A Study on Peierls Instability in Quasi-One-Dimensional-System with Interchain-Interactions. Semi-Empirical Self-Consistent-Field Molecular Orbital Approach

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It is widely known that interchain-interactions diminish the Peierls instability in a one-dimensional electronic system. We studied the electronic structure of the (-H-) chains as a model system for the quasi-one-dimensional system. We compare the result of a Hartree-Fock type calculations for a non-interaction chain, a two-chain model with interchaln-interactions, two-chain model with interchain-interactions, and a two-dimensional model in which infinite number of chains on the same plane interact with each other. The energy band and the total energy are obtained by the LCAO crystal orbital method using the CNDO/2 approximation. According to the calculated total energy in models with interchain-interactions, for both two-chain and two-dimensional models, the Peierls instability decreases, and disappears for a strong interchain-interaction.

It is widely noted that a pure-one-dimensional electronic system has instability in $2k_F$ fluctuations (here, k_F means Fermi wave number). For example, a polyacetylene (PA) is a typical one-dimensional-electronic system. When PA has equi-distant bonds, it has a metallic character because of a half occupied π-band. Actually however, PA has bond alternation (in other words, lattice distortion with $k=\pi/a$) which creates a Peierls gap, so that PA is stabilized in total energy.[1,2,3]

However, in some one-dimensional substances, for example $(SN)_x$ the Peierls instability does not appear at low temperatures.[4] For these substances, it is widely pointed out that a interchain interactions diminish the Peierls instability in a one-dimensional-electronic system. There have been some investigations on the effect of interchain-interactions for the Peierls instability. Among them, Kamimura et al. have calculated charge-response functions for a perturbation of the Coulomb potential using a non-self-consistent perturbational method in the rigid band model.[5-8] In their results, the Fermi surfaces are bent by interchain-interactions, so that nesting caused by the $2k_F$ fluctuations is not complete, and the response functions are not divergent at $2k_F$.

Kamimura et al. carried out calculations based on a rigid band model using the energy band obtained by a tight-binding approximation without self-consistency,[5,6] and with self-consistency (Local-Density-Functional formalistm).[7,8] In their treatment, however, the perturbational potential is not calculated with self-consistency. They consider the perturbation of the Coulomb potential as the fluctuation, but do not consider the bond-alternation directly. Further, though bond-alternation influences the bond-orders sensitively, their calculations do not include the change in the exchange interactions which are a function of the change in the bond-order caused by the fluctuation. Regarding pure one-dimensional systems, though Cizek,[9] Paldus[9-15] have studied the Peierls instability in a conjugated π-systems using the self-consistent Hartree-Fock method in detail, there have not been many investigations on systems including interchain interactions. Therefore, in this article we emphasize model systems with and without interchain-interactions in order to quantitatively investigate the relation between the interchain-interactions and the Peierls instability quantitatively by using a semi-empirical molecular orbital method based on Hartree-Fock theory.

Model and Method of Calculation

We consider a $(-H-)_x$ chain (Fig. 1) as a model

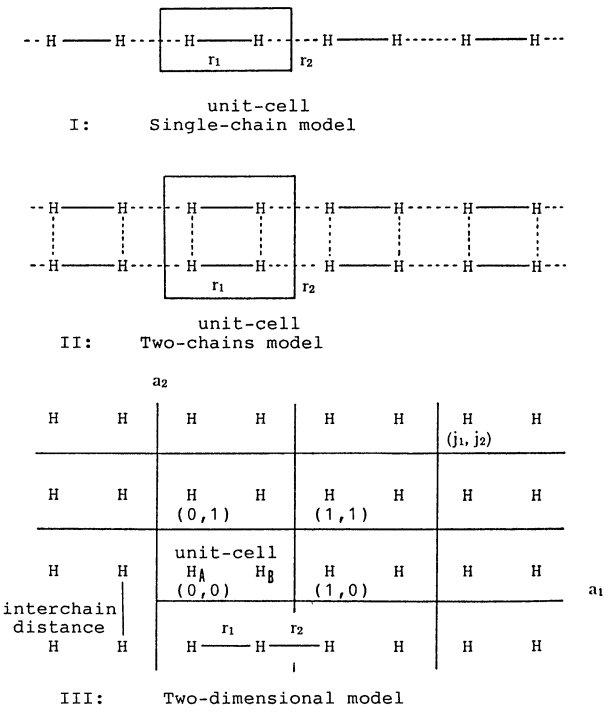

Fig. 1. Hydrogen atoms chain model.
$a=(r_1+r_2)/2$ (lattice constant).
$b=(r_2-r_1)/2$ (bond-alternation parameter).

