Parametrized Equations-of-Motion Method at the (1p-1h)+(2h-2p) Level and Its Application to Linear Polyenes

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The previously proposed idea of parametrizing the equations-of-motion method [*Int. J. Quantum Chem.*, **18**, 205 (1980)] has been worked out for the $\pi\rightarrow\pi^*$ transitions of linear polyenes. The excitation operator consists of not only 1p-1h creation and annihilation operators but also 2p-2h creation and annihilation operators. [*Bull. Chem. Soc. Jpn.*, **61**, 1103 (1988)]. The proposed scheme accounts for the effect of $\sigma\rightarrow\sigma^*$ mixings in contrast with the traditional pi-electron theories. In the present work, the two-center Coulomb integrals are evaluated by $1/R$, and all the one-center integrals on the C atom are assumed to be the same. Values of the three parameters (a, b, ζ) introduced in the scheme are so determined that the computed excitation energies of ethylene and *s-trans*-butadiene fit the observed values. The scheme has been applied to a series of all-s-trans linear polyenes through dodecahexaene. Some notable results are: (1) The $\sigma\rightarrow\sigma^*$ mixings play a significant role in lowering the excitation energies of the allowed transition to 1^1Bu; (2) the 2^1Ag state is of Ag^- type and almost free from this effect; (3) double excitations (2p-2h states) are dominant in the 2^1Ag state but practically negligible in the 1^1Bu state.

The basic idea of the equations-of-motion (EOM) method employed here is to find an excitation operator $O_\lambda^\dagger$ which creates an excited state $|\lambda>$ by its action on the ground state $|0>$:

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

The operater $O_\lambda^\dagger$ is constructed as a linear combination of creation and annihilation operators of particle-hole pairs and their products. The coefficients of the linear combination are determined in such a way that the excitation operator $O_\lambda^\dagger$ satisfies an equation which is formally the same as the equation of motion for a boson creation operator:

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

Certain molecular integrals appearing in the traditional configuration interaction (CI) calculations for the ground and excited states are eliminated in the EOM calculations because Eq. 2 is set up directly for the difference between the two states.[1)]

In a previous publication,[2)] we proposed a way to parametrize the EOM for the $\pi\rightarrow\pi^*$ transition in conjugated molecules. Emphasis was then laid on the treatment of the effect of $\sigma\rightarrow\sigma^*$ mixings. This effect, called the sigma-dynamical screening,[3)] was expected to make a significant contribution to lowering of the singlet transition energies.[2—4)] The traditional pi-electron theories like the PPP method do not explicitly account for this type fo sigma-electron screenings. In the PPP calculations on conjugated hydrocarbons, the one-center integral γ_{00} is set equal to 11 eV instead of 17 eV as evaluated by the Slater 2p orbital with the effective nuclear charge Z^*=3.18.[5)] The discrepancy was analyzed by Orloff and Sinanoglu[6)] from the view point of sigma-pi electron correlations.

The proposed semiempirical scheme is constructed on the EOM initially written for the STO-basis "Hartree-Fock" orbitals. In the final form of the scheme, however, the SCF orbitals are computed only for pi-orbitals; sigma-electrons are assumed to be localized in separate bonds (C–C and C–H). Excitation energies for $\sigma\rightarrow\sigma^*$ are all set equal to an adjustable parameter a which is expected to be around 1. Hereafter, Hartree's atomic units are employed unless otherwise specified. The one-center integrals needed in this scheme are all for the 2p orbitals of the C atom and set equal to one parameter γ_{00}=(93/256)ζ whose value is expected to be around 0.6 (i.e. 17 eV) (or ζ=1.6) as evaluated from the Slater orbitals. The two-center integrals γ_{pq} are all set equal to $1/R_{pq}$ which is the leading term in the expansion of γ_{pq} when the Slater orbitals are used. The resonance integrals β_{pq} are set to be $-bS_{pq}/R_{pq}$, where S_{pq} are the overlap integrals evaluated with the Slater orbitals, and b is an adjustable parameter which is expected to be around 1. Values of these parameters (a, b, ζ) are determined in such a way that the calculated transition energies fit the observed values for the N→T, V transitions of ethylene and butadiene.

Low-lying excited states of conjugated molecules are usually well described as linear combinations of singly excited configurations. However, the 2^1Ag state of linear polyenes is the well-known exception where doubly excited configurations are thought to be more important.[7)] Thus, in the present study, we employ the (1p-1h) plus (2p-2h) EOM[8)] which may also be termed as the 2nd higher RPA.[1b)] The proposed scheme is applied to all-trans linear polyenes through dodecahexaene.

The EOM method employed in the present work is closely related to the propagator methods. A recent review article[9)] gives ample references on these methods.

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1. Summary of the (1p-1h)+(2p-2h) EOM[8]

The following form is assumed for the excitation operator:

$$O^\dagger(\lambda SM) = \Sigma_{m\gamma}\{Y_{m\gamma}(\lambda S)C_{m\gamma}{}^\dagger(SM) - Z_{m\gamma}(\lambda S)C_{m\gamma}(\overline{SM})\}$$
$$+ \Sigma_{(m\gamma,n\delta)}\{Y^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)\Gamma_{(m\gamma,n\delta)}{}^\dagger(SM)$$
$$-Z^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)\Gamma_{(m\gamma,n\delta)}(\overline{SM})\}. \quad (3)$$

In this expression, $C_{m\gamma}{}^\dagger(SM)$ and $C_{m\gamma}(\overline{SM})$ are the creation and annihilation operator of particle-hole (1p-1h) pairs (m, γ),[1a] and $\Gamma_{(m\gamma,\, n\delta)}{}^\dagger(SM)$ and $\Gamma_{(m\gamma,\, n\delta)}(\overline{SM})$ are the creation and annihilation operators of 2p-2h states $(m\gamma,\ n\delta)$.[1b,8] They produce excited states with spin symmetry $(S,\ M)$ by their action on the closed-shell ground state $|0\rangle$. Hereafter, m and n refer to unoccupied (particle state) orbitals, and γ and δ to occupied (hole state) orbitals. They are assumed to be the Hartree-Fock (HF) orbitals. The $\Gamma_{(m\gamma,\, n\delta)}{}^\dagger$ listed in Table 1 are "orthonormal" in a sense that the 2p-2h states created by these operators acting on the Hartree-Fock ground state $|HF\rangle$ are orthonormal.

