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Yuriko Aoki and Akira Imamura

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An analytical Hückel-type approach to the relationship between Peierls instability in polyenes and interchain interaction

Yuriko Aoki

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739, Japan

Akira Imamura

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima 739, Japan and Group, PRESTO, Research Development Corporation of Japan, Tsukuba Research Consortium, Tsukuba 300-26, Japan

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We propose a convenient method to estimate the magnitude of Peierls instability in finite one- and two-dimensional (1D and 2D) polyenes from the view point of orbital symmetry. The formulas are derived in terms of in-phase and out-of-phase interactions between adjacent carbon atoms on the basis of the analytical Hückel orbitals for polyene with an arbitrary length. The stabilization energies due to bond alternation are defined for the individual energy levels. It is visually shown that bond alternation gives rise to stabilizing the occupied orbitals and destabilizing the vacant orbitals without using the k space based on periodic boundary condition in infinite polymer. This treatment is further extended to the Peierls instability in 2D polyene on the basis of the analytical Hückel orbitals derived for its regular structure. Total π and σ energies are provided as functions of bond alternation and interchain interaction. It is demonstrated that bond alternation is strongly suppressed under the existence of interchain interaction, in which interchange between occupied and unoccupied orbitals plays a crucial role. This treatment would provide a first step to investigate the relationship between crystal structure of more complicated polymer and its electronic property in connection with interchain interaction. © 1995 American Institute of Physics.

I. INTRODUCTION

Regular *trans*-polyacetylene has in its unit cell one π electron, so that the π band is half filled. Therefore, *trans*-polyacetylene in this geometry has zero band gap and will show a metallic conductivity. However, it is well known that this polymer skeleton instantaneously deforms into a bond alternant geometry, in which the unit cell extends over two sites instead of one, to get energetic stabilization. This distortion generates an energy band gap at the Fermi level and hence a metal-to-insulator transition leading to decreasing the electron conductivity. This is called the Peierls distortion¹ and is very important in connection with electronic conductivity in one-dimensional polymers, semiconduction or thermal process under bond alternation defects in polyacetylene,^{2,3} and so on. Moreover, it has been known for a long time that the electrical conductivity of organic conductors rapidly increases with pressure. The interchain coupling becomes increasingly important at high pressures and the system gradually loses its one dimensionality. It has also been reported that the three-dimensional ordering will also suppress the Peierls distortion.^{4,5}

On the other hand, the quantum chemical method for periodical polymers has been established at the SCF level^{6,7} and theoretical studies on polyacetylene have become feasible within Hartree–Fock and beyond Hartree–Fock.^{8–11} In those treatments, the formalism based on the periodic boundary condition that can be handled by the energy band theory is employed assuming that the polymer chains are infinitely long. This has enabled us to treat the Peierls instability from the viewpoint of electronic structure so that an increasing number of theoretical investigations have been reported in

the field of conducting polymers,^{12–18} one-dimensional metals^{19,20} and so on. In our laboratory, the *ab initio* perturbational method^{21–24} has also been developed to investigate the interaction between polymer and dopants.

However, *ab initio* calculations require much computer time as well as an enormous amount of disk memory, so high-dimensional polymers will become quite difficult to treat. Thus besides highly exact *ab initio* calculations employing large computers, it seems useful to develop a simple method to design conducting polymers. Su *et al.*²⁵ have studied soliton excitation with a Hückel-type Hamiltonian for the π electrons in polyacetylene treating electron–phonon coupling (SSH model). Many studies proposed in the field of solid state physics are based on the Bloch theorem for periodic boundary condition and therefore wave functions are defined in reciprocal lattice space (k space) producing imaginary number. To design highly conducting polymers, however, the wave functions in real space will be visible and more practical rather than those in k space. In this standpoint we propose a simple treatment to describe the relationship between bond alternation and electronic property in real space by starting with the analytical Hückel molecular orbitals (MOs)²⁶ of regular polyene with finite length. A simple formula indicating the strength of Peierls instability is derived for the individual energy levels of regular polyene using the symmetry of intraorbital interactions in polyene. This is based on the concept of in-phase and out-of-phase interactions between C–C bonds, which is consistent with the first order perturbation theory. Furthermore, this treatment is extended to the 2D polyene in which neighboring chains interact with each other. As the starting, analytic energy levels and MOs are derived for the regular 2D polyene and then

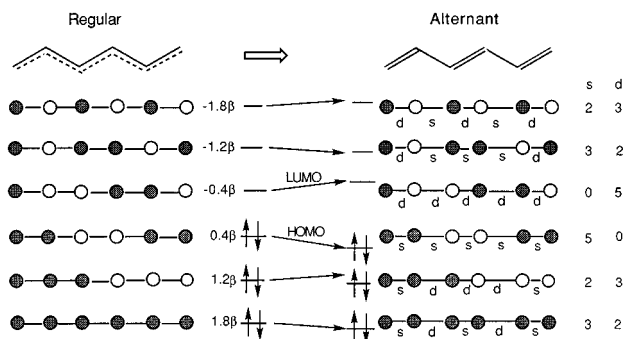


FIG. 1. Schematic energy diagram between regular and alternant structures in hexatriene. *s* stands for a stabilization and *d* stands for a destabilization caused by a bond alternation.

total energy including both of π - and σ -binding energies is formulated as a function of bond alternation and interchain interaction. It is clearly demonstrated that Peierls instability is suppressed under the existence of interchain interaction.

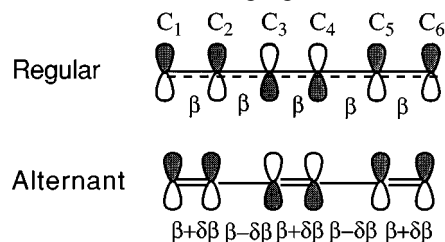
The purpose of our work is not to discuss the reliability of our results thus obtained because Hückel Hamiltonian is quite insufficient for the description, but to provide a useful tool to get information on electronic structures in various sizes of polyenes in the language of chemistry. The approach to polyene is the first step for extending our treatment to more complicated π -electron systems, molecular stacking systems and so on toward molecular designs.

II. PEIERLS INSTABILITY IN 1D POLYENE

First of all, we will begin with the primary description relating to our treatment by using the bond alternation in hexatriene for an example. We can use a concept for the bond alternation as follows: If the distance between the two carbon atoms becomes close, then in-phase interaction stabilizes the energy level and out-of-phase interaction destabilizes it. On the other hand, if the distance between the two carbon atoms becomes apart, then in-phase interaction destabilizes the energy level and out-phase interaction stabilizes it. This is substantially equivalent to the first order perturbation theory. This suggests that the number of stabilizations and destabilizations in a particular energy level will determine roughly the height of the energy level after the distortion. In Fig. 1, the schematic description is illustrated for all the energy levels of hexatriene. The energy levels after alternation are denoted according to the number of the stabilized (*s*) and the destabilized (*d*) interactions. It can be seen in the HOMO (highest occupied molecular orbital) that all the partial energies between neighboring carbon atoms contribute to stabilization, which leads to the great stability of the orbital. The reverse holds for the LUMO (lowest unoccupied molecular orbital). With respect to the lowest molecular orbital, the contribution of the stabilized partial energies is slightly greater than that of the destabilized ones, and the reverse holds for the highest molecular orbital. Consequently, it is suggested that all of the occupied orbitals contribute to the stabilization, while all of the unoccupied orbitals contribute to the destabilization. In addition, the orbitals near the Fermi level are greatly affected by the bond alternation, while the

lowest and highest orbitals are not essentially affected. This implies that the energy changes after bond alternation can be roughly estimated for individual orbitals from the numbers of the stabilized and the destabilized contributions.

