(1,2)}$ and $A^{\circ(2,2)}$ appearing in Eqs. 25—29 are constructed on the orthonormal basis set of $\Gamma^\dagger{}_{(m\gamma,n\delta)}$ in Table 1. These elements are readily obtained from the primitive elements

$$A^{\circ(1,2)}{}_{m'\gamma';\,m\gamma,\,n\delta}\,(S)$$
$$\equiv\langle HF|[C_{m'\gamma'}\,(SM),\ H,C_{m\gamma}{}^\dagger(SM)C_{n\delta}{}^\dagger(00)]|HF\rangle \tag{A. 1}$$

$$A^{\circ(2,2)}{}_{m'\gamma',\,n'\delta';\,m\gamma,\,n\delta}\,(S)$$
$$\equiv\langle HF|[(C_{m'\gamma'}{}^\dagger(SM)\ C_{n'\delta'}{}^\dagger(00))^\dagger,$$
$$H,C_{m\gamma}{}^\dagger(SM)C_{n\delta}{}^\dagger(00)]|HF\rangle \tag{A. 2}$$

To expand these primitive elements, it is convenient to have the Hamiltonian in the following form:[1a)]

$$\left.\begin{aligned}
&H=H(1)+H(2)+H(3);\\
&H(1)=\sum_i\varepsilon_i\sqrt{2}\,C_{ii}{}^\dagger(00),\\
&H(2)=\sum_{ij}[-\frac{1}{2}\sum_k V_{ikkj}+\sum_\gamma(V_{i\gamma\gamma j}-2V_{i\gamma j\gamma})]\sqrt{2}\,C_{ij}{}^\dagger(00),\\
&H(3)=\sum_{ijkl}V_{ijkl}\,C_{ik}{}^\dagger(00)\,C_{jl}{}^\dagger(00),
\end{aligned}\right\} \tag{A. 3}$$

where

$$V_{ijkl}=\langle i(1)j(2)|(r_{12})^{-1}|k(1)l(2)\rangle. \tag{A. 4}$$

In Eq. A. 3, γ refers to a hole orbital and i, j, k, l to any orbital, i.e., hole or particle. Cf. Ref. 1a for various relations useful in expanding the right-hand side of Eqs. A. 1 and A. 2.

First note that Eqs. A. 1 and A. 2 can be also written as

$$A^{\circ(1,2)}{}_{m'\gamma';\,m\gamma,\,n\delta}(S)$$
$$=\langle HF|[C_{m'\gamma'}(S0),\ H]C_{m\gamma}{}^\dagger(S0)C_{n\delta}{}^\dagger(00)|HF\rangle$$
$$+\frac{1}{2}\langle HF|HC_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)\ C_{n\delta}{}^\dagger(00)|HF\rangle \tag{A. 5}$$

$$A^{\circ(2,2)}{}_{m'\gamma',\,n'\delta';\,m\gamma,n\delta}(S)$$
$$=\langle HF|[C_{n'\delta'}(00)\ C_{m'\gamma'}(S0)[H,\ C_{m\gamma}{}^\dagger(S0)\ C_{n\delta}{}^\dagger(00)]|HF\rangle$$
$$+\frac{1}{2}\langle HF|[C_{n'\delta'}(00)C_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)\ C_{n\delta}{}^\dagger(00),\ H]|HF\rangle. \tag{A. 6}$$

In the second term of Eq. A. 5, we have

$$\langle HF|H(1)C_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)C_{n\delta}{}^\dagger(00)|HF\rangle=0 \tag{A. 7}$$

and

$$\langle HF|H(2)C_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)C_{n\delta}{}^\dagger(00)|HF\rangle$$
$$=-\langle HF|H(3)C_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)C_{n\delta}{}^\dagger(00)|HF\rangle$$
$$=\sqrt{2}\sum_{p\mu}\{\frac{1}{2}(\sum_\nu V_{\mu\nu\nu p}-\sum_q V_{\mu qqp})-2\sum_\nu V_{\mu\nu p\nu}\}\times$$
$$\langle HF|C_{p\mu}(00)C_{m'\gamma'}\,(S0)C_{m\gamma}{}^\dagger(S0)C_{n\delta}{}^\dagger(00)|HF\rangle. \tag{A. 8}$$