of a one-dimensional-electronic-conductive polymer. There are three models considered: a single $(-H-)_x$ chain (single-chain model), two $(-H-)_x$ chains parallel to each other (two-chain model), and many $(-H-)_x$ chains which aligned on the same plane periodically (two-dimensional model). The latter two are taken into account as models which include interchain-interactions; interactions are functions of the interchain-distance. We define the z-axis to be along the polymer chain direction. The lattice constant $\boldsymbol{a}$ is tentatively taken as 0.9 Å and the interchain distance is taken from 1.1 Å to 1.6 Å. The two-dimensional model is a simple lattice; 1z and 1x are the lattice vectors of the chain direction and perpendicular direction to it, respectively. In these models we define the bond alternation parameter b as $b=(r_2-r_1)/2$, which are shown in Fig. 1. The case of $b=0$ corresponds to no bond alternation; hence, a unit cell contains one H atom. However, for b not equal to 0, there is a bond alternation, and the unit cell contains two H atoms. We calculated the total energies as a function of the bond alternation parameter b in models with and without interchain-interactions; we also studied the Peierls instability caused by $\pi/\boldsymbol{a}$ lattice distortion.

Calculations of the electronic structure are performed using the self-consistent crystal-orbital method with CNDO/2 (Complete Neglect of Differential Overlap) parametrization.[16-21] Since the CNDO/2 method includes inter-electron interactions of Coulomb, exchange, and inter-core repulsion, we considered that the method is suitable for evaluating of the total energy with inter-electron repulsion semi-quantitatively.

In single-chain, two-chain, and two-dimensional models, the crystal orbitals are written as

$$\Phi_s{}^k=\sum_j\sum_p \exp(ijk)C_{ps}{}^k\,\chi_p{}^j, \tag{1}$$

Here, j, p, and s represent a unit cell, an atomic orbital, and a band state, respectively. k is a wave-number vector (for the single-chain and two-chain models, k is one-dimensional, and for the two-dimensional model, $k=(k_z,k_x)$), the points of which are selected periodically in a reciprocal lattice space.

We obtained the crystal orbitals for all of the k-points from a diagonalization of the Fock matrices,

$$\boldsymbol{F}^k\boldsymbol{C}_s{}^k=\varepsilon_s{}^k\boldsymbol{C}_s{}^k, \tag{2}$$

A definition of the Fermi energy is given by

$$2V(2\pi)^{-N}\sum_s\{\int\theta(E_F-\varepsilon_s{}^k)\mathrm{d}k\} = \text{the number of electron per unit cell} \tag{3}$$

step function $\theta(x)=0(x<0),\ 1\ (x>0)$

N: dimension 1,2,3 $\quad k: -\pi/\boldsymbol{a}<k<\pi/\boldsymbol{a}$

The density matrices in k-space are calculated by summation over the occupied orbitals with eigenvalues under the Fermi level, and given by

$$\boldsymbol{D}^k=2\sum_s^{\mathrm{occ}}\boldsymbol{C}_s{}^k(\boldsymbol{C}_S{}^k)^+ \tag{4}$$

$$P_p{}^jq^0=2V(2\pi)^{-N}\int\exp(ikj)D_{pq}{}^k\,\mathrm{d}k \tag{5}$$

$$P_A=\sum_p^{\text{on }A}P_p{}^0p^0 \tag{6}$$

At this point it is necessary for a model with interchain-interactions that we appropriately choose an interval of k-points which is small enough in order to include the effect of Fermi surface bending by the interchain interactions. In the present work, we selected 31 k-points for a single-chain model and a two-chain model, and 15×8 k-points for a two-dimensional model ($k_z\times k_x$ in reciprocal space). It is widely noted that the trapezoidal rule gives the best evaluation for the integral of the Fourier transformation in Eq. 5 for nonmetals, because there is no Fermi surface in the nonmetallic system. Thus, the density matrices $D_{pq}{}^k$ is continuous and smooth on the k-dependence.[22,23] The linear tetrahedron method is ordinally used for the LDF formalism, because only $D_p{}^0p^0$ elements are necessary for the LDF formarism; however, since all of the $D_p{}^jq^0$ elements are necessary for the Hartree-Fock method, we use the trapezoidal rule for simplicity. A problem to be solved, therefore, is still retained for the integral method in order to obtain the $D_p{}^jq^0$.

