Parametrized Equations-of-Motion Method at the (1p-1h)+(2p-2h) Level. II. Simplified Treatment of σ-π Correlations

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(Received February 13, 1990)

The previously proposed scheme of parametrized equations of motion for the π→π* transitions of linear polyenes [*Bull. Chem Soc. Jpn.*, **62**, 701(1989)] has been simplified in the treatment of the σ–π electron correlations. The simplified schemes seem to give results as accurate as the original one for the low-lying excited states.

The conventional π-electron theories including the PPP method are all constructed on the assumption of the σ–π separability.[1] This means that the electronic transitions to low-lying excited states from the ground state are explained by the transitions of π-electrons alone, leaving the σ-electron core unchanged. We have shown[2,3] that this is well justified for the transitions to triplet excited states but not for the singlet excitations. In Paper I[3], we clarified that the σ–π electron correlations involved in the π→π* transitions were two-fold. That is, the correction terms S' and T' which are equally involved both in the triplet and singlet transitions, and the dynamical screenings which are involved only in the singlet transitions. Among the three parameters a, b, and ζ appearing in the proposed scheme, a represents σ→σ* transition energies around 1 in atomic units, b, is a proportionality constant around 1 for the resonance integral, and ζ is an averaged value around 1.625 as determined by Slater's rule for the exponent coefficients of the 2s, $2p_\sigma$, and $2p_\pi$ AO's. The parameter a is involved in the evaluation of σ–π correlation effects.

In the original scheme, the dynamical screening differs for each singlet transition as the transition energy is required to evaluate it. In actual computations of the singlet transitions, we first solve the EOM (equations of motion) with the correction terms S' and T' but without the dynamical screening, and then substitute its eigenvalue for ω_λ in the dynamical screening term in the final form of the EOM. Thus, the EOM with a different dynamical screening must be solved for each singlet transition. However, in the course of actual computations, we noticed that the eigensolutions were practically unchanged regardless of the input value of ω_λ for all the lowest-energy transitions in which we are interested. In this paper, we will first show that the final results are not much altered if we input zero for ω_λ in the dynamical screening term. This will then lead to a further simplified scheme in which not only the transition energies ω_λ but also the π→π* orbital energy differences ε_π*−ε_π are set equal to zero in comparison with the parameter a on evaluation of the correction terms S' and T' as well as the dynamical screening.

1. Summary of the Parametrized EOM Proposed in Paper I[3]

Let m and n refer to the unoccupied π* orbitals, and γ and δ to the occupied π orbitals. The parametrized EOM at the (1p−1h)+(2p−2h) level is written as

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

In this matrix equation,

$$\mathscr{A}_{m\gamma,n\delta}(S) = \delta_{mn}\delta_{\gamma\delta}(\varepsilon_m - \varepsilon_\gamma) + \{-[(mn|\gamma\delta) + \delta_{mn}(T_{\gamma\delta} + T'_{\gamma\delta}) - \delta_{\gamma\delta}(T_{mn} + T'_{mn})] + (\delta_{S0})2(m\gamma|n\delta)''\}/(g_{m\gamma}g_{n\delta}), \quad (2a)$$

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

$$S_{m\gamma,n\delta} = -\sum_{p\mu}[(m\delta|p\mu)C_{p\mu,n\gamma}(0) + (n\gamma|p\mu)C_{p\mu,m\delta}(0)], \quad (3a)$$

$$T_{mn} = (1/2)\sum_\nu S_{m\nu,n\nu} \quad ; \quad T_{\gamma\delta} = -(1/2)\sum_p S_{p\gamma,p\delta}, \quad (3b)$$

$$\rho_{mn} = (1/2)\sum_{p\mu\nu}\sum_{s=0,1} C'_{m\nu,p\mu}(S)C_{n\nu,p\mu}(S) + \rho'_{mn}, \quad (4a)$$