In the second term of Eq. A. 6, we have

$$C_{n'\delta'}(00)C_{m'\gamma'}(S0)C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)|HF\rangle$$
$$=\{\delta_{m'm}\,\delta_{n'n}\,(\delta_{\gamma'\gamma}\,\delta_{\delta'\delta}-\frac{1}{2}\delta_{\gamma'\delta}\,\delta_{\delta'\gamma})$$
$$+\delta_{m'n}\,\delta_{n'm}\,(\delta_{S0}\,\delta_{\gamma'\delta}\,\delta_{\delta'\gamma}-\frac{1}{2}\delta_{\gamma'\gamma}\,\delta_{\delta'\delta})\}|HF\rangle \qquad \text{(A. 9)}$$

and a similar expression for $\langle HF|C_{n'\delta'}(00)C_{m'\gamma'}(S0)C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$. Hence, the second terms of Eqs. A. 5 and A. 6 vanish, and we have

$$A^{\circ(1,2)}{}_{m'\gamma';\,m\gamma,n\delta}(S)$$
$$=\langle HF|[C_{m'\gamma'}(S0),H]C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)|HF\rangle \qquad \text{(A. 10)}$$

$$A^{\circ(2,2)}{}_{m'\gamma',\,n'\delta';\,m\gamma,\,n\delta}(S)$$
$$=\langle HF|[C_{n'\delta'}(00)C_{m'\gamma'}(S0)[H,C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)]|HF\rangle \qquad \text{(A. 11)}$$

Now, it is useful to note the following equations:

$$[H(1),\,C_{m\gamma}{}^{\dagger}(S0)]=(\varepsilon_m-\varepsilon_\gamma)\,C_{m\gamma}{}^{\dagger}(S0) \qquad \text{(A. 12)}$$

$$[H(2),\,C_{m\gamma}{}^{\dagger}(S0)]$$
$$=\sum_i\{-\frac{1}{2}\sum_k V_{ikkm}+\sum_{\gamma''}(V_{i\gamma''\gamma''m}-2V_{i\gamma''m\gamma''})\}\,C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_j\{-\frac{1}{2}\sum_k V_{\gamma kkj}+\sum_{\gamma''}(V_{\gamma\gamma''\gamma''j}-2V_{\gamma\gamma''j\gamma''})\}\,C_{mj}{}^{\dagger}(S0) \qquad \text{(A. 13)}$$

$$[H(3),\,C_{m\gamma}{}^{\dagger}(S0)]$$
$$=-\frac{1}{2}\sum_{ik}V_{ikkm}\,C_{i\gamma}{}^{\dagger}(S0)-\frac{1}{2}\sum_{jk}V_{\gamma kkj}\,C_{mj}{}^{\dagger}(S0)$$
$$+\sum_{ij}V_{\gamma ijm}\,C_{ij}{}^{\dagger}(S0)$$
$$+\sqrt{2}\sum_{kl}\{\sum_i V_{ikml}\,C_{kl}{}^{\dagger}(00)C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_j V_{\gamma kjl}\,C_{kl}{}^{\dagger}(00)C_{mj}{}^{\dagger}(S0)\} \qquad \text{(A. 14)}$$

which amounts to

$$[H,\,C_{m\gamma}{}^{\dagger}(S0)]$$
$$=(\varepsilon_m-\varepsilon_\gamma)C_{m\gamma}{}^{\dagger}(S0)+\sum_{ij}V_{\gamma ijm}\,C_{ij}{}^{\dagger}(S0)$$
$$-\sum_i(\sum_{m''}V_{im''m''m}+\sum_{\gamma''}2V_{i\gamma''m\gamma''})C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_{j\gamma''}(V_{\gamma\gamma''\gamma''j}-2V_{\gamma\gamma''j\gamma''})C_{mj}{}^{\dagger}(S0)$$
$$+\sqrt{2}\sum_{kl}\{\sum_i V_{ikml}\,C_{kl}{}^{\dagger}(00)C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_j V_{\gamma kjl}\,C_{kl}{}^{\dagger}(00)C_{mj}{}^{\dagger}(S0)\} \qquad \text{(A. 15)}$$