With this excitation operator $O^\dagger(\lambda)$, Eq. 2 approximately leads[8] to

$$\begin{bmatrix} \mathscr{A} & \mathscr{B} & \mathscr{A}^{\circ(1,2)} & 0 \\ -\mathscr{B} & -\mathscr{A} & 0 & -\mathscr{A}^{\circ(1,2)} \\ \mathscr{A}^{\circ(2,1)} & 0 & A^{\circ(2,2)} & 0 \\ 0 & -\mathscr{A}^{\circ(2,1)} & 0 & -A^{\circ(2,2)} \end{bmatrix} \begin{bmatrix} \mathscr{Y} \\ \mathscr{Z} \\ Y^{(2)} \\ Z^{(2)} \end{bmatrix}$$
$$= \omega \begin{bmatrix} \mathscr{Y} \\ \mathscr{Z} \\ Y^{(2)} \\ Z^{(2)} \end{bmatrix}. \quad (4)$$

In this matrix equation,

$$\mathscr{Y}_{m\gamma} = g_{m\gamma}Y_{m\gamma};\ \mathscr{Z}_{m\gamma} = g_{m\gamma}Z_{m\gamma}, \quad (5)$$

$$g_{m\gamma} = (1 + \rho_{\gamma\gamma} - \rho_{mm})^{1/2}, \quad (6)$$

$$\mathscr{A}_{m\gamma,n\delta}(S) = \delta_{mn}\delta_{\gamma\delta}(\varepsilon_m - \varepsilon_\gamma)$$
$$+ \{-[(mn\,|\,\gamma\delta) + \delta_{mn}T_{\gamma\delta} - \delta_{\gamma\delta}T_{mn}]$$
$$+ (\delta_{S0})2(m\gamma\,|\,n\delta)\}/(g_{m\gamma}g_{n\delta}), \quad (7a)$$

$$\mathscr{B}_{m\gamma,n\delta}(S) = \{-(-1)^S[(m\delta\,|\,n\gamma) - S_{m\gamma,n\delta}]$$
$$+ (\delta_{S0})2(m\gamma\,|\,n\delta)\}/(g_{m\gamma}\,g_{n\delta}), \quad (7b)$$

$$S_{m\gamma,n\delta} = -\ \Sigma_{p\mu}[(m\delta\,|\,p\mu)C_{p\mu,n\gamma}(0) + (n\gamma\,|\,p\mu)C_{p\mu,m\delta}(0)], \quad (8a)$$

$$T_{mn} = (1/2)\Sigma_\nu S_{m\nu,n\nu};\ T_{\gamma\delta} = -\ (1/2)\Sigma_p S_{p\gamma,p\delta}, \quad (8b)$$

$$\rho_{mn} = (1/2)\Sigma_{p\mu\nu}\Sigma_{S=0,1}C'_{m\nu,p\mu}(S)C_{n\nu,p\mu}(S), \quad (9a)$$

$$\rho_{\gamma\delta} = -\ (1/2)\Sigma_{pq\mu}\Sigma_{S=0,1}C'_{q\gamma,p\mu}(S)C_{q\delta,p\mu}(S), \quad (9b)$$

where

$$C'(0) = [3C(0) + C(1)]/4;\ C'(1) = [C(0) + 3C(1)]/4 \quad (10)$$

and

$$C_{m\gamma,n\delta}(S) = -\ [-(-1)^S(m\delta\,|\,n\gamma)$$
$$+ (\delta_{S0})2(m\gamma\,|\,n\delta)]/(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta). \quad (11)$$

Hereafter, p and q refer to unoccupied orbitals and μ and ν to occupied orbitals. In these expressions, ε_k is the HF orbital energy and $(ij|kl)$ is the two-electron molecular integral:

$$(ij\,|\,kl) = \int[i(1)j(1)](1/r_{12})[k(2)l(2)]\ \mathrm{d}v_1\mathrm{d}v_2. \quad (12)$$

In Eq. 4,

$$\mathscr{A}^{\circ(2,1)} = \tilde{\mathscr{A}}^{\circ(1,2)}, \quad (13a)$$

$$\mathscr{A}^{\circ(1,2)}{}_{m'\gamma':(m\gamma,n\delta)}(S) = A^{\circ(1,2)}{}_{m'\gamma':(m\gamma,n\delta)}(S)/g_{m'\gamma'}, \quad (13b)$$

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

$S=M=0$	
$\Gamma_{(m\gamma,m\gamma)}{}^\dagger = C_{m\gamma}{}^\dagger(00)C_{m\gamma}{}^\dagger(00)$	
$\Gamma_{(m\gamma,n\gamma)}{}^\dagger = \sqrt{2}C_{m\gamma}{}^\dagger(00)C_{n\gamma}{}^\dagger(00)$	$(m \neq n)$
$\Gamma_{(m\gamma,m\delta)}{}^\dagger = \sqrt{2}C_{m\gamma}{}^\dagger(00)C_{m\delta}{}^\dagger(00)$	$(\gamma \neq \delta)$
$\Gamma_{(m\gamma,n\delta)_1}{}^\dagger = C_{m\gamma}{}^\dagger(00)C_{n\delta}{}^\dagger(00) + C_{m\delta}{}^\dagger(00)C_{n\gamma}{}^\dagger(00)$	$(m \neq n, \gamma \neq \delta)$
$\Gamma_{(m\gamma,n\delta)_2}{}^\dagger = (1/\sqrt{3})[C_{m\gamma}{}^\dagger(00)C_{n\delta}{}^\dagger(00) - C_{m\delta}{}^\dagger(00)C_{n\gamma}{}^\dagger(00)]$	$(m \neq n, \gamma \neq \delta)$
$S=1,\ M=0$	
$\Gamma_{(m\gamma,n\gamma)}{}^\dagger = (1/\sqrt{2})[C_{m\gamma}{}^\dagger(10)C_{n\gamma}{}^\dagger(00) - C_{n\gamma}{}^\dagger(10)C_{m\gamma}{}^\dagger(00)]$	$(m \neq n)$
$\Gamma_{(m\gamma,m\delta)}{}^\dagger = (1/\sqrt{2})[C_{m\gamma}{}^\dagger(10)C_{m\delta}{}^\dagger(00) - C_{m\delta}{}^\dagger(10)C_{m\gamma}{}^\dagger(00)]$	$(\gamma \neq \delta)$
$\Gamma_{(m\gamma,n\delta)_1}{}^\dagger = (1/2)[C_{m\gamma}{}^\dagger(10)C_{n\delta}{}^\dagger(00) - C_{n\delta}{}^\dagger(10)C_{m\gamma}{}^\dagger(00)]$ $+ [C_{m\delta}{}^\dagger(10)C_{n\gamma}{}^\dagger(00) - C_{n\gamma}{}^\dagger(10)C_{m\delta}{}^\dagger(00)]$	$(m \neq n, \gamma \neq \delta)$
$\Gamma_{(m\gamma,n\delta)_2}{}^\dagger = (1/2)[C_{m\gamma}{}^\dagger(10)C_{n\delta}{}^\dagger(00) - C_{n\delta}{}^\dagger(10)C_{m\gamma}{}^\dagger(00)$ $- C_{m\delta}{}^\dagger(10)C_{n\gamma}{}^\dagger(00) + C_{n\gamma}{}^\dagger(10)C_{m\delta}{}^\dagger(00)]$	$(m \neq n, \gamma \neq \delta)$
$\Gamma_{(m\gamma,n\delta)_3}{}^\dagger = (1/\sqrt{2})[C_{m\gamma}{}^\dagger(10)C_{n\delta}{}^\dagger(00) + C_{n\delta}{}^\dagger(10)C_{m\gamma}{}^\dagger(00)]$	$(m \neq n, \gamma \neq \delta)$

