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The Calculation of the π-Electron Orbital Energies of the Allyl Cation, Butadiene, and Cyclic Polyenes by Means of Green's Function Method

Katsumi Shimada, Sadao Okido, and Osamu Tanimoto
Department of Applied Physics, Faculty of Engineering, Osaka City University, Sumiyoshi, Osaka

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Green's function matrix method for the calculation of the orbital energies of π-electron systems, which has been discussed in previous papers, is applied to the allyl cation, butadiene, rectangular cyclobutadiene, and cyclic polyenes with various molecular lengths. The higher-order correction for the Hartree-Fock orbital energies are calculated, and in the case of butadiene the theoretical value of the ionization potential is discussed in comparison with the experimental data. The relation between the higher-order correction effect and the molecular length is illustrated in the cases of the cyclic polyenes. In particular, the breakdown of perturbation calculation based on the Hartree-Fock orbitals occurs in the case of the $C_{30}H_{30}$ molecule.

In our previous papers,[1,2] Green's function matrix method for π-electron system was discussed using several examples. These examples were of cases where the self-consistent-field (SCF) Green's function matrices can easily be calculated by the analytical method. In the present article, our method is applied to the allyl cation, butadiene, rectangular cyclobutadiene, and cyclic polyenes for the purpose of investigating the relation between the higher-order correction effect and the molecular length.

As is shown in References 1) [to be referred to as I] and 2), we are concerned with the calculation of the one-particle Green's function matrix $G(\omega)$, because the poles of $G(\omega)$ give the orbital energies. Using the perturbation method based on the Hartree-Fock orbitals, the one-particle Green's function matrix is given as follows:

$$G(\omega) = [g(\omega)^{-1} - \Sigma(\omega)]^{-1}, \tag{1}$$

where:

$$g(\omega) = [(\omega+\mu)I - (\alpha+\beta+\chi)]^{-1}. \tag{2}$$

The $g(\omega)$ matrix is Hartree-Fock Green's function matrix. (see Eq. (I.38)) The 'chemical potential', μ, is fixed at a certain value between the highest occupied level and the lowest unoccupied one. The α and β matrices are core integrals. In the following, we put:

$$\alpha_{ll} = -u - \sum_{l \neq m} \gamma_{lm}, \tag{3}$$

where u represents the ionization potential of a carbon atom in its valence state. Using the Pariser, Parr, and Pople's Hamiltonian, the elements of the Hartree-Fock field matrix, χ, are given by the following equations (from Eq. (I.31)):

$$\left.\begin{aligned} \chi_{ll} &= -i\int\frac{d\omega}{2\pi}e^{-i\omega(0-)}\{\gamma_{ll}g_{ll}(\omega)+2\sum_{p\neq l}\gamma_{lp}g_{pp}(\omega)\}, \\ \chi_{lm} &= i\gamma_{lm}\int\frac{d\omega}{2\pi}e^{-i\omega(0-)}g_{lm}(\omega) \quad (l\neq m). \end{aligned}\right\} \tag{4}$$

The self-energy part, Σ, represents the correction of higher-order effects to the Hartree-Fock orbital energies:

$$\begin{aligned} \Sigma_{lm} = \sum_{pq} \gamma_{lp}\gamma_{mq}&\int\frac{d\omega_1}{2\pi}\int\frac{d\omega_2}{2\pi} \\ &\times\{2g_{pq}(\omega_1)g_{qp}(\omega_2)g_{lm}(\omega-\omega_1+\omega_2) \\ &-g_{lq}(\omega_1)g_{qp}(\omega_2)g_{pm}(\omega-\omega_1+\omega_2)\}. \end{aligned} \tag{5}$$

(see Eq. (I.32))

The Allyl Cation

In the case of the allyl cation, the unperturbed Green's function matrix is given by:

$$g(\omega) = \begin{pmatrix} \omega+\mu-\alpha_{11}-\chi_{11} & -\beta_{12}-\chi_{12} & -\beta_{13}-\chi_{13} \\ -\beta_{12}-\chi_{12} & \omega+\mu-\alpha_{22}-\chi_{22} & -\beta_{12}-\chi_{12} \\ -\beta_{13}-\chi_{13} & -\beta_{12}-\chi_{12} & \omega+\mu-\alpha_{11}-\chi_{11} \end{pmatrix}^{-1}. \tag{6}$$