Also note that

$$[H,\,C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)]$$
$$=(\varepsilon_m+\varepsilon_n-\varepsilon_\gamma-\varepsilon_\delta)C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+\sum_{ij}\{V_{\gamma ijm}\,C_{ij}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)+V_{\delta ijn}C_{m\gamma}{}^{\dagger}(S0)C_{ij}{}^{\dagger}(00)\}$$
$$-\sum_i\{(\sum_p V_{ippm}+2\sum_\mu V_{i\mu m\mu})C_{i\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+(\sum_p V_{ippn}+2\sum_\mu V_{i\mu n\mu})C_{m\gamma}{}^{\dagger}(S0)C_{i\delta}{}^{\dagger}(00)$$
$$-\sum_{j\mu}\{(V_{\gamma\mu\mu j}-2V_{\gamma\mu j\mu})C_{mj}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+(V_{\delta\mu\mu j}-2V_{\delta\mu j\mu})C_{m\gamma}{}^{\dagger}(S0)C_{nj}{}^{\dagger}(00)\}$$
$$+\sqrt{2}\sum_{kl}[\{\sum_i V_{ikml}\,C_{kl}{}^{\dagger}(00)C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_j V_{\gamma kjl}\,C_{kl}{}^{\dagger}(00)C_{mj}{}^{\dagger}(S0)\}C_{n\delta}{}^{\dagger}(00)$$
$$+C_{m\gamma}{}^{\dagger}(S0)\{\sum_i V_{iknl}\,C_{kl}{}^{\dagger}(00)C_{i\delta}{}^{\dagger}(00)$$
$$-\sum_j V_{\delta kjl}\,C_{kl}{}^{\dagger}(00)C_{nj}{}^{\dagger}(00)\}]. \qquad \text{(A. 16)}$$

Now, from Eq. A. 15, we have

$$[C_{m'\gamma'}(S0),H]$$
$$=(\varepsilon_{m'}-\varepsilon_{\gamma'})C_{m'\gamma'}(S0)+\sum_{ij}V_{jm'\gamma'i}\,C_{ij}(S0)$$
$$-\sum_i(\sum_p V_{pm'ip}+2\sum_\mu V_{m'\mu i\mu})C_{i\gamma'}(S0)$$
$$-\sum_{j\mu}(V_{\mu j\gamma'\mu}-2V_{j\mu\gamma'\mu})C_{m'j}(S0)$$
$$+\sqrt{2}\sum_{kl}\{\sum_i V_{m'lik}\,C_{i\gamma'}(S0)C_{kl}(00)$$
$$-\sum_j V_{jl\gamma'k}\,C_{m'j}(S0)C_{kl}(00)\}. \qquad \text{(A. 17)}$$

The substitution of this expression into Eq. A. 10 gives

$$A^{\circ(1,2)}{}_{m'\gamma';m\gamma,n\delta}(S)$$
$$=\langle HF|\sqrt{2}\sum_{kl}\{\sum_i V_{m'lik}\,C_{i\gamma'}(S0)C_{kl}(00)$$
$$-\sum_j V_{jl\gamma'k}\,C_{m'j}(S0)C_{kl}(00)\}C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)|HF\rangle$$
$$=\langle HF|\sqrt{2}\sum_{q\nu}\{\sum_p V_{m'\nu pq}\,C_{p\gamma'}(S0)C_{q\nu}(00)$$
$$-\sum_\mu V_{\mu\nu\gamma'q}\,C_{m'\mu}(S0)C_{q\nu}(00)\}C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)|HF\rangle$$
$$=\sqrt{2}\{\delta_{\gamma'\gamma}\,(V_{m'\delta mn}-\frac{1}{2}V_{m'\delta nm})$$
$$+\delta_{\gamma'\delta}\,(\delta_{S0}\,V_{m'\gamma nm}-\frac{1}{2}V_{m'\gamma mn})$$
$$-\delta_{m'm}\,(V_{\gamma\delta\gamma'n}-\frac{1}{2}V_{\delta\gamma\gamma'n})-\delta_{m'n}(\delta_{S0}\,V_{\delta\gamma\gamma'm}-\frac{1}{2}V_{\gamma\delta\gamma'm})\}. \qquad \text{(A. 18)}$$