and $A^{\circ(1,2)}$ and $A^{\circ(2,2)}$ are defined by

$$A^{\circ(1,2)}{}_{m'\gamma';(m\gamma,n\delta)}(S) \equiv <HF|[C_{m'\gamma'}(S0),H,\Gamma_{(m\gamma,n\delta)}{}^{\dagger}(S0)]|HF>, \tag{14a}$$

$$\begin{aligned} &A^{\circ(2,2)}{}_{(m'\gamma',n'\delta');(m\gamma,n\delta)}(S) \\ &\quad \equiv <HF|[\Gamma_{(m'\gamma',n'\delta')}(S0),H,\Gamma_{(m\gamma,n\delta)}{}^{\dagger}(S0)]|HF>, \end{aligned} \tag{14b}$$

where $|HF>$ is the HF ground state (i.e. the noncorrelated part of $|0>$.) Referring to Table 1, we can readily obtain these elements from their primitive ones

$$\begin{aligned} &A^{\circ(1,2)}{}_{m'\gamma';m\gamma,n\delta}(S) \\ &\quad \equiv <HF|[C_{m'\gamma'}(S0),H,C_{m\gamma}{}^{+}(S0)C_{n\delta}{}^{+}(00)]|HF> \\ &\quad = \sqrt{2}\{\delta_{\gamma\gamma'}[(mm'|n\delta) - (nm'|m\delta)/2] \\ &\quad + \delta_{\delta\gamma'}[\delta_{s0}(nm'|m\gamma) - (mm'|n\gamma)/2] \\ &\quad - \delta_{mm'}[(\gamma\gamma'|n\delta) - (\delta\gamma'|n\gamma)/2] \\ &\quad -\delta_{nm'}[\delta_{s0}(\delta\gamma'|m\gamma) - (\gamma\gamma'|m\delta)/2]\}; \end{aligned} \tag{15}$$

$$\begin{aligned} &A^{\circ(2,2)}{}_{m'\gamma',n'\delta';m\gamma,n\delta}(S) \\ &\quad \equiv <HF|[(C_{m'\gamma'}{}^{+}(S0)C_{n'\delta'}{}^{+}(00))^{\dagger}, \\ &\qquad\qquad H,C_{m\gamma}{}^{+}(S0)C_{n\delta}{}^{+}(00)]|HF> \\ &\quad = \{(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta)[(\delta_{mm'}\delta_{nn'}\delta_{\gamma\gamma'}\delta_{\delta\delta'} \\ &\quad - \delta_{mm'}\delta_{nn'}\delta_{\delta\gamma'}\delta_{\gamma\delta'}/2 - \delta_{nm'}\delta_{mn'}\delta_{\gamma\gamma'}\delta_{\delta\delta'}/2) \\ &\quad + (\delta_{s0})\delta_{nm'}\delta_{mn'}\delta_{\delta\gamma'}\delta_{\gamma\delta'}] \\ &\quad + (\delta_{mm'}\delta_{nn'} - \delta_{nm'}\delta_{mn'}/2)(\gamma\gamma'|\delta\delta') \\ &\quad + ((\delta_{s0})\delta_{nm'}\delta_{mn'} - \delta_{mm'}\delta_{nn'}/2)(\delta\gamma'|\gamma\delta') \\ &\quad + (\delta_{\gamma\gamma'}\delta_{\delta\delta'} - \delta_{\delta\gamma'}\delta_{\gamma\delta'}/2)(mm'|nn') \\ &\quad + ((\delta_{s0})\delta_{\delta\gamma'}\delta_{\gamma\delta'} - \delta_{\gamma\gamma'}\delta_{\delta\delta'}/2)(mn'|nm')\} \\ &\quad + \{[\delta_{mm'}\delta_{\gamma\gamma'}2(n'\delta'|n\delta) - (\delta_{mm'}\delta_{\gamma\delta'}(n'\gamma'|n\delta) \\ &\quad + \delta_{mn'}\delta_{\gamma\gamma'}(m'\delta'|n\delta) + \delta_{nm'}\delta_{\gamma\gamma'}(n'\delta'|m\delta) \\ &\quad + \delta_{mm'}\delta_{\delta\gamma'}(n'\delta'|n\gamma)) + (1/2)(\delta_{mm'}\delta_{\delta\delta'}(n'\gamma'|n\gamma) \\ &\quad + \delta_{nn'}\delta_{\gamma\gamma'}(m'\delta'|m\delta) + \delta_{nm'}\delta_{\gamma\delta'}(n'\gamma'|m\delta) \\ &\quad + \delta_{mn'}\delta_{\delta\gamma'}(m'\delta'|n\gamma))] + (\delta_{s0})[2(\delta_{nm'}\delta_{\delta\gamma'}(n'\delta'|m\gamma) \\ &\quad + \delta_{mn'}\delta_{\gamma\delta'}(m'\gamma'|n\delta) + \delta_{nn'}\delta_{\delta\delta'}(m'\gamma'|m\gamma)) \\ &\quad - (\delta_{nn'}\delta_{\delta\gamma'}(m'\delta'|m\gamma) + \delta_{nm'}\delta_{\delta\delta'}(n'\gamma'|m\gamma) \\ &\quad + \delta_{mn'}\delta_{\delta\delta'}(m'\gamma'|n\gamma) + \delta_{nn'}\delta_{\gamma\delta'}(m'\gamma'|m\delta))]\} \\ &\quad + \{[- (\delta_{mm'}\delta_{\delta\delta'}(nn'|\gamma\gamma') + \delta_{nn'}\delta_{\gamma\gamma'}(mm'|\delta\delta') \\ &\quad + \delta_{mm'}\delta_{\gamma\gamma'}(nn'|\delta\delta') + \delta_{nn'}\delta_{\delta\delta'}(mm'|\gamma\gamma')) \\ &\quad + (1/2)(\delta_{mm'}\delta_{\gamma\delta'}(nn'|\delta\gamma') + (\delta_{mn'}\delta_{\gamma\gamma'}(nm'|\delta\delta') \\ &\quad + \delta_{nm'}\delta_{\gamma\gamma'}(mn'|\delta\delta') + \delta_{mm'}\delta_{\delta\gamma'}(nn'|\gamma\delta') \\ &\quad + \delta_{nn'}\delta_{\delta\gamma'}(mm'|\gamma\delta') + \delta_{nm'}\delta_{\delta\delta'}(mn'|\gamma\gamma') \\ &\quad + \delta_{mn'}\delta_{\delta\delta'}(nm'|\gamma\gamma') + \delta_{nn'}\delta_{\gamma\delta'}(mm'|\delta\gamma'))] \\ &\quad + (\delta_{s0})[- (\delta_{nm'}\delta_{\gamma\delta'}(mn'|\delta\gamma') + \delta_{mn'}\delta_{\delta\gamma'}(nm'|\gamma\delta') \\ &\quad + \delta_{nm'}\delta_{\delta\gamma'}(mn'|\gamma\delta') + \delta_{mn'}\delta_{\gamma\delta'}(nm'|\delta\gamma'))]\}. \end{aligned} \tag{16}$$