We consider the structural change from the regular hexatriene to the alternant one. For example, the HOMO π orbital is shown in the following figure:



As an index for the energetic stabilization after the bond alternation, the following definition is assumed using the atomic orbital (AO) coefficients:

$$\Delta \epsilon \approx -(c_1 c_2 + c_3 c_4 + c_5 c_6) + (c_2 c_3 + c_4 c_5). \quad (1)$$

The first term is related to the double bonds which contribute to stabilization (*s* in Fig. 1) due to the bonding character between C_1 and C_2 , C_3 and C_4 , or C_5 and C_6 , while to destabilization (*d* in Fig. 1) due to the antibonding character between them. To the contrary, the second term is related to the single bonds which contribute to destabilization (*d*) due to the bonding character between C_2 and C_3 or C_4 and C_5 , but to stabilization (*s*) due to the antibonding character between them.

The treatment described in the previous section is generalized by extending the system to a long polyene composed of n carbon atoms. Hückel energy levels lie closely to each other with increasing chain length. Consequently, they form an energy band composed of nearly continuous energy level distribution at an infinite polyene system. If the system maintains the equidistant geometry, the increasing of the carbon atoms leads to a metallic band structure without a finite energy gap between the HOMO and LUMO. However, as Peierls¹ has shown, one-dimensional polymers having half-filled energy bands are susceptible to a geometrical distortion leading to an energy band gap at the Fermi level and hence a metal-insulator transition. Therefore, the structure is distributed to a bond-alternant geometry giving a finite energy gap and then gains energetic stabilization. We estimate for long polyene systems the characteristic properties in the individual orbital energy levels as well as the energy band gap by means of the simple formalism shown below.

The analytical energy levels and the MOs for regular polyenes can be written in the general form²⁶⁻²⁸

$$\epsilon_i = \alpha + 2\beta \cos \theta_i, \quad (2)$$

$$\varphi_i = \sum_{r=1}^n \sqrt{\frac{2}{n+1}} \sin(r\theta_i) \chi_r \quad \theta_i = i\pi/(n+1) \quad (i=1, 2, \dots, n), \quad (3)$$

where, n is the number of carbon atoms included, χ_r stands for the π -atomic orbital on the r th carbon atom, and i indicates an energy state. We consider the stabilization energy by

the periodic bond alternation. From the coefficients in Eq. (3), the index Eq. (1) is generalized for each orbital level i and arbitrary chain length n by

$$\begin{aligned} \Delta\epsilon_i^{\text{BA}} = & \frac{4}{n+1} \delta\beta (\sin \theta_i \sin 2\theta_i + \sin 3\theta_i \sin 4\theta_i \\ & + \cdots + \sin (n-1)\theta_i \sin n\theta_i) \\ & - \frac{4}{n+1} \delta\beta (\sin 2\theta_i \sin 3\theta_i + \sin 4\theta_i \sin 5\theta_i \\ & + \cdots + \sin (n-2)\theta_i \sin (n-1)\theta_i). \end{aligned} \quad (4)$$

Supposing $\delta\beta$ be very small compared to β , we can represent the change of the orbital energy by bond alternation as linear dependence on $\delta\beta$ as usually derived by the first order perturbation theory.^{29,30} The first term of Eq. (4) is related to the double bonds and the second term to the single bonds with respect to the i th energy level. The former means that the approaching carbon atoms contribute to stabilize the polymer by an in-phase interaction, but to destabilize it by an out-of-phase interaction. Equation (4) is rewritten in the form

$$\begin{aligned} \Delta\epsilon_i^{\text{BA}} = & \frac{2}{n+1} \left(\cos \theta_i - \sum_{k=1}^K \cos (3+4(k-1))\theta_i \right. \\ & \left. + \sum_{k=1}^{K-1} \cos (5+4(k-1))\theta_i \right) \delta\beta, \end{aligned} \quad (5)$$

where, K means the number of the double bonds. By using the following relation:

$$\begin{aligned} \sum_{k=1}^K \cos [a+(k-1)b] \\ = \cos \left[a + \frac{(K-1)b}{2} \right] \sin \frac{Kb}{2} / \sin \frac{b}{2}, \end{aligned} \quad (6)$$

Eq. (5) is reduced to the simple form,

$$\Delta\epsilon_i^{\text{BA}} = \frac{2}{n+1} \frac{\sin^2 \theta_i}{\cos \theta_i} \delta\beta. \quad (7)$$

In Eq. (7), it should be pointed out that the summation on k in Eq. (5) is removed. That is to say, the stabilization energy is obtained without summing up the infinite series. This relation is graphically illustrated in Fig. 2 to elucidate its i dependency. The number of n does not affect directly on the shape of the sin and cos functions, but is related to its density of states. This causes a large effect on $\Delta\epsilon_i^{\text{BA}}$ especially in the vicinity of the 0 level where the denominator approaches zero. This results in the great stabilization of HOMO energy and the great destabilization of LUMO energy. At the lower side of the figure, the Eq. (7) is indicated for $n=100$, $\beta = -1.0$, and $\delta\beta = -0.1$ as a function of the energy level of the regular polyene. In particular, HOMO and LUMO are significantly perturbed in the opposite direction, generating an energy gap at the Fermi level. At the infinitely large n orbital energies of the HOMO and the LUMO converge, to $4\delta\beta/\pi$ and $-4\delta\beta/\pi$, respectively, while the energy levels at the lowest molecular orbital and the highest molecular orbital are not affected by the bond alternation. Then, the band-

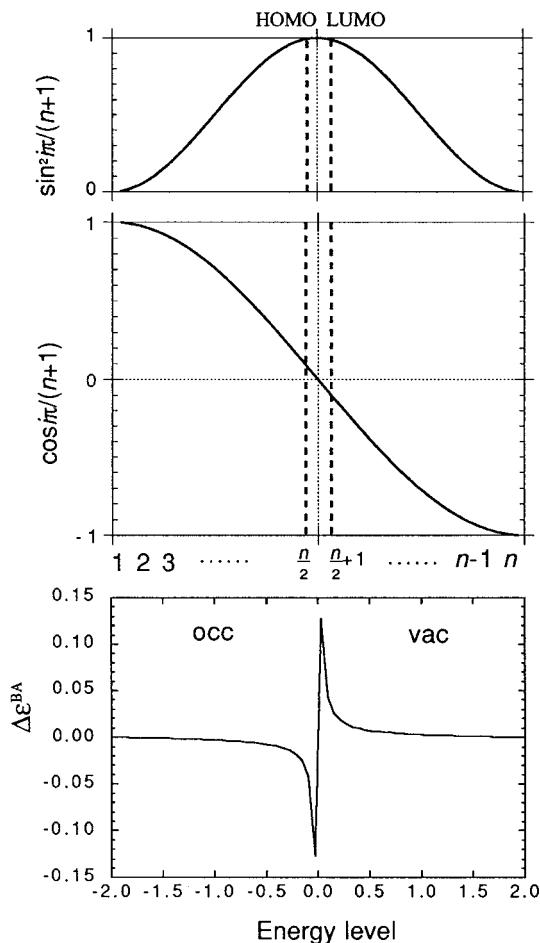


FIG. 2. Graphical representation for the numerator, denominator, and $\Delta\epsilon^{\text{BA}}$ of Eq. (7) with $\beta = -1.0$, $\delta\beta = -0.1$, and $n = 100$.

width approaches to $|2\beta - 4\delta\beta/\pi|$ for both the occupied and vacant bands. The total stabilization energy for the alternant structure is given by summing Eq. (7) upon the occupied orbitals as

$$\Delta E^{\text{BA}} = \frac{4}{n+1} \sum_{i=1}^{\text{occ}} \frac{\sin^2 \theta_i}{\cos \theta_i} \delta\beta \quad (8)$$

at the level of the Hückel method. The coefficient of $\delta\beta$ is plotted in the Fig. 3 as a function of n for both of the whole system and the unit cell.