On the other hand, the substitution of Eq. A. 16 into Eq. A. 11 gives

$$A^{\circ(2,2)}{}_{m'\gamma',n'\delta';\,m\gamma,n\delta}(S)$$
$$=\langle HF|C_{n'\delta'}(00)C_{m'\gamma'}(S0)$$
$$\times[(\varepsilon_m+\varepsilon_n-\varepsilon_\gamma-\varepsilon_\delta)C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+\sum_{p\mu}\{V_{\gamma p\mu m}\,C_{p\mu}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+V_{\delta p\mu n}C_{m\gamma}{}^{\dagger}(S0)C_{p\mu}{}^{\dagger}(00)\}$$
$$-\sum_q\{(\sum_p V_{qppm}+2\sum_\mu V_{q\mu m\mu})C_{q\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+(\sum_p V_{qppn}+2\sum_\mu V_{q\mu n\mu})C_{m\gamma}{}^{\dagger}(S0)C_{q\delta}{}^{\dagger}(00)\}$$
$$-\sum_{\nu\mu}\{(V_{\gamma\mu\mu\nu}-2V_{\gamma\mu\nu\mu})C_{m\nu}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00)$$
$$+(V_{\delta\mu\mu\nu}-2V_{\delta\mu\nu\mu})C_{m\gamma}{}^{\dagger}(S0)C_{n\nu}{}^{\dagger}(00)\}]|HF\rangle$$
$$+\langle HF|C_{n'\delta'}(00)C_{m'\gamma'}(S0)$$
$$\times\sqrt{2}\sum_{kl}[\{\sum_i V_{ikml}C_{kl}{}^{\dagger}(00)C_{i\gamma}{}^{\dagger}(S0)$$
$$-\sum_j V_{\gamma kjl}\,C_{kl}{}^{\dagger}(00)C_{mj}{}^{\dagger}(S0)\}C_{n\delta}{}^{\dagger}(00)$$
$$+C_{m\gamma}{}^{\dagger}(S0)\{\sum_i V_{iknl}\,C_{kl}{}^{\dagger}(00)C_{i\delta}{}^{\dagger}(00)$$
$$-\sum_\nu V_{\delta k\nu l}\,C_{kl}{}^{\dagger}(00)C_{n\nu}{}^{\dagger}(00)\}]|HF\rangle. \qquad \text{(A. 19)}$$

The last term of this expression can be reduced as follows: (the lasst term)

$$
\begin{aligned}
&= \langle HF|C_{n'\delta'}(00)C_{m'\gamma'}(S0)\times \\
&[-\sum_{q\nu} \{V_{\delta qm\nu}\, C_{n\gamma}{}^{\dagger}(S0) + V_{\gamma qn\nu}C_{m\delta}{}^{\dagger}(S0)\}C_{q\nu}(00) \\
&+\sum_{q} \{\sum_{p} V_{pqmn}\, C_{p\gamma}{}^{\dagger}(S0) - \sum_{\nu} V_{\gamma q\nu n}\, C_{m\nu}{}^{\dagger}(S0)\}C_{q\delta}{}^{\dagger}(00) \\
&+\sum_{\nu} \{\sum_{\mu} V_{\gamma\delta\mu\nu}\, C_{m\mu}{}^{\dagger}(S0) - \sum_{q} V_{q\delta m\nu}\, C_{q\gamma}{}^{\dagger}(S0)\}C_{n\nu}{}^{\dagger}(00) \\
&+\{\sum_{q} (\sum_{p} V_{pqmn} + 2\sum_{\nu} V_{q\nu m\nu})C_{q\gamma}{}^{\dagger}(S0) \\
&+\sum_{\mu\nu} (V_{\gamma\mu\mu\nu} - 2V_{\gamma\mu\nu\mu})C_{m\nu}{}^{\dagger}(S0) \\
&+2\sum_{q\nu} (\delta_{S0}\, V_{\gamma qm\nu} - V_{q\gamma m\nu})C_{q\nu}{}^{\dagger}(S0)\}\; C_{n\delta}{}^{\dagger}(00) \\
&+C_{m\gamma}{}^{\dagger}(S0)\{\sum_{q} (\sum_{p} V_{pqnp} + 2\sum_{\nu} V_{q\nu n\nu})C_{q\delta}{}^{\dagger}(00) \\
&+\sum_{\mu\nu} (V_{\delta\mu\mu\nu} - 2V_{\delta\mu\nu\mu})C_{n\nu}{}^{\dagger}(00) \\
&+2\sum_{q\nu} (V_{\delta qn\nu} - V_{\delta q\nu n})C_{q\nu}{}^{\dagger}(00)\}]|HF\rangle. \qquad \text{(A. 20)}
\end{aligned}
$$