In solving Eq. 4, we split it into two equations. By doing so, the order of the matrix to be diagonalized is reduced to half. They are written as follows:

$$\begin{bmatrix} \mathscr{A} - \mathscr{B} & \mathscr{A}^{\circ(1,2)} \\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix} \begin{bmatrix} \mathscr{A} + \mathscr{B} & \mathscr{A}^{\circ(1,2)} \\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix} \begin{bmatrix} \mathscr{Y} + \mathscr{X} \\ Y^{(2)} + Z^{(2)} \end{bmatrix} = \omega^2 \begin{bmatrix} \mathscr{Y} + \mathscr{X} \\ Y^{(2)} + Z^{(2)} \end{bmatrix}; \tag{17a}$$

$$\begin{bmatrix} \mathscr{A} + \mathscr{B} & A^{\circ(1,2)} \\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix} \begin{bmatrix} \mathscr{A} - \mathscr{B} & A^{\circ(1,2)} \\ \mathscr{A}^{\circ(2,1)} & A^{\circ(2,2)} \end{bmatrix} \begin{bmatrix} \mathscr{Y} - \mathscr{X} \\ Y^{(2)} - Z^{(2)} \end{bmatrix} = \omega^2 \begin{bmatrix} \mathscr{Y} - \mathscr{X} \\ Y^{(2)} - Z^{(2)} \end{bmatrix}. \tag{17b}$$

Note that the eigenvalues in these equations are ω^2.

The transition dipole moment is given by

$$\begin{aligned} \boldsymbol{D}_\lambda \equiv -<0|(\boldsymbol{r})_{op}|\lambda> = (\delta_{s0})\sqrt{2}\textstyle\sum_{m\gamma}\{\mathscr{Y}_{m\gamma}(\lambda 0) \\ + \mathscr{X}_{m\gamma}(\lambda 0)\}(g_{m\gamma}\boldsymbol{d}^{\circ}{}_{m\gamma}), \end{aligned} \tag{18}$$

where

$$\boldsymbol{d}^{\circ}{}_{m\gamma} \equiv \int m(\boldsymbol{r})\boldsymbol{r}\gamma(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r}. \tag{19}$$

Note that terms of $Y^{(2)}$ and $Z^{(2)}$ vanish in deriving the last expression of Eq. 18.[8] The oscillator strength is written

$$f_\lambda = (2/3)\omega_\lambda|\boldsymbol{D}_\lambda|^2. \tag{20}$$

It is important to note that the result in Eq. 18 has been derived on the assumption of the normalization condition $<\lambda|\lambda>=1$ or equivalently

$$\begin{aligned} &\textstyle\sum_{m\gamma}\{|\mathscr{Y}_{m\gamma}(\lambda S)|^2 - |\mathscr{X}_{m\gamma}(\lambda S)|^2\} \\ &\quad + \textstyle\sum_{(m\gamma,n\delta)}\{|Y^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)|^2 - |Z^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)|^2\} = 1. \end{aligned} \tag{21}$$

Thus, $\boldsymbol{D}_\lambda$ is indirectly affected by $Y^{(2)}$ and $Z^{(2)}$ through this normalization condition. Normalization of the eigenvectors of the reduced Eqs. 17a,b must be handled with great care so that they satisfy Eq. 21.[10]

2. Effective EOM for the $\pi \rightarrow \pi^*$ Transitions

Previously[2,3] an effective EOM for the $\pi \rightarrow \pi^*$ transitions was derived by partitioning the (1p-1h) EOM into the $\Pi \equiv (\pi^*,\pi)$ and $\Sigma \equiv (\sigma^*, \sigma)$ parts. The assumption of the zero differential overlaps between pi- and sigma-orbitals leads[4] to

$$\mathscr{A}_{\sigma^*\sigma,\pi^*\pi}(S) = \mathscr{B}_{\sigma^*\sigma,\pi^*\pi}(S) = (\delta_{s0})2(\sigma^*\sigma|\pi^*\pi)/(g_{\sigma^*\sigma}g_{\pi^*\pi}). \tag{22}$$

We shall later let $g_{\sigma^*\sigma}=1$. It was then shown[2] that the effect of the Σ part on the EOM for the Π part was to reduce the integral $(m\gamma|n\delta)$ in $\mathscr{A}$ and $\mathscr{B}$, Eq. 7, as follows:

$$(m\gamma|n\delta) \rightarrow (m\gamma|n\delta)'' = (m\gamma|n\delta) - \frac{a}{a^2 - \omega_\lambda{}^2}\, G_{m\gamma,n\delta}, \tag{23}$$

where

$$G_{m\gamma,n\delta} = 4\textstyle\sum_{\sigma^*\sigma}(m\gamma|\sigma^*\sigma)(n\delta|\sigma^*\sigma). \tag{24}$$

Henceforth, m and n refer to the π^*-orbitals, and γ and

δ to the π-orbitals. In deriving Eq. 23, we have set all the diagonal elements $\mathscr{A}_{\sigma^*\sigma,\sigma^*\sigma}$ equal to one adjustable parameter a which is expected to be around 1 (in Hartree a.u.). In order to calculate G in Eq. 24, we construct sigma-orbitals by linear combinations of sp^2 hydrids for carbon and 1s orbitals for hydrogen. Employing the approximation of complete neglect of differential overlaps between sigma-AO's and the approximation that all the charge densities of sigma-AO's be 1 and the bond orders be 1 for bonded sigma-AO's and 0 otherwise, we have

$$G_{m\gamma,n\delta} = \sum_{\eta}^{\text{sigma-bonds}} [m\gamma|\eta][n\delta|\eta], \tag{25}$$

where, for a sigma-bond (η) formed by sigma-AO's u and v,

$$[m\gamma|\eta][n\delta|\eta] \equiv [(m\gamma|uu) - (m\gamma|vv)][(n\delta|uu) - (n\delta|vv)]. \tag{26}$$