Fock matrix elements are given by Eq. 7, various integrals are given in Eqs. 8—12, and the total energy is given in Eq. 13.

$$\boldsymbol{F}^k=\sum_j\exp(ikj)\boldsymbol{F}^{j0} \tag{7}$$

$$F_p{}^jq^0=H_p{}^jq^0+G_p{}^jq^0 \tag{8}$$

$$H_p{}^0p^0=-1/2(I_p+A_p)+\gamma_A{}^0{}_A{}^0/2-\sum_B\sum_j\gamma_B{}^jA^0\,Z_B \tag{9}$$

$$H_p{}^jq^0=1/2(\beta_A+\beta_B)S_p{}^jq^0 \tag{10}$$

$$G_p{}^0p^0=\sum_B\sum_j\gamma_B{}^jA^0\,P_B-1/2\,\gamma_A{}^0{}_A{}^0\,P_p{}^0p^0 \tag{11}$$

$$G_p{}^jq^0=-1/2\gamma_p{}^jq^0\,P_p{}^jq^0 \tag{12}$$

S: overlap integral

γ: two center electron repulsion integral

total energy (per unit cell)

$$E=V(2\pi)^{-N}\int\{\mathrm{Tr}\,\boldsymbol{F}^k\boldsymbol{D}^k-1/2\mathrm{Tr}\,\boldsymbol{G}^k\,\boldsymbol{D}^k\}\,\mathrm{d}k + \sum_A\sum_B\sum_j Z_AZ_B/R_A{}^jB^0 \tag{13}$$

Now, interactions (hopping parameter $H_p{}^jq^0$ and repulsion integral $\gamma_A{}^jB^0$) are included only for the nearest-neighbor atoms in the chain direction, and the nearest-neighbor chains. Because, in the case of the nonmetal system, the exchange interaction decreases exponentially with distance due to the fact that the density matrices are continuous regarding k dependence.[22] On the other hand, in the case of a metal system, the interelectron repulsion is screened by the effect of plasma oscillation due to the electron correlation;[24-26] hence, these effects can correctly be obtained by more elaborate theories including elec-

tron correlation effects. In the case of a metal, interaction truncation is neccesary to avoid the density of the state at E_F from vanishing according to a Hartree-Fock method including long-range interelectron repulsion which is proportional to the inverse of the distance.[24]

We obtained Fock matrices from Eqs. 8—12, and calculated the crystal orbitals again from Eq. 2; iteration of this procedure was repeated until the density matrices converged adequately. We then determined the self-consistent orbitals, and calculated some properties using the SCF orbitals such as band structure, and total energy given by Eq. 13.

Results of Calculation

The total energy is shown as a function of the bond alternation parameter, b, for a system without interchain interactions in Fig. 2. When b=0, the non-bond-alternation case, we obtained two solutions, one of which is a symmetry-adapted solution for a translational operation with a distance a of 0.9 Å; the other is a symmetry-broken solution (which has symmetry for the translational operation with the distance of two unit cells, 1.8 Å). Since the first solution has no band gap, it should be metallic. The second is a Bond-Order-Alternant-Wave (BOAW) solution which has a band gap of 6.9 eV. The second solution was obtained by starting SCF calculations with an initial guess symmetry broken density matrix selected by trial-and- error. The total energy of the BOAW solution is 0.09 eV lower than that of the metallic one. This result suggests that the metallic solution of the system is unstable and easily transfers to the BOAW solution by a small perturbation potential. In the present work we did not try to obtain the Charge-Density-Wave (CDW) solution with partial charges on respective atoms, since we paid our attention to the bond alternation in the systems. In the BOAW solution, the total energy decreases in the b=0—0.15 region shown in Fig. 2; thus, at b=0, a non-bond-alternant system is unstable. The band structure is shown for this single chain model in Fig. 3, indicating the characteristic feature of the Peierls instability for the BOAW solution.