Thus, Eq. A. 19 becomes

$$
\begin{aligned}
&A^{\circ(2,2)}{}_{m'\gamma',n'\delta';\, m\gamma,n\delta}\,(S) \\
&= \langle HF|C_{n'\delta'}(00)C_{m'\gamma'}(S0)\times \\
&[(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta)\; C_{m\gamma}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00) \\
&+\sum_{q\nu} \{(2V_{\delta qn\nu} - V_{\delta q\nu n})C_{m\gamma}{}^{\dagger}(S0)C_{q\nu}{}^{\dagger}(00) \\
&+(\delta_{S0}\, 2V_{\gamma qm\nu} - V_{q\gamma m\nu})C_{q\nu}{}^{\dagger}(S0)C_{n\delta}{}^{\dagger}(00) \\
&-\sum_{q\nu} \{V_{\delta qm\nu}\, C_{n\gamma}{}^{\dagger}(S0) + V_{\gamma qn\nu}\, C_{m\delta}{}^{\dagger}(S0)\}C_{q\nu}{}^{\dagger}(00) \\
&+\sum_{q} \{\sum_{p} V_{pqmn}\, C_{p\gamma}{}^{\dagger}(S0) - \sum_{\nu} V_{\gamma q\nu n}\, C_{m\nu}{}^{\dagger}(S0)\}C_{q\delta}{}^{\dagger}(00) \\
&+\sum_{\nu} \{\sum_{\mu} V_{\gamma\delta\mu\nu}\, C_{m\mu}{}^{\dagger}(S0) \\
&-\sum_{q} V_{q\delta m\nu}\, C_{q\gamma}{}^{\dagger}(S0)\}C_{n\nu}{}^{\dagger}(00)]|HF\rangle. \qquad \text{(A. 21)}
\end{aligned}
$$

After some tedious calculations using Eq. A. 9 in the last expression, we finally obtain