The residue of the (lm) element of the Green's function matrix is denoted as R_{lm}:

$$R_{lm} = \frac{1}{2\pi i}\int d\omega e^{-i\omega(0-)}g_{lm}(\omega). \tag{7}$$

It can easily be seen that R_{lm} have the following relations:

$$\left.\begin{aligned} &2R_{11} + R_{22} = 1, \\ &R_{13} = R_{11}, \\ &R_{11}R_{22} = R_{12}^2 \end{aligned}\right\} \tag{8}$$

and

$$(\alpha_{11}-\alpha_{22}+\beta_{13}+\chi_{13})R_{12} = (\beta_{12}+\chi_{12})(1-2R_{22}).$$

The self-consistency conditions (4) are, then, written as:

$$\left.\begin{aligned} &(4\gamma_{12}-\gamma_{11}-2\gamma_{13})R_{22} = 2\chi_{11} - \gamma_{11} - 2\gamma_{13}, \\ &-\gamma_{12}R_{12} = \chi_{12}, \\ &(\gamma_{11}-2\gamma_{12})R_{22} = \chi_{22} - 2\gamma_{12}, \\ &\gamma_{13}R_{22} = 2\chi_{13}+\gamma_{13}. \end{aligned}\right\} \tag{9}$$

From these relations, the following algebraic equation is obtained:

$$\begin{aligned} A_1^2R_{22}^4 + A_1(2A_2-A_1)R_{22}^3 + \{A_2(A_2-2A_1)+8\beta_{12}^2\}R_{22}^2 \\ - (A_2^2+8\beta_{12}^2)R_{22} + 2\beta_{12}^2 = 0, \end{aligned} \tag{10}$$

where:

$$\left.\begin{aligned} A_1 &= -\frac{3}{2}\gamma_{11} + 2\gamma_{12} - \frac{1}{2}\gamma_{13}, \\ A_2 &= \alpha_{11} - \alpha_{22} + \frac{1}{2}\gamma_{11} - \gamma_{12} + \frac{1}{2}\gamma_{13} + \beta_{13}. \end{aligned}\right\} \tag{11}$$

Using the solution for R_{22} in the above equation (10), the Hartree-Fock field, χ, is obtained from Eq. (9). The orbital energies, ω_1, ω_2 and ω_3 ($\omega_1<\omega_2<\omega_3$), in the SCF approximation are easily obtained by the use of Eq. (2); they are listed in Table 1. The element of the SCF Green's function matrix is represented as;

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1) O. Tanimoto and K. Shimada, *Mol. Phys.*, **23**, 745 (1972).
2) K. Shimada and O, Tanimoto, *ibid.*, **23** 765 (1972).

TABLE 1. THE ORBITAL ENERGIES OF THE ALLYL CATION (IN eV)

	Semi-empirical[3]	Löwdin orbitals(1)	Löwdin orbitals(2)
γ_{11}	10.84	17.62	
γ_{12}	7.52	8.92	
γ_{13}	5.63	5.57	
β_{12}	−2.85	−2.68	
β_{13}	−0.45	0	−0.45
u	11.42	11.54	
ω_3	−5.860 (−5.651)	−4.281 (−3.192)	−4.399 (−3.469)
ω_2	−9.761 (−9.659)	−8.933 (−8.519)	−8.493 (−8.080)
ω_1	−21.31 (−21.23)	−20.18 (−19.69)	−20.47 (−19.97)

The values in the bracket are the result of the SCF calculation. (1) As the values of the coulomb-integrals, those in the case of benzene[4] are adopted. (2) The value of β_{13} is used that of semi-empirical case.

TABLE 2.

(lm)	A_{lm}	B_{lm}	C_{lm}
11	A_{11}	0.5	$0.5-A_{11}$
22	$1-2A_{11}$	0	$2A_{11}$
12	A_{12}	0	$-A_{12}$
13	A_{11}	−0.5	$0.5-A_{11}$

$$g_{lm}(\omega) = \frac{A_{lm}}{\omega-\omega_1-i\delta} + \frac{B_{lm}}{\omega-\omega_2+i\delta} + \frac{C_{lm}}{\omega-\omega_3+i\delta}, \qquad (12)$$

where A_{lm}, B_{lm}, and C_{lm} are certain constants simply related to one another, as is shown in Table 2. From the theorem of residues:

$$\begin{aligned}\int\frac{\mathrm{d}\omega_1}{2\pi}\frac{\mathrm{d}\omega_2}{2\pi}g_{ij}(\omega_1)g_{kl}(\omega_2)g_{mn}(\omega-\omega_1+\omega_2) \\ = \frac{A_{ij}B_{kl}A_{mn}}{\omega-2\omega_1+\omega_2} + \frac{A_{ij}C_{kl}A_{mn}}{\omega-2\omega_1+\omega_3} + \frac{B_{ij}A_{kl}B_{mn}}{\omega+\omega_1-2\omega_2} \\ + \frac{B_{ij}A_{kl}C_{mn}+C_{ij}A_{kl}B_{mn}}{\omega+\omega_1-\omega_2-\omega_3} + \frac{C_{ij}A_{kl}C_{mn}}{\omega+\omega_1-2\omega_3}.\end{aligned} \qquad (13)$$

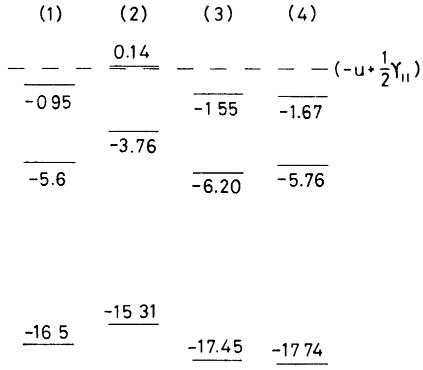

Fig. 1. The orbital energies of the allyl cation measured from the standard $-u+1/2\,\gamma_{11}$.
Case (1) is the result that is in the Salem's text and cases (2), (3) and (4) correspond to the first, second and third column in Table 1, respectively.

Using Eqs. (13) and (5), the orbital energies including the correlation effect were calculated from the secular equation (1); they are shown in Fig. 1, along with the results in Salem's text.[5] The orbital energies are measured from the standard $-u+\gamma_{11}/2$. In the case of the semi-empirical parameters, unlike the other cases, the highest energy level appears above the origin of the energy level. With regard to the electron-density distribution, we have the following relations:

$q_{22} > 2q_{11}$ (Case (2) in Fig. 1)

and:

$q_{22} < 2q_{11}$ (Cases (1), (3) and (4) in Fig. 1)

as q_{ii} is the electron-occupation number at the carbon atom, i. It shows the feature of the semi-empirical parameters that the correction for the Hartree-Fock orbital energies is smaller than that in other cases.

Butadiene

In the case of butadiene, the SCF Green's function matrix is given by:

$$g(\omega) = \begin{pmatrix} \omega+\mu-\alpha_{11}-\chi_{11} & -\beta_{12}-\chi_{12} & -\beta_{13}-\chi_{13} & -\beta_{14}-\chi_{14} \\ -\beta_{12}-\chi_{12} & \omega+\mu-\alpha_{22}-\chi_{22} & -\beta_{23}-\chi_{23} & -\beta_{13}-\chi_{13} \\ -\beta_{13}-\chi_{13} & -\beta_{23}-\chi_{23} & \omega+\mu-\alpha_{22}-\chi_{22} & -\beta_{12}-\chi_{12} \\ -\beta_{14}-\chi_{14} & -\beta_{13}-\chi_{13} & -\beta_{12}-\chi_{12} & \omega+\mu-\alpha_{11}-\chi_{11} \end{pmatrix}^{-1}. \qquad (14)$$

For even alternant hydrocarbons, the theorem proved by Pople[6] states that:

$$P_{rr} = 2\frac{1}{2\pi i}\int \mathrm{d}\omega\, \mathrm{e}^{-i\omega(0-)}g_{rr}(\omega) = 1. \qquad (15)$$

From the above theorem, the following relation is obtained:

$$\alpha_{rr} + \chi_{rr} = \text{constant} \equiv \mu, \qquad (16)$$

where the chemical potential, μ, is set at the center of the level scheme. The relation:

$$\beta_{13} + \chi_{13} = 0 \qquad (17)$$

is derived from the pairing theorem.[7] Using these relations, the elements of the SCF Green's function can be written thus:

$$\begin{aligned} g_{lm}(\omega) = \frac{a_{lm}}{\omega-\beta_+-i\delta} + \frac{b_{lm}}{\omega+\beta_++i\delta} \\ + \frac{c_{lm}}{\omega-\beta_--i\delta} + \frac{d_{lm}}{\omega+\beta_-+i\delta}, \end{aligned} \qquad (18)$$

where, assuming that $\beta_{12}=\beta_{13}\equiv\beta$ and $\beta_{14}=0$:

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[3] H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955) R. Pariser and R, G, Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953),

[4] R. G. Parr, "The Quantum Theory of Molecular Electronic Structure", Benjamin, New York (1963), p. 67.