$$\rho_{\gamma\delta} = -(1/2)\sum_{pq\mu}\sum_{s=0,1} C'_{q\gamma,p\mu}(S)C_{q\delta,p\mu}(S) + \rho'_{\gamma\delta}, \quad (4b)$$

$$g_{m\gamma} = (1 + \rho_{\gamma\gamma} - \rho_{mm})^{1/2}, \quad (4c)$$

where

$$C'(0) = [3C(0) + C(1)]/4 \; ; \; C'(1) = [C(0) + 3C(1)]/4 \quad (5)$$

and

$$C_{m\gamma,n\delta}(S) = -[-(-1)^S(m\delta|n\gamma) + (\delta_{S0})2(m\gamma|n\delta)]/(\varepsilon_m + \varepsilon_n - \varepsilon_\gamma - \varepsilon_\delta). \quad (6)$$

In these equations, S=0 and 1 refer to the singlet and triplet transitions, respectively. Hereafter, p and q refer to unoccupied orbitals and μ and ν to occupied orbitals. ε_k's are the HF orbital energies and $(ij|kl)$'s are the two-electron molecular integrals:

$$(ij|kl) = \iint [i(1)j(1)](1/r_{12})[k(2)l(2)]\mathrm{d}v_1\mathrm{d}v_2. \quad (7)$$

In Eq. 1,

$$\tilde{\mathscr{A}}^{\circ(2,1)} = \mathscr{A}^{\circ(1,2)}, \quad (8)$$

and the matrix elements of $\mathscr{A}^{\circ(1,2)}$ and $\mathrm{A}^{\circ(2,2)}$ are given in paper I. The dynamical screening by σ-electrons enters in Eqs. 2a and 2b as

$$(m\gamma|n\delta)'' = (m\gamma|n\delta) - \frac{a}{a^2 - \omega_\lambda^2} G_{m\gamma,n\delta}, \quad (9)$$

where

$$G_{m\gamma,n\delta} = 4\sum_{\sigma^*\sigma}(m\gamma|\sigma^*\sigma)(n\delta|\sigma^*\sigma). \quad (10)$$

For the evaluation of G in Eq. 10, see Paper I. On the other hand, the correction terms S' and T' in Eqs. 2b and 2a are given by

$$S'_{m\gamma,n\delta} = (1/2)[\mathrm{a} + \varepsilon_m - \varepsilon_\delta)^{-1} + (\mathrm{a} + \varepsilon_n - \varepsilon_\gamma)^{-1}]G_{m\delta,n\gamma}, \quad (11a)$$

$$T'_{mn} = (1/2)\sum_\pi S'_{m\pi,n\pi} \; ; \; T'_{\gamma\delta} = -(1/2)\sum_{\pi^*} S'_{\pi^*\gamma,\pi^*\delta}. \quad (11b)$$

The correction terms ρ' in Eqs. 4a and 4b are given by

$$\rho'_{mm} = (1/2)\sum_\pi G_{m\pi,m\pi}/(a + \varepsilon_m - \varepsilon_\pi)^2; \quad (12a)$$

$$\rho'_{\gamma\gamma} = -(1/2)\sum_{\pi^*} G_{\pi^*\gamma,\pi^*\gamma}/(a + \varepsilon_{\pi^*} - \varepsilon_\gamma)^2. \quad (12b)$$

Assuming that the eigenvectors are normalized as

$$\sum_{m\gamma}\{|\mathscr{Y}_{m\gamma}(\lambda S)|^2 - |\mathscr{Y}_{m\gamma}(\lambda S)|^2\} + \sum_{(m\gamma,n\delta)}\{|Y^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)|^2 - |Z^{(2)}{}_{(m\gamma,n\delta)}(\lambda S)^2\} = 1, \quad (13)$$

we have the transition dipole moment

$$\boldsymbol{D}_\lambda = (\delta_{S0})N_\lambda^{-1}\sqrt{2}\sum_{m\gamma}\{\mathscr{Y}_{m\gamma}(\lambda 0) + \mathscr{Y}_{m\gamma}(\lambda 0)\}(g_{m\gamma}\boldsymbol{d}^\circ{}_{m\gamma}), \quad (14)$$