Next, a two-chain model with an interchain distance of 1.2 Å was calculated as a system with interchain interactions. The energy band split into two components from interchain interactions. One component is a symmetric crystal orbital with respect to two chains; the another is antisymmetric. In the non-bond alternation case (b=0), the energy band is occupied under E_F by electrons (Fig. 4), and a metallic solution is obtained. The Fermi wave number, k_F, is shifted from $\pi/2a$ in proportion to the energy splitting

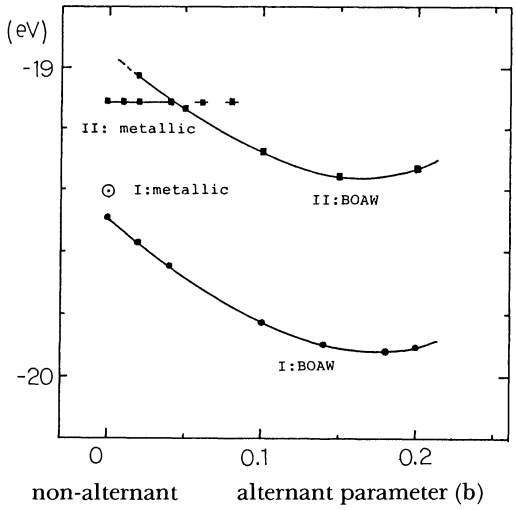

Fig. 2. The total energies per atom (in eV) vs. bond alternation parameter b.
I: single-chain model with the lattice constant a=0.9 Å.
II: two-chains model with the lattice constant with a=0.9 Å and with the interchain distance of 1.2 Å.

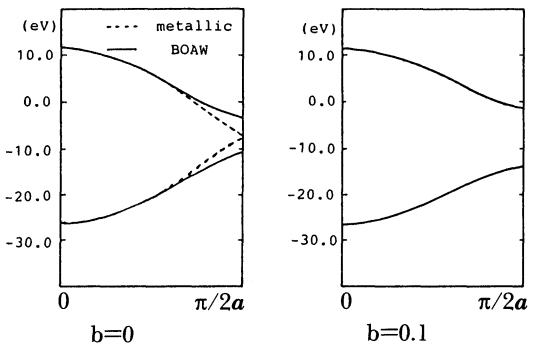

Fig. 3. The energy band structure for the single-chain model.

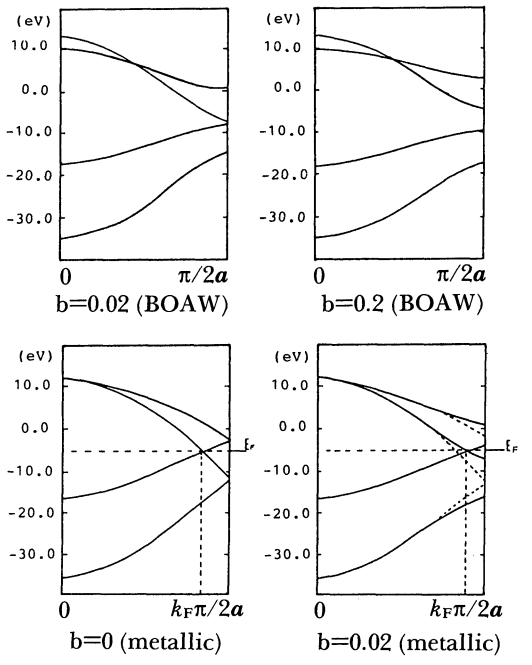

Fig. 4. The energy band structure for the two-chains model.

between the symmetric and the antisymmetric bands. It is noteworthy that the effect of π/a distortion to the total energy decreases because of the Peierls gap by the π/a distortion created far from the Fermi level in k-space. In other words, the system does not obtain a stabilization energy by changing the energy level about $k=\pi/2a$, caused by a bond-alternation (Fig. 4). We can therefore expect that the larger the interchain interaction is, the more stable toward π/a distortion is the two-chain model system. The $2k_F$ distortion which gives the Peierls instability in this system is incommensurate with the lattice constant a; it thus gives a smaller instability than π/a distortion, i.e., the bond-alternation. The calculated total energies are also shown for the two-chain model in Fig. 2, indicating that the metallic solution is obtained in the region b=0—0.04. The total energy for the metallic solution scarcely changes in this region. We can therefore say that the Peierls instability in the system with the interchain-interaction is much smaller than that without interchain-interactions. In the region of b over 0.04 the electronic state transfers from the metallic state to a nonmetallic state with BOAW (Fig. 2). The Peierls gap is then larger than the band splitting caused by interchain-interactions as shown in Fig. 4 (b=0.2 of BOAW). The total energy for the BOAW state in the two-chain model decreases with an increase of b in the region b=0.04—0.15 (Fig. 2).