[5] L. Salem, "The Molecular Orbital Theory of Conjugated Systems", Benjamin, New York (1966), p. 68.

[6] J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

[7] A, D, McLachlan, *Mol. Phys.*, **4**, 49 (1961).

TABLE 3.

(lm)	a_{lm}	b_{lm}	c_{lm}	d_{lm}
11	a_{11}	a_{11}	a_{22}	a_{22}
22	a_{22}	a_{22}	a_{11}	a_{11}
12	a_{12}	$-a_{12}$	a_{12}	$-a_{12}$
13	a_{12}	a_{12}	$-a_{12}$	$-a_{12}$
14	a_{11}	$-a_{11}$	$-a_{22}$	a_{22}
23	a_{22}	$-a_{22}$	$-a_{11}$	a_{11}

$$\left.\begin{aligned} \beta_+ &= -\frac{1}{2}[\{(\beta+\chi_{23}-\chi_{14})^2+4(\beta+\chi_{12})^2\}^{1/2} \\ &\qquad -\beta-\chi_{14}-\chi_{23}], \\ \beta_- &= -\frac{1}{2}[\{(\beta+\chi_{23}-\chi_{14})^2+4(\beta+\chi_{12})^2\}^{1/2} \\ &\qquad +\beta+\chi_{14}+\chi_{23}]. \end{aligned}\right\} \quad (19)$$

The relations among the coefficients, a_{lm}, b_{lm}, c_{lm}, and d_{lm}, in Eq. (18) are given in Table 3, and

$$\left.\begin{aligned} a_{11} &= \frac{1}{4}[1+(\beta+\chi_{23}-\chi_{14})\{(\beta+\chi_{23}-\chi_{14})^2 \\ &\qquad +4(\beta+\chi_{12})^2\}^{-1/2}], \\ a_{22} &= \frac{1}{2}-a_{11}, \\ a_{12} &= -\frac{1}{2}(\beta+\chi_{12})\{(\beta+\chi_{23}-\chi_{14})^2 \\ &\qquad +4(\beta+\chi_{12})^2\}^{-1/2}=\sqrt{(a_{11}a_{22})}. \end{aligned}\right\} \quad (20)$$

From these equations and Eq. (4), the following equations can easily be obtained:

$$\left.\begin{aligned} \chi_{11} &= \frac{1}{2}\gamma_{11}+\gamma_{12}+\gamma_{13}+\gamma_{14}, \\ \chi_{22} &= \frac{1}{2}\gamma_{22}+\gamma_{12}+\gamma_{13}+\gamma_{23}, \\ \chi_{12} &= 2\beta\gamma_{12}\chi_{23}/(\beta\gamma_{23}-A\chi_{23}), \\ \chi_{14} &= -(\gamma_{14}/\gamma_{23})\chi_{23} \end{aligned}\right\} \quad (21)$$

and

$$\begin{aligned} &4A^2\chi_{23}{}^4 - 8\beta\gamma_{23}A\chi_{23}{}^3 + (20\beta^2-A^2)\gamma_{23}{}^2\chi_{23}{}^2 \\ &\qquad + 2\beta\gamma_{23}{}^3A\chi_{23} - \beta^2\gamma_{23}{}^4 = 0, \end{aligned} \quad (22)$$

where:

$$A = 2\gamma_{12} - \gamma_{23} - \gamma_{14}. \quad (23)$$

Eq. (22) has two real solutions. We choose the solution which satisfies the condition:

$$\beta + \chi_{23} < 0. \quad (24)$$

The orbital energies, including the correlation effect, are obtained and the numerical results are listed in Table 4, together with the SCF orbital energies. In other to compare the present results with the experimental results, the ionization potential is calculated. Using Slater orbitals, the ionization potential of *trans*-butadiene is calculated as below:

$$I_{\text{calc}} = u - \frac{1}{2}\gamma_{11} - \omega = 9.01\ \text{eV} \quad (8.80\ \text{eV})$$

where ω is the energy of the higher occupied orbital given in Table 4 and where u=11.54 eV is used.