The gap between HOMO and LUMO after alternation is given by

$$\begin{aligned} \Delta_s^{\text{BA}}(1D) = & -4\beta \sin \frac{\pi}{2(n+1)} - \frac{4\delta\beta}{n+1} \\ & \times \text{cosec} \frac{\pi}{2(n+1)} \cos^2 \frac{\pi}{2(n+1)}. \end{aligned} \quad (9)$$

The first term is concerned to the band gap for the equidistant geometry which approaches zero with increasing n , and the second term is added to the gap after bond alternation.

The density of states (DOS) is approximately derived as

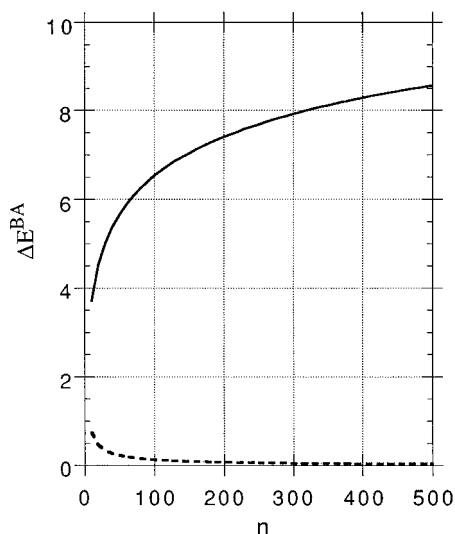


FIG. 3. Total stabilization energies by Eq. (8) as a function of n . The solid line — represents ΔE^{BA} for the total system and the broken line ---- represents $2\Delta E^{\text{BA}}/n$ for the per unit cell.

$$\frac{d\theta_i}{|d\epsilon^{\text{BA}}|} \cong -\frac{1}{2\beta} \operatorname{cosec} \theta_i - \frac{\delta\beta}{2(n+1)\beta^2} \times \operatorname{cosec} \theta_i (1 + \sec^2 \theta_i). \quad (10)$$

The first term is referred to the DOS for the regular polyene by Eq. (2), and the second term is to the effect of the bond alternation by Eq. (7). The contribution of $\sec^2 \theta$ in the second term leads to the substantial difference from the DOS of the regular polyene. Figure 4 shows an example of DOS curves for alternant polyenes with $n=50$, $\beta=-1.0$, and $\delta\beta=0 \sim -0.15$. The term with respect to $\sec^2 \theta$ in the vicinity of the $\theta=\pi/2$ results in the large DOS near the HOMO level ($4\delta\beta/\pi$) and the LUMO level ($-4\delta\beta/\pi$).

III. REGULAR 2D POLYENE

A. Analytical solution for regular 2D polyene

We want to extend the index given by Eq. (7) to the estimation of Peierls instability in 2D polyene. However, analytical solution like Eqs. (2) and (3) for regular 1D poly-

ene is not given for regular 2D polyene, as far as we know. Therefore, as a starting of the application, analytical energy levels and MOs are derived for regular 2D polyene and then the effect of the bond alternation is examined, according to Fig. 5. In this section we describe the characteristic features of the electronic states of regular 2D polyene.

In the frame work of the Hückel theory, the nearest neighbor chain interactions are taken into account. However, as shown in Fig. 6, several neighbor site interaction between chains should be taken into account. In our expression, $\gamma^{(0)}$ means the nearest neighbor interaction between chains, $\gamma^{(1)}, \gamma^{(2)}, \dots, \gamma^{(Q)}$ mean first, second \dots , Q th neighbor interactions, respectively. The interacting matrix element between i th MO on p th chain and i' th MO on p' th chain, $\tilde{H}_{ii'}^{(pp')}$, is represented by

$$\tilde{H}_{ii'}^{(p,p')} = \frac{2}{n+1} \sum_r^n \sum_{r'}^n \sin \frac{r i^{(p)} \pi}{n+1} \times \sin \frac{r' i'^{(p')} \pi}{n+1} H_{rr'}^{(p,p')}, \quad (11)$$

where $H_{rr'}^{(p,p')}$ is the integral between r th AO in p th chain and r' th AO in p' th chain. If only the interaction $\gamma^{(0)}$ in Fig. 6 is taken into account, then Eq. (11) becomes

$$\tilde{H}_{ii'}^{(p,p')}[Q=0] = \delta_{ii'} (\delta_{p',p} \epsilon_i + \delta_{p',p \pm 1} \gamma^{(0)}). \quad (12)$$

However, in general, interchain interaction should be given by including several neighbor interactions. Therefore, AO based matrix element between chains in Eq. (11) should be written as the second term in

$$H_{rr'}^{(p,p')}[Q] = \delta_{p',p} (\delta_{r',r} \alpha + \delta_{r',r \pm 1} \beta) + \delta_{p',p \pm 1} \sum_{q=0}^Q \delta_{r',r \pm q} \gamma^{(q)}. \quad (13)$$

In the above, the summation on q assumes that the chain is infinitely long. Considering the end effect in Eq. (13), the MO based matrix element, Eq. (11), can be generally expressed as

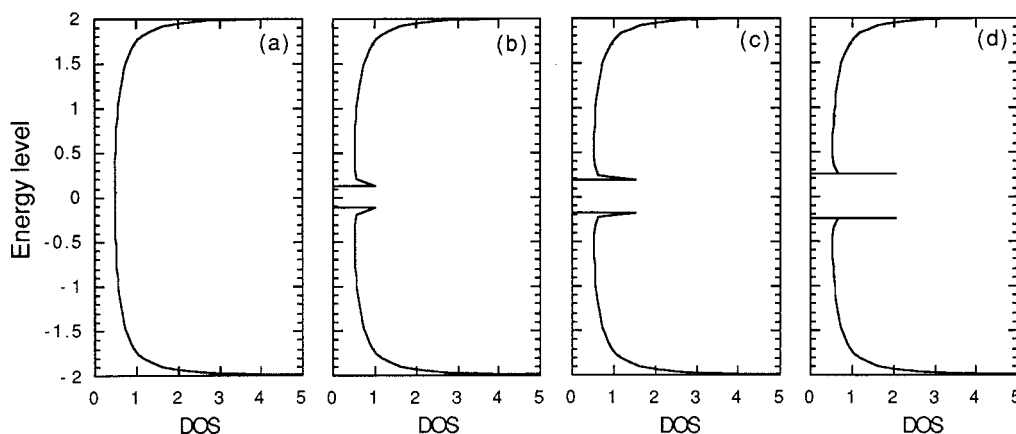


FIG. 4. The DOS after bond alternation ($n=50$, $\beta=-1.0$) by Eq. (10). (a) $\delta\beta=0.0$ (regular polyene) (b) $\delta\beta=-0.05$ (c) $\delta\beta=-0.10$ (d) $\delta\beta=-0.15$.