In dealing with the 2p-2h states, we shall consider only those of pi-electrons and ignore any 2p-2h states in which sigma-electrons are involved. Then, our effective EOM for pi-electrons takes the same form as Eq. 4 or 17 with m and n referring to the π^*-orbitals and γ and δ to the π-orbitals. Only the difference is that the integral $(m\gamma|n\delta)$ in Eq. 7 should be replaced by $(m\gamma|n\delta)''$ given in Eq. 23. In computing the S, T, and ρ in Eqs. 8a—9b, however, note that the summations of p and q run over both π^* and σ^*, and the summations of μ and ν run over both π and σ. Therefore, if these summations are restricted to running over only π- and π^*-orbitals in the effective EOM for the $\pi \rightarrow \pi^*$ transitions, one must add to these S, T, and ρ the following correction terms S', T', and ρ', respectively, due to correlations with sigma-electrons. As is shown in Appendix A, they are written as

$$S'_{m\gamma,n\delta} = (1/2)[(a + \varepsilon_m - \varepsilon_\delta)^{-1} + (a + \varepsilon_n - \varepsilon_\gamma)^{-1}]G_{m\delta,n\gamma}, \tag{27}$$

$$T'_{mn} = (1/2)\sum_{\pi} S'_{m\pi,n\pi}\,;\; T'_{\gamma\delta} = -(1/2)\sum_{\pi^*} S'_{\pi^*\gamma,\pi^*\delta}, \tag{28}$$

$$\rho'_{mm} = (1/2)\sum_{\pi} G_{m\pi,m\pi}/(a + \varepsilon_m - \varepsilon_\pi)^2; \tag{29a}$$

$$\rho'_{\gamma\gamma} = -(1/2)\sum_{\pi^*} G_{\pi^*\gamma,\pi^*\gamma}/(a + \varepsilon_{\pi^*} - \varepsilon_\gamma)^2. \tag{29b}$$

When Eq. 4 or 17, with the replacement of Eq. 23, is solved for pi-electrons, the normalization condition in Eq. 21 is satisfied for the amplitudes of pi-electrons. Then, the norm $<\lambda|\lambda>$ becomes greater than 1 due to contributions from the amplitudes of sigma-electrons. As is shown in Appendix B, we have

$$\begin{aligned} N_\lambda^2 &\equiv <\lambda|\lambda> \\ &\cong 1 + \\ &(\delta_{s0})\frac{4a\omega_\lambda}{(a^2 - \omega_\lambda^2)^2} \sum_{\pi_1^*\pi_1}\sum_{\pi_2^*\pi_2}(G_{\pi_1^*\pi_1,\pi_2^*\pi_2}/[g_{\pi_1^*\pi_1}\,g_{\pi_2^*\pi_2}]) \\ &\times \{\mathscr{Y}_{\pi_1^*\pi_1}(\lambda) + \mathscr{Z}_{\pi_1^*\pi_1}(\lambda)\}\{\mathscr{Y}_{\pi_2^*\pi_2}(\lambda) + \mathscr{Z}_{\pi_2^*\pi_2}(\lambda)\}. \end{aligned} \tag{30}$$

Thus, the transition dipole moment in Eq. 18 should be written as

$$\boldsymbol{D}_\lambda = (\delta_{s0})N_\lambda^{-1}\sqrt{2}\sum_{m\gamma}\{\mathscr{Y}_{m\gamma}(\lambda 0) + \mathscr{Z}_{m\gamma}(\lambda 0)\}(g_{m\gamma}\boldsymbol{d}^\circ_{m\gamma}). \tag{31}$$

3. Parametrization

A parameter a has been already introduced as an averaged energy for the $\sigma \rightarrow \sigma^*$ excitations. In evaluating the two-electron integrals, we have been employing the zero-differential overlap (ZDO) approximation. For these integrals, we only have the following types:

$$\begin{aligned} (ij|kl) = {} & \sum_p C^{(i)}{}_p C^{(j)}{}_p C^{(k)}{}_p C^{(l)}{}_p \gamma_{pp} \\ & + \sum_{\substack{p \\ (p\neq q)}}\sum_q C^{(i)}{}_p C^{(j)}{}_p C^{(k)}{}_q C^{(l)}{}_q \gamma_{pq}; \end{aligned} \tag{32a}$$

$$(ij|u_q u_q) = C^{(i)}{}_q C^{(j)}{}_q \gamma'_{qu_q} + \sum_{p(\neq q)} C^{(i)}{}_p C^{(j)}{}_p \gamma'_{pu_q}, \tag{32b}$$

where i, j, k, and l refer to π and/or π^* MO's and u_q is a sigma-AO at atom q. The coefficients $C^{(k)}{}_p$ are of the SCF pi-MO k. We set

$$\gamma_{pp} = \gamma'_{pu_p} = \gamma_{00} \equiv (93/256)\zeta; \tag{33a}$$

$$\gamma_{pq} = \gamma'_{pu_q} = 1/R_{pq} \quad (p \neq q), \tag{33b}$$

where R_{pq} is the distance between atoms p and q.

Now, the SCF-MO's for pi-electrons are obtained according to the usual procedure.[11] The coefficients of the LCAO-MO's and the orbital energies satisfy the equations

$$\sum_s F_{rs} C^{(i)}{}_s = \varepsilon_i C^{(i)}{}_r, \tag{34}$$

where the Fock matrix elements are, in the ZDO approximation,

$$F_{rr} = H_{rr} + (1/2)P_{rr}\gamma_{rr} + \sum_{s(\neq r)} P_{ss}\gamma_{rs}; \tag{35a}$$

$$F_{rs} = H_{rs} - (1/2)P_{rs}\gamma_{rs} \qquad (r \neq s), \tag{35b}$$

and

$$P_{rs} \equiv 2\sum_i^{occ} C^{(i)}{}_r C^{(i)}{}_s. \tag{36}$$

The diagonal elements H_{rr} of the core Hamiltonian operator are approximated as

$$H_{rr} = U_{rr} - \sum_{s(\neq r)} \gamma_{rs}, \tag{37}$$

where the one-center terms U_{rr} are all the same (U_0) for carbon atoms. We set

$$U_{rr} = U_0 = -0.4101 \text{ (the negative of I.P. for C(2p))}, \tag{38}$$

although any other value of U_0 suffices for the present purpose as we need only the orbital coefficients and the orbital energy differences rather than the absolute values of ε_k. The off-diagonal core matrix elements H_{rs} are approximated to be the resonance integrals. Here we employ Ohno's proposal[12] that

$$\beta_{rs} = (\gamma_{rs} - 2/R_{rs})S_{rs}. \tag{39}$$

We therefore set

$$H_{rs} = \beta_{rs} = -bS_{rs}/R_{rs}, \tag{40}$$

where b is an adjustable parameter whose value is expected to be around 1 and S_{rs} is the overlap integral

$$S_{rs} = [1 + \rho + (2/5)\rho^2 + (1/15)\rho^3]\exp(-\rho); \quad \rho \equiv \zeta R_{rs}. \tag{41}$$

Note that the simple replacement of γ_{rs} by $1/R_{rs}$ in Ohno's formula corresponds to letting $b=1$ in Eq. 40.

4. Application to Linear Polyenes

The effective EOM with adjustable parameters described in the preceding sections is now applied to the $\pi \rightarrow \pi^*$ transitions of all-*s*-trans linear polyenes.

(i) Determination of the Values of a, b, and ζ. Values of the parameters a, b, and ζ are determined in such a way that the computed transition energies fit the observed values for the N→T, V transitions of ethylene and butadience. The assignment of 4.6 eV to the N→T and 7.6 eV to the N→V of ethylene is well established.[13] On the other hand, the ordering of the lowest excited states of *s-trans*-butadiene has been a subject of considerable controversy.[7,13–21] In the present work, we employ the assignment proposed by Doering in his electron impact study,[20a] i.e., 5.9 eV for the optically allowed ^{1}Bu state and 5.8 eV for the 2^1Ag state. The value for the ^{1}Bu state seems well established both in UV spectral[19] and electron impact[20] studies.