TABLE 4. NUMERICAL RESULTS OF π-ELECTRON ORBITAL ENERGIES IN BUTADIENE MOLECULE

	Slater orbitals[8]		Hall orbitals[9]
	cis-	*trans-*	*trans-*
γ_{11}	16.93		17.26
γ_{22}	16.93		17.56
γ_{12}	9.24		9.03
γ_{23}	8.69		8.63
γ_{13}	5.52		5.48
γ_{14}	4.68	3.83	3.78
β	−2.68		−2.68
χ_{12}	−4.37	−4.39	−4.28
χ_{23}	−1.42	−1.35	−1.37
χ_{14}	0.763	0.595	0.598
ω^{SCF}	±5.79 ±9.12	±5.72 ±9.16	±5.62 ±9.06
ω	±6.04 ±9.02	±5.93 ±8.99	±5.92 ±8.92
Δ $(\Delta=\omega-\omega^{\text{SCF}})$	±0.25 ∓0.10	±0.21 ∓0.17	±0.30 ∓0.14

The value in brackets is the result of the SCF calculation. The experimental value was given by Price and Walsh[10] as:

$$I_{\text{expt}} = 9.07\ \text{eV}.$$

Thus, our result is in good agreement with the experimental value. The effect of orbital reorganization during the ionization process was investigated by Devaquat and Salem.[11] Using the perturbation theory, they found only a small correction to the I_{SCF} value for the ionization potential in the SCF scheme; the correction is about 0.1 eV for closed-shell systems, such as the allyl cation or butadiene. On the other hand, the correlation energies obtained with our method are 0.2—0.5 eV, except for the semi-empirical parameters. Hence, the deviations in the orbital energies from the SCF values are determined by the correlation effect rather than by the orbital-distortion effect.

The Rectangular Cyclobutadiene

Here we will derive the equations for the orbital energies of the rectangular cyclobutadiene. From the SCF Green's function matrix:

$$g(\omega) = \begin{pmatrix} \omega & -\beta-\chi_{12} & 0 & -\beta'-\chi_{14} \\ -\beta-\chi_{12} & \omega & -\beta'-\chi_{14} & 0 \\ 0 & -\beta'-\chi_{14} & \omega & -\beta-\chi_{12} \\ -\beta'-\chi_{14} & 0 & -\beta-\chi_{12} & \omega \end{pmatrix}^{-1}. \quad (25)$$

we obtain the following self-consistency conditions:

$$\left.\begin{aligned} \chi_{11} &= \frac{1}{2}\gamma_{11}+\gamma_{12}+\gamma_{13}+\gamma_{14}, \\ \chi_{12} &= -\frac{1}{2}\gamma_{12}, \\ \chi_{13} &= \chi_{14} = 0. \end{aligned}\right\} \quad (26)$$

We also obtain the orbital energies, $\omega_{\text{SCF}}=\pm\beta_\pm$,

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[8] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

[9] G. G. Hall, *Trans. Faraday Soc.*, **50**, 773 (1954).

[10] W. C. Price and A. D. W. Walsh, *Proc. Roy. Soc.*, Ser. A, **174**, 220 (1940).

[11] A. Devaquet and L. Salem, *J. Chim. Phys.*, **62**, 1267 (1965).

where:

$$\beta_\pm = \beta \pm \beta' - \frac{1}{2}\gamma_{12}. \tag{27}$$

The matrix element of the self-energy part is given by:

$$\begin{aligned}\Sigma_{lm} = \frac{a}{4}\Big(&\frac{1}{\omega+3\beta_+} + \frac{(-1)^{l+m}}{\omega-3\beta_+} + \frac{\alpha_{lm}}{\omega+3\beta_-} \\ &+ \frac{(-1)^{l+m}\alpha_{lm}}{\omega-3\beta_-}\Big) + \frac{b}{4}\Big(\frac{1}{\omega+\beta_++2\beta_-} + \frac{(-1)^{l+m}}{\omega-\beta_+-2\beta_-} \\ &+ \frac{\alpha_{lm}}{\omega+2\beta_++\beta_-} + \frac{(-1)^{l+m}\alpha_{lm}}{\omega-2\beta_+-\beta_-}\Big),\end{aligned} \tag{28}$$

where:

$$\left.\begin{aligned} a &= \frac{1}{16}\{(\gamma_{11}-\gamma_{12})^2-(\gamma_{11}-\gamma_{13})^2+(\gamma_{11}-\gamma_{14})^2 \\ &\quad +(\gamma_{12}-\gamma_{13})^2+(\gamma_{13}-\gamma_{14})^2-(\gamma_{12}-\gamma_{14})^2\}, \\ b &= \frac{1}{16}\{3(\gamma_{11}-\gamma_{12})^2+(\gamma_{11}-\gamma_{13})^2-(\gamma_{11}-\gamma_{14})^2 \\ &\quad -(\gamma_{12}-\gamma_{13})^2+7(\gamma_{13}-\gamma_{14})^2+(\gamma_{12}-\gamma_{14})^2\}\end{aligned}\right\} \tag{29}$$