Finally, we calculated the energy band for the two dimensional model. The orbital energy is a function of k_x and k_z, so that the Fermi surface is bent by large interchain interactions. Therefore, the stabilization in the total energy which is caused by the Peierls gap by π/a distortion is much diminished for the reason mentioned above. The calculated energy band and the Fermi surface are shown in Fig. 5.

We calculated the energy bands and the total energies of the two-dimensional model with interchain distances of 1.6, 1.4, 1.2, 1.1 Å (indicated in Figs. 6 and 7). When the distance is 1.6 Å, there is a metallic solution in the region b=0—0.04 (III_A in Fig. 6). It is shown that the instability of the total energy for the two-dimensional model is considerably less than that for a system without interchain interactions. The second derivative of the total energy with respect to b, however, is negative for the relatively large interchain distances (III_A in Fig. 6). Therefore, at b=0, the non-bond-alternation case, the state is metallic, but unstable with respect to bond-alternation. For the case of III_A, we obtained the BOAW solution in the region of b over 0.06; the total energy is minimum at b=0.16 and is inferred to be lower than that in the metallic case in the region b=0—0.04 from approximate calculations. The metallic solution at the point of b=0 is thus probably unstable for III_A. When the interchain distance is 1.4 Å, the result is as also shown in Fig. 6 (III_B). The tendency is similar to the case with interchain distance of 1.6 Å; the second derivative of the total energy increases. In the case that the interchain distance is 1.2 Å, the total energy is as shown in Fig. 6 (III_C). Metallic solutions were obtained in the region b=0—0.04, where the second derivative of the total

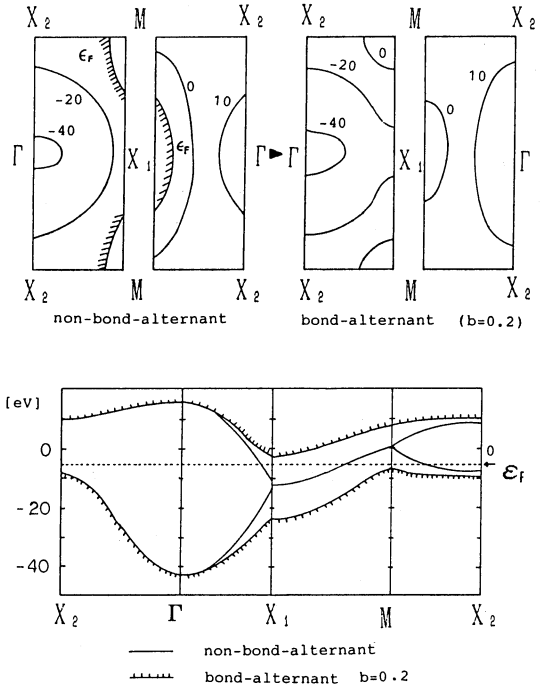

Fig. 5. The energy band structure for the two-dimensional model. The interchain distance is 1.2 Å.

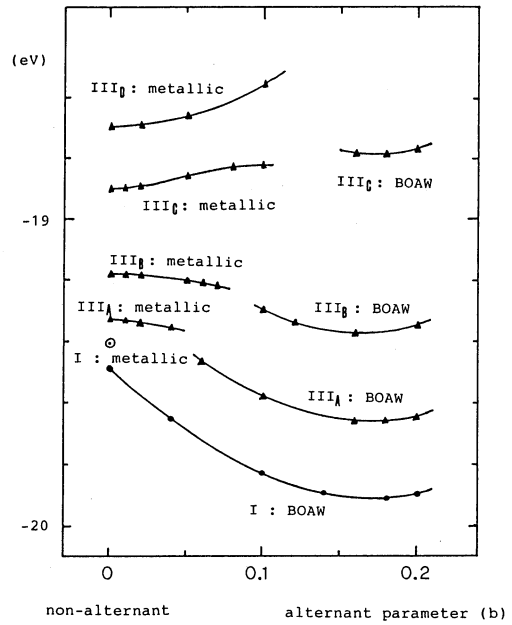

Fig. 6. The total energies per atom (in eV) vs bond alternation parameter b for the two dimensional model with the lattice constant a=0.9 Å.
III_A : the interchain distance of 1.6 Å.
III_B : the interchain distance of 1.4 Å.
III_C : the interchain distance of 1.2 Å.
III_D : the interchain distance of 1.1 Å.
I : the single-chain model.