These four values are used to determine values of the three parameters a, b, and ζ in the vicinity of $a=1$, $b=1$, and $\zeta=1.6$. An optimized set of values has been obtained as $a=1.10$, $b=1.05$, and $\zeta=1.65$. With these parameter values, we obtain 4.21 eV, 6.65 eV for the T, V states of ethylene, and 5.72 eV, 5.83 eV for the ^{1}Bu, 2^1Ag states of butadiene, respectively.

(ii) Computational Details. Input data of molecular geometries are as follows. The planar shape with the C_{2h} symmetry (D_{2h} for ethylene) is assumed for all the polyene molecules. For ethylene, *s-trans*-butadiene, and *s-trans*-hexatriene, the following experimental data[22] are used: R(C=C)=1.337 Å, R(C–H)=1.103 Å, and ∠HCH=116.2° for ethylene, R(C=C)=1.3405 Å, R(C–C)=1.463 Å, R(C–H)=1.090 Å (averaged), and ∠CCC=123.3° for butadiene, and R(C=C)=1.337 Å at both ends and 1.367 Å at center, R(C–C)=1.457 Å, ∠CCC=121.7° (outer), and 124.4° (inner) for hexatriene. The angular conformation of the CH_2 group at both ends of butadiene and hexatriene is assumed to be the same as that of ethylene. All the ∠CCH's, except at both ends, are assumed to be the same, and R(C–H)=1.09 Å is assumed for all the C–H bonds. For longer polyenes, we set R(C=C)=1.367 Å (but 1.337 Å at both ends), R(C–C)=1.457 Å, R(C–H)=1.09 Å and ∠HCH=∠CCH=∠CCC=120°.

With these molecular geometries and a given set of parameters a, b, and ζ, the SCF-MO's for pi-electrons are obtained by solving the secular equations of Eq. 34. Then, the matrices $\mathscr{A}$, $\mathscr{B}$, $\mathscr{A}^{\circ(1,2)}$, and $A^{\circ(2,2)}$ are constructed including the S', T', and ρ' described in Section 2, and Eq. 17a or 17b is solved for ω. For each singlet transition, the molecular integrals $(m\gamma|n\delta)$ of $\mathscr{A}$ and $\mathscr{B}$ are replaced by the reduced quantities $(m\gamma|n\delta)''$ with the previously obtained eigenvalue of ω, and Eq. 17a or 17b with these new $\mathscr{A}$ and $\mathscr{B}$ is solved to give final results for the singlet transition. As mentioned above, great care is needed in normalization of the eigenvectors in this case.[10]

(iii) Results. The transition energies computed with the parameter values ($a=1.10$, $b=1.05$, and $\zeta=1.65$) are listed in Table 2. The weight of (2p-2h) components, i.e. the value of the second term in Eq. 21, is also given in parentheses for each transition. For the allowed transitions, 1^1Ag→1^1Bu, the oscillator strengths are given in square brackets. Due to the correction of Eq. 23, i.e. the sigma-dynamical screening effect, the transition energy for the 1^1Bu state was reduced by 1.56 eV for ethylene, 1.16 eV for butadiene, 1.05 eV for hexatriene, 1.03 eV for octatetraene, 1.00 eV for decapentaene, and 1.00 eV for dodecahexaene. Such reduction was negligibly small for the 2^1Ag states: 0.02 eV for butadiene, 0.01 eV for hexatriene, 0.003 eV for octatetraene, and so forth. All of these 2^1Ag states were of Ag^- type. The observed values for ^{1}Bu listed in Table 2 are all taken from Table 2 of Ref. 7. They agree very well with those more recently given by Leopold et al.,[23] i.e., 5.74 eV for butadiene, 4.93 eV for hexatriene, and 4.41 eV for octatetraene. Ramasesha and Soos[24a] gave values of the oscillator strength per site by their "exact" PPP calculations. They are 0.169 for hexatriene, 0.164 for octatetraene, and 0.159 for decapentaene, which may be compared with our values 0.193, 0.184, and 0.180, respectively. The oscillator strength f is plotted against the number of double bonds in Fig. 1. The f value of the s-trans linear polyene with 11 double bonds is that of β-carotene which was deduced from its absorption intensities in various organic solvents[25] using the dielectric theory proposed by Shibuya.[26] The transition energies for 1^3Bu, 1^3Ag, 1^1Bu, and 2^1Ag are plotted in Fig. 2.

5. Discussion

The numerical results presented in the preceding Section appear fairly reasonable as a whole. As is seen

Table 2. Computed Transition Energies (in eV) to the Low-Lying Valence States of All-s-Trans Linear Polyenes

	^{3}Bu	(obsd)	^{3}Ag	(obsd)	^{1}Bu	(obsd)[a]	2^{1}Ag	(obsd)[a]
Butadiene	3.44 (0.05)	3.2[b]	4.61 (0.01)	4.95[b]	5.72 (0.007) [0.85]	5.91	5.83 (0.73)	
Hexatriene	2.88 (0.08)	2.7[c]	4.04 (0.06)	4.2[c]	4.93 (0.02) [1.16]	4.93	4.89 (0.77)	
Octatetraene	2.58 (0.11)	2.1[d]	3.48 (0.08)	3.6[d]	4.42 (0.02) [1.47]	4.40	4.21 (0.79)	3.97
Decapentaene	2.41 (0.13)		3.11 (0.10)		4.08 (0.03) [1.80]	4.02	3.86 (0.81)	3.48
Dodecahexaene	2.32 (0.14)		2.85 (0.12)		3.83 (0.029) [2.137]	3.65	3.67 (0.82)	2.91

Values in parentheses are the weights of (2p–2h) components, and values in square brackets are the oscillator strengths. a) All taken from the review article of Hudson et al.[7] b) From Doering.[20a] c) R. McDiarmid, A. Sabljic, and J. P. Doering, *J. Am. Chem. Soc.*, **107**, 826 (1985). d) M. Allan, L. Neuhaus, and E. Haselbach, *Helv. Chim. Acta*, **67**, 1776 (1984).