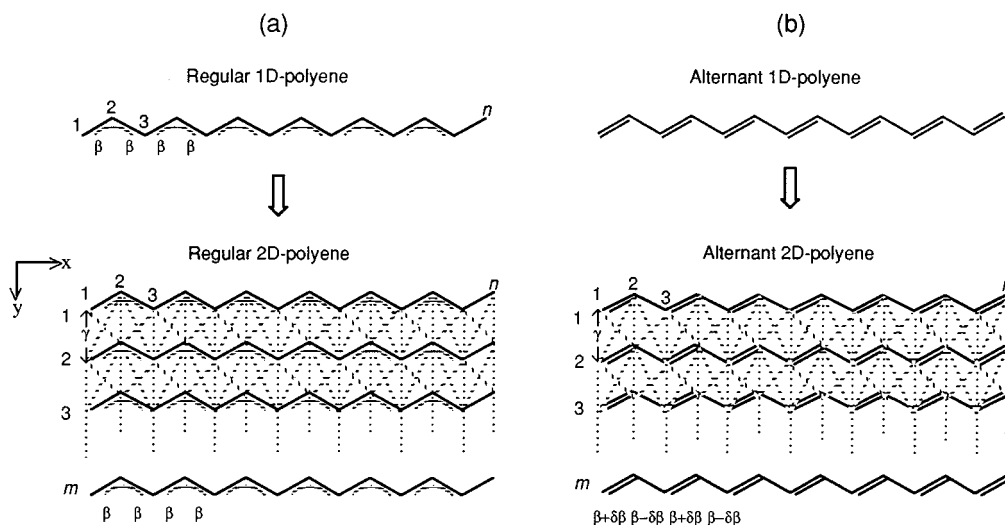


FIG. 5. A model for interchain interaction in (a) regular and (b) alternant 2D polyenes. Polyene chains are arranged within the plain including the single polyene or stacked with each other in the direction perpendicular to the plain.

$$\begin{aligned}
 \tilde{H}_{ii'}^{(p,p')}[Q] &= \delta_{ii'} \delta_{p',p} \epsilon_i + \delta_{ii'} \delta_{p',p \pm 1} \gamma^{(0)} + \delta_{ii'} \delta_{p',p \pm 2} \\
 &\times \sum_{q=1}^Q \cos \frac{qi^{(p')} \pi}{n+1} \gamma^{(q)} + \delta_{p',p \pm 1} \frac{2}{n+1} \\
 &\times \{1 + (-1)^{i+i'}\} \sum_{q=2}^Q \sum_{k=1}^q \sin \frac{ki^{(p)} \pi}{n+1} \\
 &\times \sin \frac{(q-k)i^{(p')} \pi}{n+1} \gamma^{(q)}. \quad (14)
 \end{aligned}$$

The first term is the intrachain interaction, the second term the contribution from the nearest neighbor interaction, $\gamma^{(0)}$, between chains, the third term the contributions from the first neighbor, $\gamma^{(1)}$, to the Q th neighbor, $\gamma^{(Q)}$, interactions between chains under assuming that the chain is infinitely long, and the fourth term the correction for the end effect ignored in the third term. However, when $Q=1$, the fourth term becomes completely zero. Therefore, Eq. (14) can be greatly simplified as

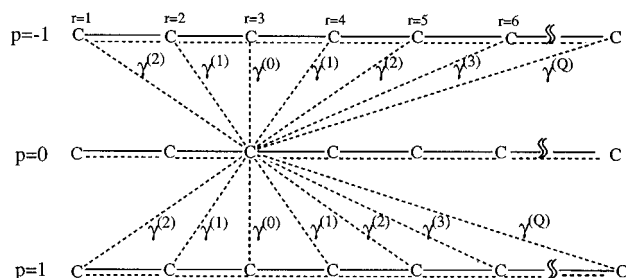


FIG. 6. Interchain interaction $\gamma^{(q)}$ ($q = 1, 2, \dots, Q$) between nearest neighbor chains.

$$\begin{aligned}
 \tilde{H}_{ii'}^{(p,p')}[Q] &\cong \tilde{H}_{ii'}^{(p,p')}[Q=1] \\
 &= \delta_{ii'} \left\{ \delta_{p',p} \epsilon_i + \delta_{p',p \pm 1} \left(\gamma^{(0)} \right. \right. \\
 &\quad \left. \left. + 2 \gamma^{(1)} \cos \frac{i^{(p')} \pi}{n+1} \right) \right\}. \quad (15)
 \end{aligned}$$

The $(n \times m)^2$ MO based matrix elements for the whole interacting system are represented as

$$\tilde{H} = \begin{bmatrix}
 \begin{array}{c|c|c|c|c}
 p=1 & 2 & 3 & \dots & m \\
 \hline
 \begin{array}{c} \epsilon_1 \quad \epsilon_2 \quad 0 \\ 0 \quad \epsilon_n \end{array} & \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad 0 \\ 0 \quad \Gamma_n \end{array} & \begin{array}{c} 0 \\ 0 \end{array} & \begin{array}{c} 0 \\ 0 \end{array} & \begin{array}{c} 0 \\ 0 \end{array} \\
 \hline
 \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad 0 \\ 0 \quad \Gamma_n \end{array} & \begin{array}{c} \epsilon_1 \quad \epsilon_2 \quad 0 \\ 0 \quad \epsilon_n \end{array} & \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad 0 \\ 0 \quad \Gamma_n \end{array} & \begin{array}{c} 0 \\ 0 \end{array} & \begin{array}{c} 0 \\ 0 \end{array} \\
 \hline
 0 & \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad 0 \\ 0 \quad \Gamma_n \end{array} & \begin{array}{c} \epsilon_1 \quad \epsilon_2 \quad 0 \\ 0 \quad \epsilon_n \end{array} & \begin{array}{c} \Gamma_1 \quad \Gamma_2 \quad 0 \\ 0 \quad \Gamma_n \end{array} & \begin{array}{c} 0 \\ 0 \end{array}
 \end{array}
 \end{bmatrix} \quad (16)$$

where

$$\Gamma_i = \gamma^{(0)} + 2 \gamma^{(1)} \cos \frac{i \pi}{n+1}. \quad (17)$$

In Eq. (16), the diagonal submatrices correspond to the terms within each single polyene that are already diagonalized. The off-diagonal submatrices, the interchain interactions, are confined to nearest neighbor chain interaction. The diagonal elements of those submatrices are the integrals between same i th MOs which belong to the neighboring chains with each other. The off-diagonal elements of them become zero, because the interaction integral given by Eq. (17) has no elements between different energy levels, i and $i' (\neq i)$, as far as $Q=1$ is assumed. Nonzero values appear, when the contribution from $Q \geq 2$ in Eq. (14) is taken into account, because end effects from the fourth term remain. These terms cause a slight interaction between different MOs, i and $i' (\neq i)$. However, this contribution ($Q \geq 2$) is negligible because of the small value of the $\gamma^{(q)}$ for $q \geq 2$. In addition, trigonometric sine functions in these terms approach zero with increasing n . As a result, the contribution from $Q \geq 2$ can be neglected and thus Eq. (14) can be adequately approximated by Eq. (15).

On the other hand, if the polyene is long enough that the fourth term in Eq. (14), end effect of the chain, becomes almost zero, the interacting matrix element can be written by

$$\Gamma_i = \gamma^{(0)} + 2 \left(\gamma^{(1)} \cos \frac{i\pi}{n+1} + \gamma^{(2)} \cos \frac{2i\pi}{n+1} + \gamma^{(3)} \cos \frac{3i\pi}{n+1} + \cdots + \gamma^{(Q)} \cos \frac{Qi\pi}{n+1} \right), \quad (18)$$

where the second term expanded by $\gamma^{(q)}$ corresponds to the third term of Eq. (14). By this reason, Γ_i in Eq. (16) can be also defined by Eq. (18) instead of Eq. (17).