where

$$\boldsymbol{d}^\circ{}_{m\gamma} \equiv -\int m(\boldsymbol{r})\boldsymbol{r}\gamma(\boldsymbol{r})\mathrm{d}^3r \quad (15)$$

and N_λ is a renormalization constant given by

$$N_\lambda^2 - 1 = (\delta_{S0})\frac{4a\omega_\lambda}{(a^2 - \omega_\lambda^2)^2}\sum_{\pi_1{}^*\pi_1}\sum_{\pi_2{}^*\pi_2}(G_{\pi_1{}^*\pi_1,\pi_2{}^*\pi_2}/[g_{\pi_1{}^*\pi_1}g_{\pi_2{}^*\pi_2}]) \times[\mathscr{Y}_{\pi_1{}^*\pi_1}(\lambda 0) + \mathscr{Y}_{\pi_1{}^*\pi_1}(\lambda 0)][\mathscr{Y}_{\pi_2{}^*\pi_2}(\lambda 0) + \mathscr{Y}_{\pi_2{}^*\pi_2}(\lambda 0)]. \quad (16)$$

The oscillator strength is given by

$$f_\lambda = (2/3)\omega_\lambda|\boldsymbol{D}_\lambda|^2. \quad (17)$$

2. Simplified Treatment of the σ-π Correlations

The correction term in Eq. 9 for the dynamical screening by σ-electrons involves ω_π which is different for each transition λ. This makes the whole calculations quite laborious because the low-lying excited states often change places in their energy-level ordering as we include the dynamical screening in the EOM. In the course of actual calculations, however, we noticed that the final results of these lowest singlet transitions were practically unaltered irrespective of the input value for ω_λ. We therefore propose to set ω_λ/a=0 in evaluating the dynamical screening. This is referred to as the Simplified Version I in this paper. Table 1 shows the results obtained by the use of the same set of the parameter values as in Paper I. Note

Table 1. Computed Transition Energies (in eV) to the Low-Lying Valence States of All-*trans* Linear Polyenes by the Simplified Version I with the Parameter Values: a=1.10, b=1.05, ζ=1.65

	^3B_u	(obsd)	^3A_g	(obsd)	^1B_u	(obsd)[a]	2^1A_g	(obsd)[a]
Butadiene	3.44	3.2[b]	4.61	4.95[b]	5.79	5.91	5.84	
	(3.44)		(4.61)		(5.72)		(5.83)	
Hexatriene	2.88	2.7[c]	4.03	4.2[c]	4.98	4.93	4.90	
	(2.88)		(4.04)		(4.93)		(4.89)	
Octatetraene	2.57	2.1[d]	3.48	3.6[d]	4.46	4.40	4.21	3.97
	(2.58)		(3.48)		(4.42)		(4.21)	
Decapentaene	2.41		3.11		4.11	4.02	3.86	3.48
	(2.41)		(3.11)		(4.08)		(3.86)	

Values in parentheses are the transition energies obtained by the original scheme with the same set of the parameter values (cf. Paper I). a) All taken from the review article of B. S. Hudson, B. E. Kohler, and K. Schulten, "Excited States," ed by E. C. Lim, Academic Press, New York (1982), Vol. 6, pp. 1—95. b) J. P. Doering, *J. Chem. Phys.* **70**, 3902 (1979). 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).

that the results show marvelous agreement with the original ones.