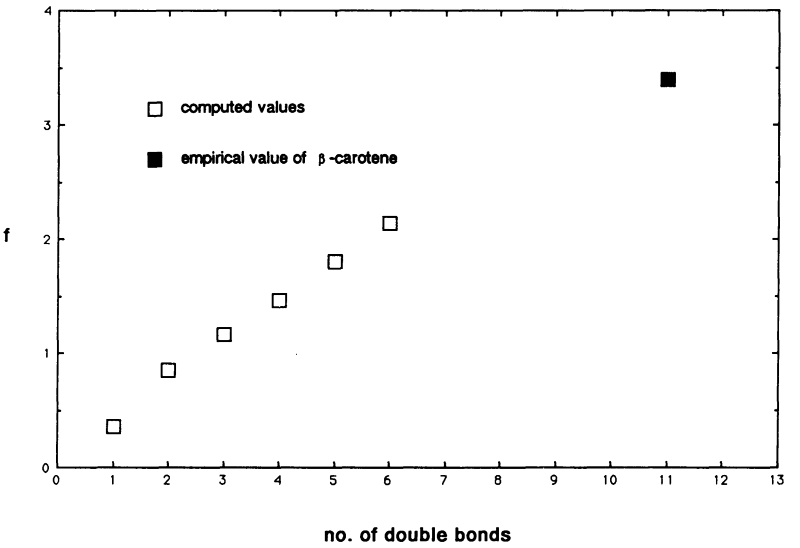

Fig. 1. The oscillator strength (*f*) of the 1^{1}Bu transition of all-s-trans linear polyenes against the number of double bonds. The empirical value of β-carotene was deduced from its absorption intensities in various organic solvents[25] using the dielectric theory.[26]

in Fig. 1, the plot of the calculated oscillator strengths well extrapolates to the "empirical" value of β-carotene. The computed transition energies of the allowed ^{1}Bu states are all in excellent agreement with experiment. The 2^{1}Ag states, which mostly lie below the allowed ^{1}Bu states, were found to be essentially dominated by the 2p-2h states. This agrees with the widely accepted notion.[7] Figure 2 indicates that these transition energies converge to certain finite values as the number of double bonds increases.

We have tried to see whether a pure pi-electron EOM scheme is possibly constructed. This means that not only the sigma-dynamical screening Eq. 23 is omitted but also the correction terms S', T', and ρ' are ignored. In this case we would have only two parameters b and ζ. This, however, was not successful: The EOM became instable for the triplet transitions. The inclusion of the correction terms S' and T' was

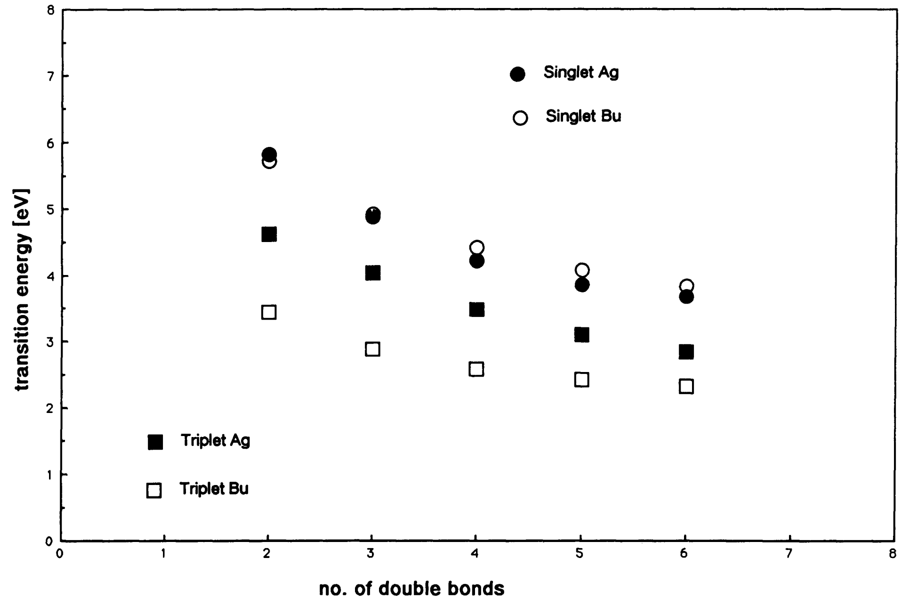

Fig. 2. Calculated transition energies for the four lowest excited valence states (1^3Bu, 1^3Ag, 1^1Bu, 2^1Ag) of all-s-trans linear polyenes against the number of double bonds.

essential. Parametrization at the RPA level would also fail, as the RPA fails for the triplet transitions already in its non-empirical treatment.[1)]

Great interest in polyacetylene $(CH)_x$ as an electronic material has stimulated some recent investigations of the low-lying excitations in linear polyenes.[24,27–29)] Gutsev et al.[27)] employed the Discrete Variational Xα method, but all the other investigators[24,28–29)] employed schemes in the framework of the PPP approximation. Hemley et al.[30)] employed an extended PPP-CI theory to analyze the absorption spectra of the $1A_g \to 1^1B_u$ transition of jet-cooled hexatriene.[23b)]

Application of the present scheme to nonlinear conjugated hydrocarbons is straightforward,and such a study is currently in progress.

Appendix A: The Correction Terms S', T', and ρ'

From Eq. 8a, we have

$$S'_{m\gamma,n\delta} = -\ \Sigma_{\sigma^*\sigma}[(m\delta|\sigma^*\sigma)C_{\sigma^*\sigma,n\gamma}(0) + (n\gamma|\sigma^*\sigma)C_{\sigma^*\sigma,m\delta}(0)], \tag{A$\cdot$1}$$

where m and n refer to the π^*-orbitals and γ and δ to the π-orbitals. Note that in the summation of Eq. 8a, the terms for $(p,\mu)=(\pi^*, \sigma)$ and (σ^*, π) vanish due to the symmetry or to the ZDO approximation between the pi- and sigma-orbitals. Using Eq. 11, we have

$$C_{\sigma^*\sigma,n\gamma}(0) = -\ 2(\sigma^*\sigma|n\gamma)/(\varepsilon_n - \varepsilon_\gamma + a), \tag{A$\cdot$2}$$

and a similar expression for $C_{\sigma^*\sigma,m\delta}(0)$. In deriving Eq. A. 2, we have let all the $\varepsilon_{\sigma^*}-\varepsilon_\sigma=a$ according to the approximation introduced in Section 2, and $(\sigma^*\gamma|n\sigma)=0$ due to the ZDO approximation. Substituting these expressions in Eq. A. 1 and using the G defined by Eq. 24, we obtain

$$S'_{m\gamma,n\delta} = (1/2)[(\varepsilon_m - \varepsilon_\delta + a)^{-1} + (\varepsilon_n - \varepsilon_\gamma + a)^{-1}]G_{m\delta,n\gamma}. \tag{A$\cdot$3}$$

To derive T', first note that $S_{m\sigma,n\sigma}=S_{\sigma^*\gamma,\sigma^*\delta}=0$ due to the ZDO approximation. Then, from Eq. 8b together with the result Eq. A. 3, we have

$$T'_{mn} = (1/2)\Sigma_\pi S'_{m\pi,n\pi};\ T'_{\gamma\delta} = -(1/2)\Sigma_{\pi^*}S'_{\pi^*\gamma,\pi^*\delta}. \tag{A$\cdot$4}$$