It can be seen from Eq. (16) that the individual energy levels in a polyene interact only with the same energy levels which belong to the nearest neighbor chain. It is clear that the large $(n \times m)^2$ problem can be therefore reduced to the m^2 problem for each i as follows:

$$\begin{matrix} p=1 & 2 & \cdots & m \end{matrix} \quad \left| \begin{array}{cccc} \epsilon_i - \epsilon & \Gamma_i & & \\ \Gamma_i & \epsilon_i - \epsilon & \Gamma_i & 0 \\ & \Gamma_i & \epsilon_i - \epsilon & \\ 0 & & \ddots & \\ & & & \epsilon_i - \epsilon \end{array} \right| = 0 \quad (i=1,2,\dots,n). \quad (19)$$

This means that the eigenvalue problem is individually given for the particular level i of the original single polyene, and hence treated independently from other levels. Equation (19) has the same form as the usual Hückel secular equation for polyene except the diagonal elements are replaced by energy levels ϵ_i of the single polyene instead of its Coulomb integral α , and the off-diagonal matrix elements Γ_i instead of resonance integral β . In a similar manner as the analytical solution for single polyene, the orbital energies and MOs for regular 2D polyene are written by

$$\epsilon_i^j[Q=1] = \epsilon_i + 2\Gamma_i \cos \theta_j, \quad (20)$$

$$\varphi_i^j = \sum_{p=1}^m \sqrt{\frac{2}{m+1}} \sin(p\theta_j) \varphi_i, \quad \theta_j = j\pi/(m+1), \quad (j=1,2,\dots,m), \quad (21)$$

respectively. $\epsilon_i (i=1,2,\dots,n)$ in Eq. (20) are orbital energies for a single polyene given by Eq. (2). The second term of Eq. (20) means that every $\epsilon_i (i=1,2,\dots,n)$ splits into m after taking the interaction between chains into account. The magnitude of the splitting depends on Γ_i for each level i . φ_i in Eq. (21) are the MOs for a single polyene given by Eq. (3).

B. Orbital energy and molecular orbital for $Q=0$

The higher order terms than the first in the parenthesis of Eq. (18) can be neglected because of the small value of $\gamma^{(q)} (q \geq 2)$. Therefore, the use of Eq. (17) as Γ_i seems to be sufficiently reasonable. However, at first, we want to simplify it furthermore by taking only $Q=0$ into account. By neglecting $\gamma^{(1)}$ from Eq. (15), the matrix element between chains is simply defined as

$$\tilde{H}_{ii'}^{(p,p')} \equiv \delta_{ii'} (\delta_{p',p} \epsilon_i + \delta_{p',p \pm 1} \gamma^{(0)}). \quad (22)$$

The secular equation to be solved becomes

$$\begin{matrix} p=1 & 2 & \cdots & m \end{matrix} \quad \left| \begin{array}{cccc} \epsilon_i - \epsilon & \gamma^{(0)} & & \\ \gamma^{(0)} & \epsilon_i - \epsilon & \gamma^{(0)} & 0 \\ & \gamma^{(0)} & \epsilon_i - \epsilon & \\ 0 & & \ddots & \\ & & & \epsilon_i - \epsilon \end{array} \right| = 0 \quad (i=1,2,\dots,n), \quad (23)$$

giving the following energy levels:

$$\epsilon_i^j[Q=0] = \epsilon_i + 2\gamma^{(0)} \cos \theta_j. \quad (24)$$

The magnitude of the orbital splitting after interchain interaction does not depend on i , differing from Eq. (20) that depends on i .

Now, we describe the properties of the energy levels given by Eq. (24) and the molecular orbital by Eq. (21), which are analytically derived for the 2D polyene composed of m chains. For example, the orbital energies for the double chain ($m=2$) are given by

$$\epsilon_i^j[Q=0] = \epsilon_i \pm \gamma^{(0)}, \quad (i=1,2,\dots,n), \quad (25)$$

for the triple chain ($m=3$) by

$$\epsilon_i^j[Q=0] = \epsilon_i \pm \sqrt{2}\gamma^{(0)}, 0 \quad (i=1,2,\dots,n). \quad (26)$$

Equations (25) and (26) are consistent to the solutions obtained from the 2×2 and 3×3 MO based secular equations by Eq. (23), respectively. The energy diagrams are shown in Fig. 7 for $\gamma^{(0)} = -1$, which are also consistent with those obtained by the usual diagonalization of the AO based Hückel matrix for the whole system.

From Eq. (21), molecular orbitals are written as functions of n and m by

TABLE I. k values by Eq. (29) for various n and m .

$n \backslash m$	1	2	3	4	5	6	7	8	9	10
2		1.000	0.707	0.618	0.577	0.555	0.541	0.532	0.526	0.521
4		0.618	0.437	0.382	0.357	0.343	0.334	0.329	0.325	0.322
6		0.445	0.315	0.275	0.257	0.247	0.241	0.237	0.234	0.232
8		0.347	0.246	0.215	0.201	0.193	0.188	0.185	0.183	0.181
10		0.285	0.201	0.176	0.164	0.158	0.154	0.151	0.150	0.148
12		0.241	0.170	0.149	0.139	0.134	0.130	0.128	0.127	0.126
14		0.209	0.148	0.129	0.121	0.116	0.113	0.111	0.110	0.109
16		0.185	0.130	0.114	0.107	0.102	0.100	0.098	0.097	0.096
18		0.165	0.117	0.102	0.095	0.092	0.089	0.088	0.087	0.086
20		0.149	0.106	0.092	0.086	0.083	0.081	0.080	0.079	0.078

C. Effect of $\gamma^{(1)}$ on the electronic structure

Again, we consider the case of $Q=1$, that is, Eq. (20) having Eq. (17) as the Γ_i . In the case of $Q=0$, the magnitude of m splitting by interchain interaction does not depend on the level i . In other words, every level denoted by i ($=1, 2, \dots, n$) is individually interacted with same magnitude. In the case of $Q>0$, on the other hand, the magnitude depends on each level i as shown in Fig. 8 in which the energy diagram of $2C_6H_8$ for $Q=1$ is drawn in comparison with that for $Q=0$. The energy levels are denoted as a function of $-\beta$. As an example of strong interaction between chains, $\gamma^{(0)}$ is assumed to be β and $\gamma^{(1)}$ is to be 0.07β , calculated by using Eq. (41) as mentioned later. It shows that in the case of $Q=0$ the individual energy levels are split into two by ± 1.0 , but in the case of $Q=1$ the splitting depends on individual energy levels, affected by additional interaction $\gamma^{(1)}$. However, it is of interest that the total energy is nevertheless unaffected by the reason mentioned below.