$$
\begin{aligned}
&A^{\circ(2,2)}{}_{m'\gamma',n'\delta';\, m\gamma,n\delta}\,(S) \\
&= \{(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta)\times \\
&[(\delta_{m'm}\, \delta_{n'n}\, \delta_{\gamma'\gamma}\, \delta_{\delta'\delta} - \frac{1}{2}\, \delta_{m'm}\, \delta_{n'n}\, \delta_{\gamma'\delta}\, \delta_{\delta'\gamma} \\
&-\frac{1}{2}\, \delta_{m'n}\, \delta_{n'm}\, \delta_{\gamma'\gamma}\, \delta_{\delta'\delta}) + (\delta_{S0})\; \delta_{m'n}\, \delta_{n'm}\, \delta_{\gamma'\delta}\, \delta_{\delta'\gamma}] \\
&+(\delta_{m'm}\, \delta_{n'n} - \frac{1}{2}\, \delta_{m'n}\, \delta_{n'm})\; V_{\gamma\delta\gamma'\delta'} \\
&+((\delta_{S0})\; \delta_{m'n}\, \delta_{n'm} - \frac{1}{2}\, \delta_{m'n}\, \delta_{n'n})V_{\gamma\delta\delta'\gamma'} \\
&+(\delta_{\gamma'\gamma}\, \delta_{\delta'\delta} - \frac{1}{2}\, \delta_{\gamma'\delta}\, \delta_{\delta'\gamma})\; V_{m'n'mn} \\
&+((\delta_{S0})\; \delta_{\gamma'\delta}\, \delta_{\delta'\gamma} - \frac{1}{2}\, \delta_{\gamma'\gamma}\, \delta_{\delta'\delta})V_{n'm'mn}\} \\
&+\{[\delta_{m'm}\, \delta_{\gamma'\gamma}\, (2V_{\delta n'n\delta'}) - (\delta_{m'm}\, \delta_{\delta'\gamma}\, V_{\delta n'n\gamma'} + \delta_{n'm}\, \delta_{\gamma'\gamma}\, V_{\delta m'n\delta'} \\
&+\delta_{m'n}\, \delta_{\gamma'\gamma}\, V_{\delta n'm\delta'} + \delta_{m'm}\, \delta_{\gamma'\delta}\, V_{\gamma n'n\delta'}) \\
&+\frac{1}{2}(\delta_{m'm}\, \delta_{\delta'\delta}\, V_{\gamma n'n\gamma'} + \delta_{n'n}\, \delta_{\gamma'\gamma}\, V_{\delta m'm\delta'} \\
&+\delta_{m'n}\, \delta_{\delta'\gamma}\, V_{\delta n'm\gamma'} + \delta_{n'm}\, \delta_{\gamma'\delta}\, V_{\gamma m'n\delta'})] \\
&+(\delta_{S0})\; [2(\delta_{m'n}\, \delta_{\gamma'\delta}\, V_{\gamma n'm\delta'} \\
&+\delta_{n'm}\, \delta_{\delta'\gamma}\, V_{\delta m'n\gamma'} + \delta_{n'n}\, \delta_{\delta'\delta}\, V_{\gamma m'm\gamma'}) \\
&-(\delta_{n'n}\, \delta_{\gamma'\delta}\, V_{\gamma m'm\delta'} + \delta_{m'n}\, \delta_{\delta'\delta}\, V_{\gamma n'm\gamma'})] \\
&+(\delta_{n'm}\, \delta_{\delta'\delta}\, V_{\gamma m'n\gamma'} + \delta_{n'n}\, \delta_{\delta'\gamma}\, V_{\delta m'm\gamma'})]\} \\
&+\{[-\delta_{m'm}\, \delta_{\delta'\delta}\, V_{\gamma n'\gamma'n} + \delta_{n'n}\, \delta_{\gamma'\gamma}\, V_{\delta m'\delta'm} \\
&+\delta_{m'm}\, \delta_{\gamma'\gamma}\, V_{\delta n'\delta'n} + \delta_{n'n}\, \delta_{\delta'\delta}\, V_{\gamma m'\gamma'm}) \\
&+\frac{1}{2}\,(\delta_{m'm}\, \delta_{\delta'\gamma}\, V_{\delta n'\gamma'n} + \delta_{n'm}\, \delta_{\gamma'\gamma}\, V_{\delta m'\delta'n} + \delta_{m'n}\, \delta_{\gamma'\gamma}\, V_{\delta n'\delta'm} \\
&+\delta_{m'm}\, \delta_{\gamma'\delta}\, V_{\gamma n'\delta'n} + \delta_{n'n}\, \delta_{\gamma'\delta}\, V_{\gamma m'\delta'm} + \delta_{m'n}\, \delta_{\delta'\delta}\, V_{\gamma n'\gamma'm} \\
&+\delta_{n'm}\, \delta_{\delta'\delta}\, V_{\gamma m'\gamma'n} + \delta_{n'n}\, \delta_{\delta'\gamma}\, V_{\delta m'\gamma'm})] \\
&+(\delta_{S0})\; [-(\delta_{m'n}\, \delta_{\delta'\gamma}\, V_{\delta n'\gamma'm} + \delta_{n'm}\, \delta_{\gamma'\delta}\, V_{\gamma m'\delta'n} \\
&+\delta_{m'n}\, \delta_{\gamma'\delta}\, V_{\gamma n'\delta'm} + \delta_{n'm}\, \delta_{\delta'\gamma}\, V_{\delta m'\gamma'n})]\}. \qquad \text{(A. 22)}
\end{aligned}
$$

Note that all the terms in the second braces are of particle-hole "exchange integral" type and those in the third braces are of particle-hole "Coulomb integral" type.

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