We then propose to make further approximation that the orbital energy differences $\varepsilon_{\pi^*}-\varepsilon_{\pi}$ appearing in Eqs. 11—12, as well as ω_λ, are ignored in dealing with the σ-π electron correlations, i.e.,

$$\omega_\lambda/a = (\varepsilon_{\pi^*} - \varepsilon_{\pi})/a = 0. \tag{18}$$

This is referred to as the Simplified Version II in this paper. In this approximation, we would have

$$(m\gamma|n\delta)'' = (m\gamma|n\delta) - G_{m\gamma,n\delta}/a, \tag{19}$$

$$S'_{m\gamma,n\delta} = G_{m\delta,n\gamma}/a, \tag{20a}$$

$$T'_{mn} = (1/2)(\sum_{\pi} G_{m\pi,n\pi})/a \ ;$$

$$T'_{\gamma\delta} = -(1/2)(\sum_{\pi^*} G_{\pi^*\delta,\pi^*\gamma})/a. \tag{20b}$$

$$\rho'_{mm} = (1/2)(\sum_{\pi} G_{m\pi,m\pi})/a^2 \ ; \tag{21a}$$

$$\rho'_{\gamma\gamma} = -(1/2)(\sum_{\pi^*} G_{\pi^*\gamma,\pi^*\gamma})/a^2, \tag{21b}$$

and

$$N_\lambda = 1. \tag{22}$$

With this approximation, we now have

$$\mathscr{A}_{m\gamma,n\delta}(S) = \delta_{mn}\delta_{\gamma\delta}(\varepsilon_m - \varepsilon_\gamma) + \{-[(mn|\gamma\delta)'' + \delta_{mn}T_{\gamma\delta} - \delta_{\gamma\delta}T_{mn}] + (\delta_{S0})2(m\gamma|n\delta)''\}/(g_{m\gamma}g_{n\delta}), \tag{23a}$$

$$\mathscr{B}_{m\gamma,n\delta}(S) = \{-(-1)^S[(m\delta|n\gamma)'' - S_{m\gamma,n\delta}] + (\delta_{S0})2(m\gamma|n\delta)''\}/(g_{m\gamma}g_{n\delta}), \tag{23b}$$

where $(m\gamma|\,n\delta)''$ and $(m\delta|\,n\gamma)''$ are given by Eq. 19 and

$$(mn|\gamma\delta)'' = (mn|\gamma\delta) - (1/2)(\delta_{mn}\sum_{\pi^*} G_{\pi^*\delta,\pi^*\gamma} + \delta_{\gamma\delta}\sum_{\pi} G_{m\pi,n\pi})/a. \tag{24}$$

3. Numerical Examination and Discussions

Numerical computations were made for the $\pi\rightarrow\pi^*$ transitions of linear polyenes, using the same molecular geometries as described in Paper I.

We have already shown, in Table 1, the results of the Simplified Version I ($\omega_\lambda/a=0$). The results were remarkably close to those of the original version, although the same parameter values as found in the original version were used without further optimization, i.e. (a=1.10, b=1.05, ζ=1.65).

Table 2 shows the results of the Simplified Version II ($\omega_\lambda/a=(\varepsilon_{\pi^*}-\varepsilon_{\pi})/a=0$) when the same set of the parameter values was used. These results are rather poor. Thus we looked for a better set of the parameter values. The results with an optimized set (a=1.10, b=1.05, ζ=1.65) are shown in the column II of Table 3. The results of the transition energies are reasonably good compared to those of the original scheme in spite of the approximations introduced here. Note however that the oscillator strength for the allowed transition 1^1B_u tends to become smaller than that of the original scheme as the molecule gets longer. We have noticed that the transition to the second allowed state (2^1B_u) shows just the opposite behavior. This is in accord with the behavior of the weight of the (1p—1h) components in these transitions. The 2^1B_u states are essentially doubly-excited states. In the case of decapentaene, the first and second ^1B_u transitions are separated by only 0.06 eV in this scheme but 0.42 eV in the original scheme. Their oscillator strengths were changed to 1.44 and 0.256 from the original 1.80 and 0.010, while the weights of the (2p-2h) components were changed to 0.132 and 0.690 from the original 0.026 and 0.766, respectively. Such changes are much smaller in the case of octatetraene. (Here, the two lowest ^1B_u states are separated by 0.23 eV in this scheme and 0.61 eV in the original scheme. The oscillator strengths were changed to 1.35 and 0.04 from 1.47 and