and

$$\alpha_{11} = \alpha_{12} = -\alpha_{13} = -\alpha_{14} = 1. \tag{30}$$

The orbital energies, $\omega = \pm\omega_\pm$, are given by the following equations:

$$\omega_+ = \beta_+ + \frac{a}{\omega_+ + 3\beta_+} + \frac{b}{\omega_+ + \beta_+ + 2\beta_-} \tag{31}$$

and

$$\omega_- = \beta_- + \frac{a}{\omega_- + 3\beta_-} + \frac{b}{\omega_- + 2\beta_+ + \beta_-}. \tag{32}$$

The Cyclic Polyenes

For the purpose of investigating the relation between the correlation energies and the molecular length, we will discuss the cyclic polyenes here. The systems of $4n+2$ π-electrons are considered in the following discussion. For the sake of simplicity, only the nearest-neighbour interactions are taken into account. The SCF Green's function, $g_{4n+2}(\omega)$, is given as below:

$$g_{4n+2}(\omega) = \begin{pmatrix} \omega & d & 0 & \cdots & d \\ d & \omega & d & \cdots & 0 \\ 0 & d & \omega & \cdots & 0 \\ \cdot & \cdot & \cdot & & \cdot \\ \cdot & \cdot & \cdot & & \cdot \\ d & 0 & 0 & \cdots & \omega \end{pmatrix}^{-1}, \tag{33}$$

where we put $\mu = \alpha + \chi_{ll}$ and $d = -\beta - \chi_{l,l\pm1}$. The poles of this Green's function matrix are given by:[12]

$$\det|g_{4n+2}(\omega)^{-1}| = -4d^{4n+2}\sin^2(2n+1)\theta = 0, \tag{34}$$

where:

$$\omega = -2d\cos\theta. \tag{35}$$

The solutions of the above equation are:

$$\theta_r = \frac{r}{2n+1}\pi, \tag{36}$$

where:

$$\left.\begin{aligned} &r = 0,\ 2n+1 \\ &r = 1, 2, \cdots, 2n \text{ (doubly degenerated levels).}\end{aligned}\right\} \tag{37}$$

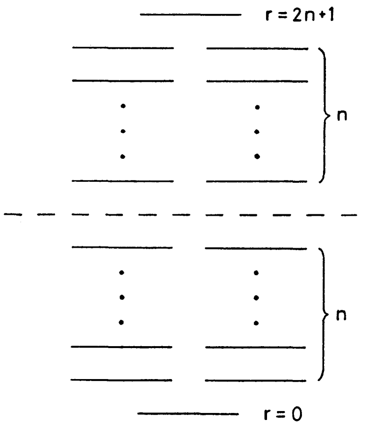

Fig. 2. The schematic orbital energies of the cyclic polyenes with $4n+2$ π-electrons.

The $4n+2$ suffix in $g_{4n+2}(\omega)$ will be disregarded hereafter for the sake of simplicity. The (lm) element of $g(\omega)$ is obtained thus:

$$g_{lm}(\omega) = \frac{\cos(2n+1+l-m)\theta}{2d\sin\theta\sin(2n+1)\theta}. \tag{38}$$

On the other hand, as is shown in Fig. 2, $g_{lm}(\omega)$ is written in the following form:

$$g_{lm}(\omega) = \sum_{r=0}^{n}\frac{a_{lm;r}}{\omega-\omega_r-i\delta} + \sum_{r=n+1}^{2n+1}\frac{b_{lm;r}}{\omega-\omega_r+i\delta}. \tag{39}$$

The transformation of the variables, ω to θ, is convenient for the following evaluation. Then, the contour on the complex plane is distorted to that shown in Fig. 3.

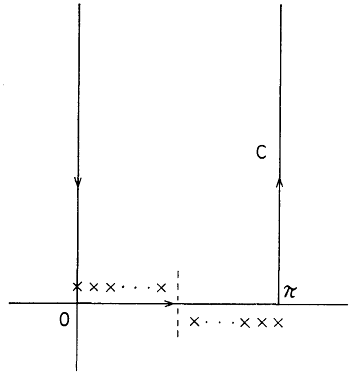

Fig. 3. The contour in the complex θ plane. The mark × denotes the poles of the one-particle Green's function.