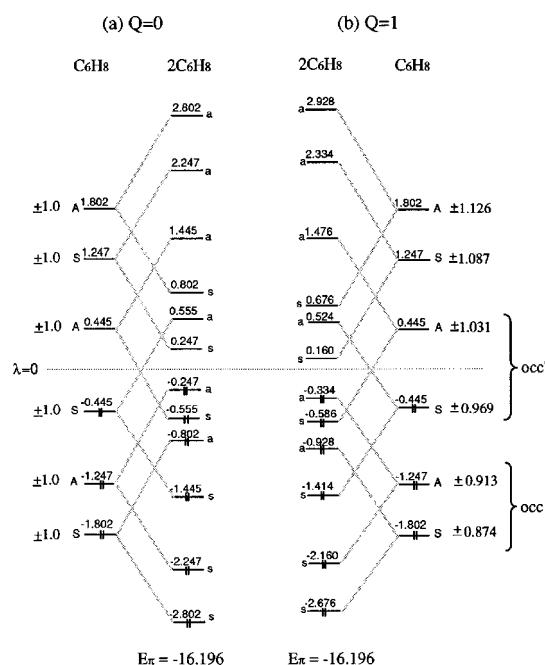


FIG. 8. Energy diagrams for interchain interactions of hexatriene double ($m=2$) chains for (a) $Q=0$ and (b) $Q=1$. The energy levels are written as a function of $-\beta$. $\gamma^{(0)}$ is assumed to be β and $\gamma^{(1)}$ to be 0.07β . The notation occ in (b) means the fully occupied i th level after interchain interaction and occ' the partially occupied i th level.

The total π energy of 2D polyene for the case of $Q=1$ is given by summing up the occupied (i, j) pairs of Eq. (20) as

$$E_{\pi} = 2 \sum_{(i,j)}^{\text{occ}} \epsilon_i^j [Q=1] \\ = 2 \left(\sum_{(i,j)}^{\text{occ}} \epsilon_i^j [Q=0] + 4 \gamma^{(1)} \sum_{(i,j)}^{\text{occ}} \cos \theta_i \cos \theta_j \right). \quad (30)$$

In the above, Γ_i in Eq. (20) is substituted by Eq. (17) and the first term is given by Eq. (24). The second term of Eq. (30) becomes

$$\sum_{(i,j)}^{\text{occ}} \cos \frac{i\pi}{n+1} \cos \frac{j\pi}{m+1} \\ = \sum_i^{\text{occ}} \cos \frac{i\pi}{n+1} \sum_{j=1}^m \cos \frac{j\pi}{m+1} \\ + \sum_i^{\text{occ}'} \cos \frac{i\pi}{n+1} \sum_{j=1}^{m'} \cos \frac{j\pi}{m+1}. \quad (31)$$

The occ means that the summation is running on i which has fully occupied m orbitals on j as shown in Fig. 8. The occ' (even number) is running on i which has both of occupied ($j=1 \sim m'$) and unoccupied ($j=m'+1 \sim m$) orbitals on j . In the above equation, the first term gives zero, because the summation on j becomes zero. The second term gives also zero, because

$$\sum_i^{\text{occ}'} \cos \frac{i\pi}{n+1} \sum_{j=1}^{m'} \cos \frac{j\pi}{m+1} \\ = \sum_i^{\text{occ}'/2} \left(\cos \frac{i\pi}{n+1} \sum_{j=1}^{m'} \cos \frac{j\pi}{m+1} \right. \\ \left. + \cos \frac{(n-i+1)\pi}{n+1} \sum_{j=1}^{m'} \cos \frac{j\pi}{m+1} \right) \\ = \sum_i^{\text{occ}'/2} \cos \frac{i\pi}{n+1} \sum_{j=1}^m \cos \frac{j\pi}{m+1} = 0. \quad (32)$$

The occ'/2 means that i is running on occ' less than $\lambda=0$. Consequently, the summation in the second term of Eq. (30) gives zero, so that additional interaction $\gamma^{(1)}$ does not affect

on the total π energy for $Q=0$. As a result, Eq. (30) is simply written as

$$E_{\pi} = 2 \sum_{(i,j)}^{\text{occ}} \epsilon_i^j [Q=1] = 2 \sum_{(i,j)}^{\text{occ}} \epsilon_i^j [Q=0]. \quad (33)$$

This proves that the total π energy in Fig. 8 is not changed even by including $\gamma^{(1)}$ and can be calculated only from the orbital energies for $Q=0$ given by Eq. (24).

The energy gap between HOMO and LUMO for $Q=1$ is represented by

$$\begin{aligned} \Delta_g^{\text{BA}}(2D)[Q=1] &= \Delta_g^{\text{BA}}(2D)[Q=0] + 4\gamma^{(1)} \\ &\times \left(\cos \frac{i_L \pi}{n+1} \cos \frac{j_L \pi}{m+1} \right. \\ &\quad \left. - \cos \frac{i_H \pi}{n+1} \cos \frac{j_H \pi}{m+1} \right). \end{aligned} \quad (34)$$

The second term means the effect of $\gamma^{(1)}$ on the energy gap for $Q=0$, where the LUMO corresponds to the j_L th orbital split from the i_L th orbital and the HOMO corresponds to the i_H th orbital split from the j_H th orbital. By using the relations $i_L = n - i_H + 1$ and $j_L = n - j_H + 1$, the second term becomes zero. As a result, as well as is the total π energy, the energy gap is also not changed by including $\gamma^{(1)}$, that is

$$\Delta_g^{\text{BA}}(2D)[Q=1] = \Delta_g^{\text{BA}}(2D)[Q=0]. \quad (35)$$

It will be advantageous that those important properties of electronic structures can be discussed only with the contribution $\gamma^{(0)}$, nevertheless $\gamma^{(1)}$ seems to be rather important. Therefore, we deal with the case of $Q=0$ given by Eq. (24) in the following discussion.

IV. ALTERNANT 2D POLYENE

A. Analytical solution for alternant 2D polyene

Next, we consider the effect of bond alternation on 2D polyene. In this section, the relationship between interchain interaction and Peierls instability will be derived. The total energy is given by the sum of π and σ electronic energies for the bond alternated 2D polyene as a function of β and $\gamma^{(0)}$.

At first, to define total π energy of bond alternated 2D polyene, we start with the energy levels of alternant single polyenes as already derived in Sec. II. This treatment corresponds to Fig. 5(b). On the basis of the orbital energy after bond alternation, the secular equation for 2D polyene is approximately expressed by an extension of Eq. (23) as

$$\begin{vmatrix} \epsilon_i + \Delta \epsilon_i^{\text{BA}} - \epsilon & \gamma^{(0)} & \cdots & 0 \\ \gamma^{(0)} & \epsilon_i + \Delta \epsilon_i^{\text{BA}} - \epsilon & \gamma^{(0)} & 0 \\ & \gamma^{(0)} & \epsilon_i + \Delta \epsilon_i^{\text{BA}} - \epsilon & \\ 0 & & & \ddots \\ & & & \epsilon_i + \Delta \epsilon_i^{\text{BA}} - \epsilon \end{vmatrix} = 0, \quad (36)$$

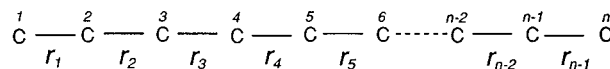


FIG. 9. Numberings of sites and bonds in polyene.

where $\epsilon_i + \Delta \epsilon_i^{\text{BA}}$ are substituted as the diagonal matrix elements in place of ϵ_i in Eq. (23). In this formula, we assume that the magnitude of the interchain interaction is not changed even after the bond alternation occurs. The molecular orbitals of regular polyene are also assumed to remain unchanged and thus the MO based matrix elements given by Eq. (22) to be held. As well as the regular 2D polyene, Eq. (36) leads to the analytical solution

$$\epsilon_i^j \text{BA} = \epsilon_i + \Delta \epsilon_i^{\text{BA}} + 2\gamma^{(0)} \cos \theta_j. \quad (37)$$

This shows that the energy levels for alternant 2D polyene are given by the sum of Eqs. (7) and (24).