Table 2. Computed Transition Energies (in eV) to the Low-Lying Valence States of All-*trans* Linear Polyenes by the Simplified Version II with the Same Set of the Parameter Values as in Table 1: a=1.10, b=1.05, ζ=1.65

	^3B_u	(obsd)[a]	^3A_g	(obsd)[a]	^1B_u	(obsd)[a]	2^1A_g	(obsd)[a]
Butadiene	3.69	3.2	4.81	4.95	5.93	5.91	5.90	
	(3.44)		(4.61)		(5.72)		(5.83)	
Hexatriene	3.19	2.7	4.25	4.2	5.18	4.93	4.97	
	(2.88)		(4.04)		(4.93)		(4.89)	
Octatetraene	2.90	2.1	3.74	3.6	4.71	4.40	4.28	3.97
	(2.58)		(3.48)		(4.42)		(4.21)	
Decapentaene	2.57		3.39		4.38	4.02	3.93	3.48
	(2.41)		(3.11)		(4.08)		(3.86)	

Values in parentheses are the transition energies obtained by the original scheme with the same set of the parameter values (cf. Paper I). a) The same as in Table 1.

Table 3. Computed Transition Energies (in eV) and Oscillator Strengths to the Low-Lying Valence States of All-*trans* Linear Polyenes by the Simplified Versions II and IIr with the Optimized Parameter Values

	^3B_u		^3A_g		^1B_u		2^1A_g	
	II	IIr	II	IIr	II	IIr	II	IIr
Butadiene	3.40	3.36	4.47	4.44	5.70 [0.79]	5.68 [0.80] ([0.85])	5.48	5.47
Hexatriene	2.91	2.86	3.93	3.90	4.97 [1.06]	4.93 [1.07] ([1.16])	4.60	4.59
Octatetraene	2.64	2.59	3.44	3.40	4.50 [1.35]	4.46 ([1.37]) ([1.47])	3.96	3.95
Decapentaene	2.50	2.44	3.11	3.06	4.18 [1.44]	4.13 [1.60] ([1.80])	3.63	3.62

II stands for the Simplified Version II with the parameter values (a=1.19, b=0.98, ζ=1.64), and IIr for the Simplified Version IIr with (a=1.19, b=0.98, ζ=1.64, r=0.07). Values in the square brackets are the oscillator strengths, and those in parentheses under IIr of ^1B_u are by the original scheme of Paper I.

0.01, while the (2p-2h) weights were changed to 0.035 and 0.776 from 0.022 and 0.758).

In addition to the two approximations described above, we also treated $r=\omega_\lambda/a=(\varepsilon_{\pi^*}-\varepsilon_\pi)/a$ as an adjustable parameter. This is referred to as the Simplified Version IIr. The best fit parameters turned out to be the same as the Simplified Version II for a, b, and ζ except that r=0.07. The results are shown in the column IIr of Table 3. It is clear that this introduction of the new parameter r does not much affect the results for the transition energies but improves the results for the oscillator strengths. In the case of decapentaene, the first and second ^1B_u transitions are separated by 0.09 eV, their oscillator strengths are 1.60 and 0.11, and their (2p-2h) weights are 0.068 and 0.750. (In the case of octatetraene, these values are 0.26 eV; 1.37, 0.03; 0.032, 0.776).

In the following paper of this series, we shall treat the two-center integrals more carefully than just setting equal to 1/R. This would hopefully improve the whole results of the transition energies and oscillator strengths. We shall then find newly optimized parameter values for both linear and non-linear π-electron systems.

Computations were partly carried out using facilities of the Computer Centers both at Shinshu University and the University of Tokyo. We also acknowledge the computational assistance of Mr. Hidetoshi Hara.

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3) T. Shibuya, T. Funada, and S. Narita, *Bull. Chem. Soc. Jpn.*, **62**, 701 (1989), hereafter referred to as Paper I, where some other related articles are also given.