The residues are given by:

$$\begin{aligned} a_{lm;r} &= \lim_{\omega\to\omega_r}(\omega-\omega_r)\sum_j\frac{a_{lm;j}}{\omega-\omega_j} \\ &= \lim_{\theta\to\theta_r} w_r(\theta-\theta_r)\frac{\cos(2n+1+l-m)\theta}{\sin(2n+1)\theta} \\ &= \frac{w_r}{2n+1}\cos\frac{(l-m)r}{2n+1}\pi, \end{aligned} \tag{40}$$

$$b_{lm;r} = a_{lm;2n+1-r} = (-1)^{l-m}a_{lm;r}, \tag{41}$$

where, as the pole, $r=0$, exists on the contour, c, and as the other poles are included within c, we have:

$$w_0 = 1/2, \text{ and } w_r = 1 \text{ for } 1 \leqq r \leqq n. \tag{42}$$

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[12] C. Coulson, *Proc. Roy. Soc., Ser. A*, **164**, 383 (1938).

Using Eq. (4) and the relations:

$$\left.\begin{aligned}&\sum_r \alpha_{ll;r} = \sum_{r=0}^{n} \frac{w_r}{2n+1} = \frac{1}{2n+1}\left(n+\frac{1}{2}\right) = \frac{1}{2}\\ &\text{and}\\ &\sum_r a_{l,l\pm1;r} = \frac{1}{2n+1}\left(\sum_{r=0}^{n}\cos\frac{r\pi}{2n+1} - \frac{1}{2}\right),\end{aligned}\right\} \tag{43}$$

we obtained the self-consistency conditions:

$$\left.\begin{aligned}&\chi_{ll} = \frac{1}{2}\gamma_0 + 2\gamma_1,\\ &\chi_{l,l\pm1;r} = -\frac{1}{2n+1}\,\frac{\cos\dfrac{n\pi}{2n+1}}{1-\cos\dfrac{\pi}{2n+1}}\end{aligned}\right\} \tag{44}$$

where $\gamma_0 = \gamma_{ll}$ and $\gamma_1 = \gamma_{l,l\pm1}$. Hence, we obtain the next relations:

$$\left.\begin{aligned}&\mu = \alpha + \chi_{ll} = \alpha + \frac{1}{2}\gamma_0 + 2\gamma_1 = -u + \frac{1}{2}\gamma_0,\\ &d = -\beta + \frac{\gamma_1}{2n+1}\,\frac{\cos\dfrac{n\pi}{2n+1}}{1-\cos\dfrac{\pi}{2n+1}}\quad .\end{aligned}\right\} \tag{45}$$

The SCF orbital energies are obtained by using $\omega_r^{\mathrm{SCF}} = -2d\cos\theta_r \equiv \beta_r$. The (lm) element of $\sum(\omega)$ can easily be obtained:

$$\textstyle\sum_{lm}(\omega) = \sum_{rst} B_{rst}(lm)\left[\dfrac{1}{\omega+\beta_r+\beta_s+\beta_t} + \dfrac{(-1)^{l+m}}{\omega-\beta_r-\beta_s-\beta_t}\right], \tag{46}$$

where the coefficient, $B_{rst}(lm)$, is given by:

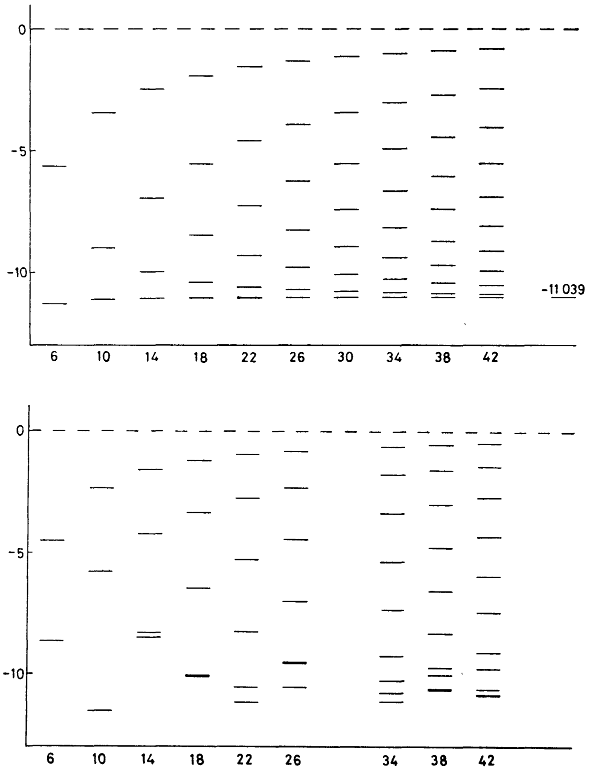

Fig. 4. The orbital energies of the cyclic polyenes of the SCF method and these including the correlation effect.