In a similar manner as Eqs. (9) and (28), energy gap in alternant 2D polyene is given by

$$\begin{aligned} \Delta_g^{\text{BA}}(2D) &= -4\beta \sin \frac{\pi}{2(n+1)} - \frac{4\delta\beta}{n+1} \\ &\times \text{cosec} \frac{\pi}{2(n+1)} \cos^2 \frac{\pi}{2(n+1)} \\ &+ 4\gamma^{(0)} \cos \frac{\pi}{m+1}. \end{aligned} \quad (38)$$

Written for reference, in the large n and m limitations, the band gap becomes

$$\begin{aligned} \lim_{m \rightarrow \infty} \lim_{n \rightarrow \infty} \Delta_g^{\text{BA}}(2D) &= \lim_{n \rightarrow \infty} \left(-\frac{8}{\pi} \delta\beta + 4\gamma^{(0)} \cos \frac{\pi}{m+1} \right) \\ &= -\frac{8}{\pi} \delta\beta + 4\gamma^{(0)}. \end{aligned} \quad (39)$$

This means that whether an energy gap occurs or not is determined by both the magnitudes of $\delta\beta$ and $\gamma^{(0)}$. Thus we can get a simple relation. That is, if the condition

$$|\gamma^{(0)}| \geq \frac{2}{\pi} |\delta\beta| \quad (40)$$

is satisfied, in other words, the interchain interaction is stronger than some degree of the bond alternation, then the band gap may disappear leading to high conductivity.

B. Total π and σ energies of alternant 2D polyene

To represent the total π energy as a function of the change of bond length, the resonance integral should be estimated corresponding to the bond length r_l , which are numbered as shown in Fig. 9. We assume β_l to be an exponential function of the form^{31,32}

$$\beta_l / \beta = \exp [\zeta(r_m - r_l)], \quad (41)$$

where $\zeta=4.599 \text{ \AA}^{-1}$ is adopted, $r_m(=1.397 \text{ \AA})$ is the C–C bond length of benzene molecule, and β is the resonance integral of π electrons in benzene. Total energy is measured in units of $|\beta|$ in the following. For simplicity, by neglecting the end effects on the bond length, we assume the change of bond length to be constant through the chain,

$$|r_m - r_l| = |\Delta r_l| \cong \Delta r \geq 0. \quad (42)$$

From Eq. (41), the change in resonance integral due to bond alternation is approximated by

$$\delta\beta \cong \{\exp(\zeta \cdot \Delta r) - 1\}\beta. \quad (43)$$

Using Eqs. (2), (7), (37), and (43), total π energy is expressed as a function of Δr by

$$\begin{aligned} E_\pi(\Delta r) &= 2 \sum_{(i,j)}^{\text{occ}} \epsilon_i^{j \text{ BA}}[Q=0], \\ &= 2 \sum_{(i,j)}^{\text{occ}} \left[\alpha + 2\beta \cos \theta_i + \frac{2}{n+1} \frac{\sin^2 \theta_i}{\cos \theta_i} \right. \\ &\quad \left. \times \{\exp(\zeta \cdot \Delta r) - 1\} \beta + 2\gamma^{(0)} \cos \theta_j \right]. \quad (44) \end{aligned}$$

To obtain the total energy as a function of bond alternation, we should define not only π energy, but also σ energy. Previously, in order to describe the local equilibrium electronic structure in a large system, a recursion method was applied for the estimation of π -binding energy.³¹ In this treatment, an expansion by second- and fourth-order terms around the pure σ -bond length(r_σ) was used for the σ -binding energy. In the present work, it is assumed that the total σ energy can be simply expressed by the harmonic oscillator approximation using only a second order term about the displacement from r_σ ,

$$E_\sigma = \sum_{l=1}^{n-1} k_2(r_\sigma - r_l)^2. \quad (45)$$

k_2 is a parameter which is determined by the condition that the length of a double bond which is far from the end is equal to the equilibrium double bond length $r_d(=1.344 \text{ \AA})$ obtained by *ab initio* optimization.¹⁵ The pure σ bond length(r_σ) is assumed to be 1.52 \AA .³² Using the definition of Eq. (42), Eq. (45) is rewritten as a function of Δr by

$$\begin{aligned} E_\sigma(\Delta r) &= k_2\{(n-1)\Delta r^2 + 2\Delta r(r_\sigma - r_m) \\ &\quad + (n-1)(r_\sigma - r_m)^2\}. \quad (46) \end{aligned}$$

In the present treatment, σ energy in connection with interchain interaction (y direction in Fig. 5) is neglected, because energetic behavior of π energy is strongly perturbed by the interchain interaction as described in Sec. III, while that of σ energy may not be substantially changed.

Consequently, the total energy is given by the sum of the σ and π energies as

$$E(\Delta r) = E_\pi(\Delta r) + E_\sigma(\Delta r). \quad (47)$$

To minimize the total energy, the equilibrium bond length should satisfy the condition,

$$\left. \frac{\partial E(\Delta r)}{\partial \Delta r} \right|_{\Delta r=r_{\text{BA}}} = 0, \quad (48)$$

where $r_{\text{BA}}=r_m-r_d=0.053 \text{ \AA}$. From the above condition, k_2 is derived as

$$\begin{aligned} k_2 &= 2\zeta \exp(\zeta \cdot \Delta r_{\text{BA}}) [(n+1)\{(n-1)\Delta r_{\text{BA}} \\ &\quad + (r_\sigma - r_m)\}]^{-1} \sum_i^{\text{occ}} \left(\sin^2 \frac{i\pi}{n+1} \left/ \cos \frac{i\pi}{n+1} \right| |\beta| \right). \quad (49) \end{aligned}$$

For $n=50$, k_2 is determined to be $6.14|\beta|/\text{\AA}^2$.

By using above force constant k_2 for σ energy, the Δr dependency of the total energy given by Eq. (47) is examined for various $\gamma^{(0)}(=0.0, 0.25, 0.50, \text{ and } 0.75)$ and $m=2-5$ as shown in Fig. 10(a)–10(d), respectively. In a single polyene, bond alternant structure ($\Delta r \neq 0$) is preferred for π -binding energy. That is, total π energy is stabilized with increasing $\delta\beta$ (or Δr) as described in Sec. II. On the contrary, regular one ($\Delta r=0$) is always preferred for σ -binding energy as seen from Eq. (46). Δr_{eq} at the equilibrium structure is determined by the sum of both contributions, σ and π . In the present calculations, k_2 is determined so that Δr that minimizes the total energy is adjusted to be r_{BA} so as to satisfy the condition Eq. (48). When the interaction between chains is rather small, that is, while one dimensionality is maintained high, Δr_{eq} lies in the vicinity of r_{BA} . However, when two dimensionality becomes dominant, Δr comes close to zero even in π energy. As a result, Δr_{eq} decreases with increasing $\gamma^{(0)}$, leading to a regular structure for sufficiently large $\gamma^{(0)}$. With respect to m dependency, the smaller Δr_{eq} tends to be energetically minimum with increasing m within even number or within odd one at the same $\gamma^{(0)}$. However, it may be found that Δr_{eq} of even number of chains approaches zero somewhat faster than that of odd number of chains with increasing $\gamma^{(0)}$. For, when m is odd, the number of antisymmetric orbitals on particular i th level is more than that of symmetric orbitals by one that remains unchanged from the original energy level of the single polyene as shown in Fig. 7. These extra antisymmetric orbitals that maintain one dimensionality may be considered to prefer the bond alternation.