The derivation of ρ' is more complicated. Substituting Eq. 10 together with Eq. 11 into Eq. 9a, we obtain

$$\begin{aligned}\rho_{mm} = {} & (1/2)\Sigma_{p\mu\nu}[3(p\mu|m\nu)^2 - 2(p\mu|m\nu)(p\nu|m\mu) \\ & + (p\nu|m\mu)^2]/(\varepsilon_p + \varepsilon_m - \varepsilon_\mu - \varepsilon_\nu)^2\end{aligned} \tag{A$\cdot$5}$$

where m refers to the π^*-orbitals, but p to both π^* and σ^*, and μ and ν to both π and σ. We note that the terms in the summation of Eq. A. 5 vanish due to the ZDO approximation if both μ and ν are σ. Similarly, the terms with $\mu\nu=\sigma\pi$ or $\pi\sigma$ are nonvanishing only if $p=\sigma^*$. Therefore,

$$\rho'_{mm} = (1/2)\Sigma_\pi\Sigma_{\sigma^*\sigma}4(\sigma^*\sigma|m\pi)^2/(\varepsilon_m - \varepsilon_\pi + \varepsilon_{\sigma^*} - \varepsilon_\sigma)^2. \tag{A$\cdot$6}$$

Letting all the $\varepsilon_{\sigma^*}-\varepsilon_\sigma=a$, we obtain Eq. 29a. The expression of $\rho'_{\gamma\gamma}$ in Eq. 29b is derived in a similar manner.

Appendix B: The Normalization Constant N_λ^{-1} in Eq. 30

Originally the normalization condition $\langle\lambda|\lambda\rangle=1$ was assumed as in Eq. 21. For the effective EOM for pi-electrons, however, the summations in Eq. 21 run over the 1p-1h and 2p-2h states of pi-electrons only. Thus, $N_\lambda^2=\langle\lambda|\lambda\rangle$ differs from 1 and becomes greater than 1 due to the contribution from the terms of sigma-electrons. In our model, the mixing of $\sigma\rightarrow\sigma^*$ is considered only at the level of 1p-1h states. Therefore,

$$N_\lambda^2 - 1 = \Sigma_{\sigma^*\sigma}\{|\mathscr{Y}_{\sigma^*\sigma}(\lambda)|^2 - |\mathscr{X}_{\sigma^*\sigma}(\lambda)|^2\}$$

$$\equiv [\mathscr{Y}_\Sigma(\lambda) \ - \mathscr{X}_\Sigma(\lambda)] \begin{bmatrix} \mathscr{Y}_\Sigma(\lambda) \\ \mathscr{X}_\Sigma(\lambda) \end{bmatrix}. \quad \text{(B.1)}$$

As was shown earlier,[3]

$$\begin{bmatrix} \mathscr{Y}_\Sigma(\lambda) \\ \mathscr{X}_\Sigma(\lambda) \end{bmatrix} =$$

$$- \begin{bmatrix} (\mathscr{A}_{\Sigma\Sigma} - \omega_\lambda) & \mathscr{B}_{\Sigma\Sigma} \\ -\mathscr{B}_{\Sigma\Sigma} & -(\mathscr{A}_{\Sigma\Sigma} + \omega_\lambda) \end{bmatrix}^{-1} \begin{bmatrix} \mathscr{B}_{\Sigma\Pi} & \mathscr{A}_{\Sigma\Pi} \\ -\mathscr{A}_{\Sigma\Pi} & -\mathscr{B}_{\Sigma\Pi} \end{bmatrix} \begin{bmatrix} \mathscr{Y}_\Pi(\lambda) \\ \mathscr{X}_\Pi(\lambda) \end{bmatrix}. \quad \text{(B.2)}$$

Letting $\mathscr{B}_{\Sigma\Sigma}=0$ and using Eq. 22, we have

$$\begin{bmatrix} \mathscr{Y}_\Sigma(\lambda) \\ \mathscr{X}_\Sigma(\lambda) \end{bmatrix} = \begin{bmatrix} -(\mathscr{A}_{\Sigma\Sigma} - \omega_\lambda)^{-1} \ \mathscr{A}_{\Sigma\Pi} \ \{\mathscr{Y}_\Pi(\lambda) + \mathscr{X}_\Pi(\lambda)\} \\ (\mathscr{A}_{\Sigma\Sigma} + \omega_\lambda)^{-1} \ \mathscr{A}_{\Sigma\Pi} \ \{\mathscr{Y}_\Pi(\lambda) + \mathscr{X}_\Pi(\lambda)\} \end{bmatrix}. \quad \text{(B.3)}$$

So that,

$$\begin{aligned} N_\lambda^2 - 1 = {} & |(\mathscr{A}_{\Sigma\Sigma} - \omega_\lambda)^{-1}\mathscr{A}_{\Sigma\Pi}\{\mathscr{Y}_\Pi(\lambda) + \mathscr{X}_\Pi(\lambda)\}|^2 \\ & - |(\mathscr{A}_{\Sigma\Sigma} + \omega_\lambda)^{-1}\mathscr{A}_{\Sigma\Pi}\{\mathscr{Y}_\Pi(\lambda) + \mathscr{X}_\Pi(\lambda)\}|^2 \\ = {} & [\frac{1}{(a-\omega_\lambda)^2} - \frac{1}{(a+\omega_\lambda)^2}]\Sigma_{\pi_1{}^*\pi_1}\Sigma_{\pi_2{}^*\pi_2}\Sigma_{\sigma^*\sigma} \\ & \{\mathscr{Y}_{\pi_1{}^*\pi_1}(\lambda) + \mathscr{X}_{\pi_1{}^*\pi_1}(\lambda)\} \ \mathscr{A}_{\pi_1{}^*\pi_1,\sigma^*\sigma}(S) \\ & \times \mathscr{A}_{\sigma^*\sigma,\pi_2{}^*\pi_2}(S)\{\mathscr{Y}_{\pi_2{}^*\pi_2}(\lambda) + \mathscr{X}_{\pi_2{}^*\pi_2}(\lambda)\} \end{aligned} \quad \text{(B·4)}$$

In deriving the last expression, we have let $\mathscr{A}_{\sigma^*\sigma,\sigma^*\sigma}=a$ and all the off-diagonal elements of $\mathscr{A}_{\Sigma\Sigma}$ be 0. Now, referring to Eqs. 22 and 24 and letting $g_{\sigma^*\sigma}=1$, we obtain

$$\begin{aligned} N_\lambda^2 - 1 = {} & (\delta_{s0}) \frac{4a\omega_\lambda}{(a^2 - \omega_\lambda{}^2)^2} \Sigma_{\pi_1{}^*\pi_1}\Sigma_{\pi_2{}^*\pi_2} \\ & (G_{\pi_1{}^*\pi_1,\pi_2{}^*\pi_2}/[g_{\pi_1{}^*\pi_1}g_{\pi_2{}^*\pi_2}]) \{\mathscr{Y}_{\pi_1{}^*\pi_1}(\lambda) + \mathscr{X}_{\pi_1{}^*\pi_1}(\lambda)\} \\ & \times \{\mathscr{Y}_{\pi_2{}^*\pi_2}(\lambda) + \mathscr{X}_{\pi_2{}^*\pi_2}(\lambda)\}. \end{aligned} \quad \text{(B·5)}$$

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