$$B_{rst}(lm) = \sum_{pq} \gamma_{lp}\gamma_{mq}(-1)^{p+q}[2a_{pq;r}a_{qp;s}a_{lm;t} - a_{lq;r}a_{qp;s}a_{pm;t}]. \tag{47}$$

TABLE 5. THE ORBITAL ENERGIES OF THE CYCLIC POLYENES

	6	10	14	18	22	26	30	34	38	42
(1)	±5.653	±3.440	±2.467	±1.922	±1.574	±1.332	±1.155	±1.019	±0.912	±0.825
	±11.31	±9.007	±6.912	±5.534	±4.594	±3.919	±3.414	±3.023	±2.711	±2.458
		±11.13	±9.989	±8.478	±7.242	±6.279	±5.525	±4.924	±4.437	±4.035
			±11.09	±10.40	±9.303	±8.273	±7.393	±6.657	±6.041	±5.522
				±11.07	±10.61	±9.786	±8.939	±8.164	±7.481	±6.886
					±11.06	±10.73	±10.09	±9.392	±8.716	±8.096
						±11.05	±10.81	±10.30	±9.714	±9.125
							±11.05	±10.86	±10.45	±9.950
								±11.05	±10.90	±10.55
									±11.05	±10.92
										±11.04
(2)	±4.507	±2.360	±1.602	±1.214	±0.977	±0.818		±0.617	±0.550	±0.496
	±8.644	±5.781	±4.243	±3.340	±2.744	±2.328		±1.785	±1.598	±1.447
		±11.52	±8.304	±6.454	±5.262	±4.434		±3.362	±2.996	±2.701
			±8.495	±10.05	±8.265	±7.001		±5.341	±4.770	±4.307
				±10.10	±10.54	±9.520		±7.324	±6.558	±5.934
					±11.18	±9.571		±9.255	±8.309	±7.534
						±11.05		±10.27	±9.722	±9.097
								±10.78	±10.03	±9.787
								±11.12	±10.60	±10.61
									±10.60	±10.84
										±10.85

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13) The Löwdin orbital parameters for benzene in Ref. 4 are used.

In the nearest-neighbour-interaction approximation, Eqs. (34) and (35) hold if ω and d are transformed to $\omega-\Sigma_{11}(\omega)$ and $d-\Sigma_{12}(\omega)$ respectively; that is,

$$-4[d-\Sigma_{12}(\omega)]^{4n+2}\sin^2(2n+1)\theta = 0. \tag{48}$$

Therefore,

$$\omega_r - \Sigma_{11}(\omega_r) = -2[d-\Sigma_{12}(\omega_r)]\cos\theta_r \tag{49}$$

is obtained, where θ_r is given by Eq. (36). Using these parameters[13];

$$\gamma_0 = 17.62\,\text{eV} \text{ and } \gamma_1 = 8.92\,\text{eV},$$

the numerical calculations are executed. The numerical results for $n=1-10$ are listed in Table 5 and are illustrated in Fig. 4.

In the case of the Hartree-Fock approximation, the energy of the $r=0$ level (the lowest occupied orbital), as measured from the center of the level scheme, monotonously increases as the π-electron number, $m=4n+2$, increases. At the limit, $m\to\infty$, the value of the lowest orbital energy approaches -11.039 eV in the case of the above-mentioned parameters. However, the orbital energies of occupied levels belonging to the other quantum number, r, monotonously decrease. By including the higher-order correction, these monotonous properties are broken down (see Fig. 4). The extremely close levels appear in the lower part of the level scheme. Furthermore, at $m=30$, the relation:

$$\omega_2 = \omega_5 + \omega_6 + \omega_7$$

is accidentally satisfied and the perturbation calculation is not adequate. The deviations from the Hartree-Fock orbital decrease as m increases, and the orbital energies approach the Hartree-Fock levels.