Finally, we propose a simple interpretation for the aforementioned results. As shown in Figs. 11(a) and 11(b), we consider the case that $\gamma^{(0)}$ is so small, that is Eq. (40) is not satisfied, the interchange between occupied and unoccupied orbitals does not occur. In this case, Peierls distortion that stabilizes the occupied orbitals therefore leads to the stabilization in total energy. On the other hand, as shown in Figs. 11(c) and 11(d), in the case that $\gamma^{(0)}$ is so large that interchange between occupied and unoccupied orbitals occurs, the level which was unoccupied in the original single polyene becomes to lie lower than $\lambda=0$ after the interchain interaction and also the level which was occupied in the original single polyene becomes to lie upper than $\lambda=0$. As a result, so long as Eq. (40) is satisfied, the larger the interchain interaction $\gamma^{(0)}$, the greater the total π energy is stabilized. It was

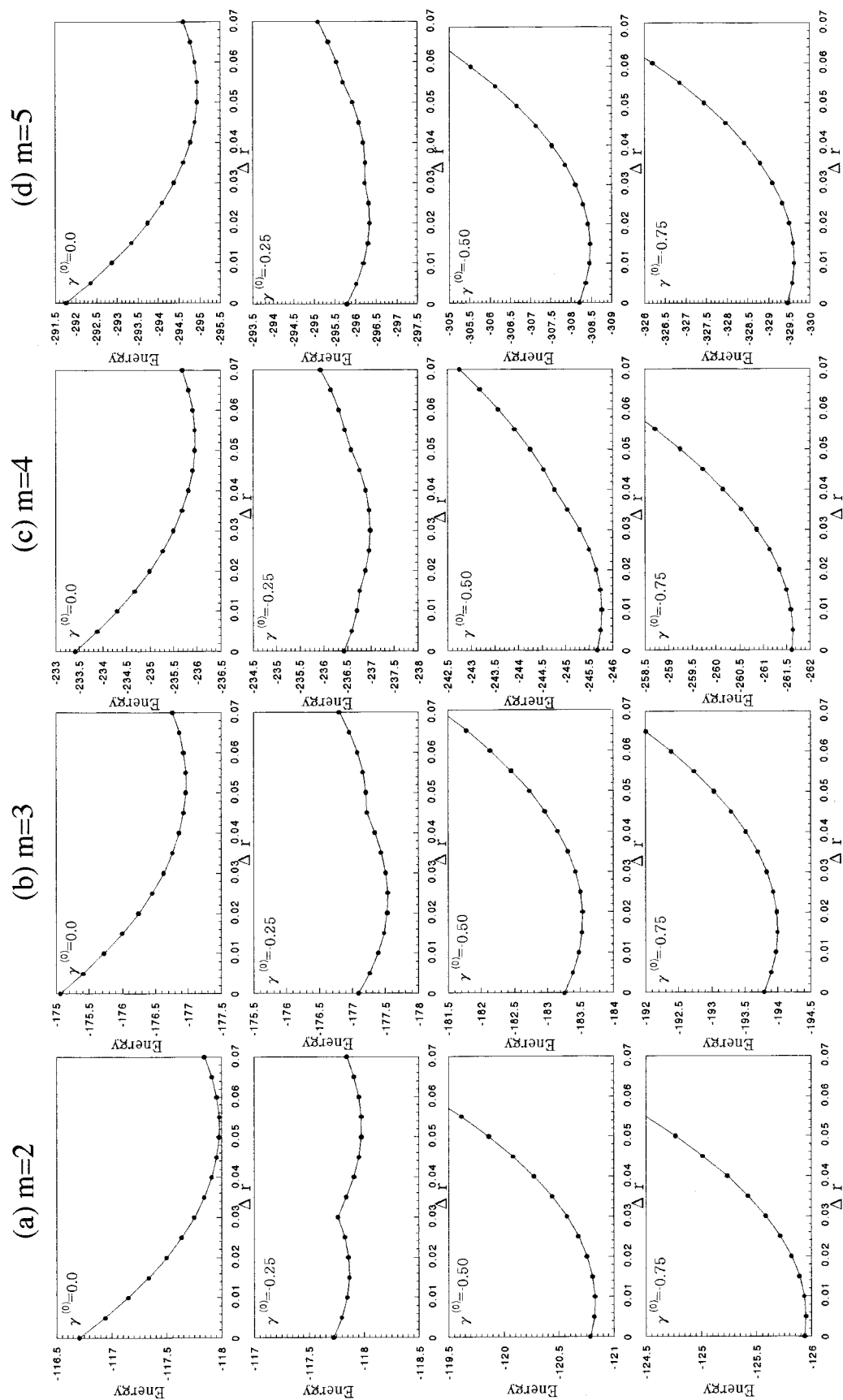


FIG. 10. Total energies including σ and π contributions in 2D polyene as a function of Δr for various m and $\gamma^{(0)}$.

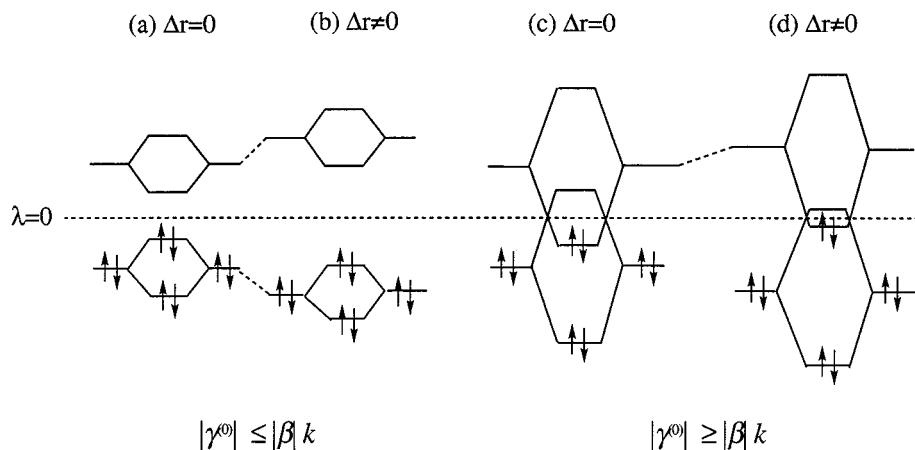


FIG. 11. Schematic illustration for energetic behavior near HOMO and LUMO under bond alternation and interchain interaction.

finally proved that even if σ energy is included, the above mentioned feature in π energy is substantially retained.

V. CONCLUSION

In the present paper we have presented a simple treatment for the estimation of Peierls instability in 1D and 2D polyenes with arbitrary sizes of chains. First, a simple formula that gives the magnitude of bond alternation is derived from the concept of in-phase and out-of-phase interactions in finite 1D polyene in real space without \mathbf{k} vectors. It is visually demonstrated that HOMO contributes to great stabilization toward the distortion, while LUMO to great destabilization against the distortion. Our treatment is applied to the Peierls instability in finite 2D polyene. As the starting of the investigation, analytical energy levels and MOs for regular 2D polyene with equidistant C–C bonds are derived from the interaction matrix elements based on the MOs for a single polyene.

Using the analytical solution thus obtained, a simple formula for the alternant 2D polyene is also derived on the basis of the energy levels of alternant 1D polyene. Total energy including π and σ systems is defined and the relationship between bond alternation and interchain interaction is discussed. It has been proved that Peierls instability is strongly suppressed under large interchain interaction, and in this case the interchange between occupied and unoccupied orbitals plays a crucial role.

Our treatment would provide a simple concept for estimating the Peierls instability and be applicable to other structural distortions not only in polyene but also in other π -electron systems. This treatment would be further feasible to investigate the relationship between crystal structure of molecular stacking system and its energy band structure. We would expect that applications to more realistic systems would provide a theoretical insight on designing highly conductive polymers in connection with interchain interaction.

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