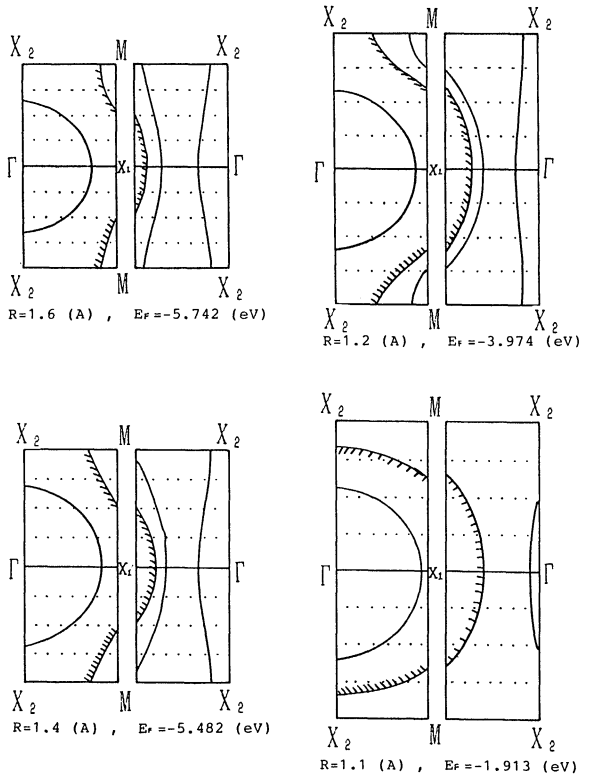

Fig. 7. The shape of the Fermi surface of two-dimensional model at the b=0 point (non-alternant system).
Γ=(0, 0), X_1: along the chain direction.
E_F: Fermi level (in eV), R: Interchain distance (in A), Selected k-points: 15×8 in the first Brillouin zone.

energy becomes positive. In region b=0.16—0.2 we obtained BOAW solutions; the total energy is higher than in the metallic case at b=0. Those arguments mean that the metallic solution at point b=0 with an interchain distance less than 1.4 Å is stable. In the case that the interchain distance is 1.1 Å, the total energy is as shown in Fig. 6 (III_D). From this figure it is obvious that the metallic solution becomes more stable.

The shapes of the Fermi surface are shown in Fig. 7. When the interchain distance is in the range 1.6—1.4 Å, the curvature of the Fermi surface is not so large. This system can be considered to be a typical quasi-one-dimensional metal. However, these systems are unstable. When the interchain distance is in the range 1.4—1.2 Å, the Fermi surface is distorted strongly, and the properties of this system become those of a two-dimensional system. When the interchain distance is 1.2—1.1 Å, the Fermi surface is completely closed. Therefore, this state can be considered to be a complete two-dimensional metal.

Conclusion

According to our results of a CNDO/2 calculation for $(-H-)_x$, as the interchain interactions increase, the system becomes stable at b=0. Particularly, when the interchain distance is smaller than 1.2 Å, the metallic state is expected to exist with considerably large stability: that is, the Peierls instability in this system is completely diminished. When the interchain distance is small enough, the Fermi surface is completely closed; this system becomes two-dimensional metal.

Regarding hydrogen metal, there have been some theoretical and experimental investigations concerning various physicochemical properties at high pressure. Most of those were studied by the Local-Density-Functional formarism, but part were studied by the Hartree-Fock theorem.[27-35]

Some problems to be solved in our study are as follows:

1) The selection of the k point in reciprocal-lattice space and the integration method for a Fourier transformation about metal.

2) Method for solving the SCF problem.

3) The SCF solution except for the BOAW state. For example, CDW, SDW.

4) A method to truncate interactions. In the present work, we took account of only nearest-neighbor interactions.

5) In relation to 3), 4), a treatment of the electron correlation.

Nevertheless, the obtained results given in this article shed light on the relation between the interchain interactions and Peierls instability of a quasi-one-dimensional system quantitatively. Moreover, the result of a two-chain model indicates that a system of two appropriate identical polymers with a strong inter-chain interaction is expected to be metallic upon diminishing the Peierls instability. That is, we can say that there should be a clue to designing conductive polymer systems.

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