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A Through Space/Bond Interaction Analysis of the Shape of the Band Structure of Polyacetylene

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The band structure of all-*trans*-polyacetylene is examined by using through space/bond interaction analysis. It is found that the cross-term in the perturbation expansion between two kinds of interactions governs the band shape near the gap: One kind is the interaction within the backbone, and the other is that between the backbone and the side chain. The relationship between the band structure and the symmetry of the interacting orbitals is also discussed.

The relationship between the structure of a polymer and its electronic states has attracted considerable attention from the theoretical point of view. All-*trans*-polyacetylene is a simple linear conjugated π system and is an insulator with a degenerate ground state because of the alternation of the C–C bond length. The electronic properties of pure polyacetylene have been investigated by using the Hartree-Fock tight-binding approximation both within one-electron pictures[1–9] and including electron-correlation effects.[10,11] There are other methods, for example, using the X_α approach[12,13] and the GKS potential,[14] which give better agreements with the experimental data than do the RHF results. Many theoretical studies show that the conductivity of such a system is intimately related to the distortion of the symmetry attributable to the bond alternation, which gives rise to the formation of a gap between the HOMO π band and the LUMO π^* band.[15–19] This polymer has recently been the focus of enormous interest because of the discovery that the conductivity can be controlled by doping with electron donors and acceptors.[20–27]. Brêdas et al. showed, at the level of the ab initio method, that there is a relationship between the structural change in the bond alternation and the magnitude of the charge-transfer interaction between the polyacetylene and dopants.[28,29] Kertész carried out three-dimensional energy band calculations on highly doped donor and acceptor compounds of polyacetylene based on the rigid-band model[30] and discussed the interaction of the polymer π orbital with the orbitals of the dopants.[31] These facts imply that the conductivity of a Peierls-distorted[32] linear chain is strongly dependent on the environment of polymers in connection with the gap between the top of the filled π-electron valence band and the bottom of the unfilled π^*-electron conduction band.

On the other hand, there have been few studies of the energy band of σ electron orbitals, which are considered to be hardly responsible at all for the conductivity. Hoffmann's group has developed a chemical and theoretical approach to the electronic structures of solids, which mainly have two-dimensional layers, at the level of the extended Hückel method. In their studies, the band structures including σ orbitals of many inorganic crystals have been predicted and interpreted successfully in terms of the symmetry of the crystal orbitals. In order to obtain some insight into the behavior of the σ orbitals near the gap, we ourselves have extended the concept of the interaction of orbitals through-space and through-bonds, a concept that has been presented by Hoffmann et al.,[33] to a polymer system. In our previous paper,[34] this method was applied to the lone-pair orbitals of polynitrilomethylidyne, and it was found that the relationship between the energy band and the interaction of atomic orbitals can be interpreted in terms of the symmetry of the crystal orbitals. In the present article, we use this method for characterizing the electronic properties of polyacetylene on the presumption that the band structure with a high conductivity must be reflected in the interaction between orbitals near the gap. We expect that this analysis will provide information useful for the prediction of various properties of the polymers.

Calculation of Band Structure

The crystal orbital method has been described in the literature.[8,35] The necessary equations will, therefore, merely be listed below in explanation of the through space/bond interaction analysis. The ab initio crystal orbital method used in this study is based on the general SCF tight-binding LCAO formalism,[36] which corresponds essentially to Roothaan's Hartree-Fock equation for molecules.[37] A delocalized wave function of a single electron in the periodic potential of a one-dimensional crystal is represented as a linear combination of Bloch basis orbitals, which are symmetry-adapted combinations of atomic orbitals, χ_r, in this form:

$$\phi_i^k(r_1)=(2N+1)^{-1/2}\sum_{m=-N}^{+N}\sum_{r}^{n_r}\exp(ikR_m)C_{ir}(k)\chi_r(r_1-R_m) \tag{1}$$

where k denotes a wavenumber vector in the first Brillouin zone, and i, an energy band. The $\chi_r(r_1-R_m)$ term stands for an atomic orbital localized in the m-th cell at $R_m(m=0, 1, 2, \cdots, N)$, while $2N+1$ is the number of elementary cells. For a given atomic basis and in the restricted HF-Roothaan scheme, the optimal set of one-electron wave functions, $\phi_i^k(r_1)$, is obtained by solving the following equations:

$$\sum_{S} C_{is}(k)[F_{rs}(k) - S_{rs}(k)E_i(k)] = 0 \qquad (2)$$

$$r = 1, 2, \text{------} ,n_r$$

where,

$$F_{rs}(k) = \sum_{m=-M}^{+M} \exp(ikR_m)F_{rs}^{Om}(R_m), \qquad (3)$$

$$S_{rs}(k) = \sum_{m=-M}^{+M} \exp(ikR_m)S_{rs}^{Om}(R_m), \qquad (4)$$

whose solutions at various k points in BZ provide the band structure of $E_i(k)$. F_{rs}^{Om} is the Fock matrix element between the r-th atomic orbital χ_r in the central cell and the s-th atomic orbital χ_s^m in the m-th cell. S_{rs}^{Om} is the overlap integral between these orbitals.

Based on this scheme, the polymer Gaussian 74 program has been extensively developed by Suhai et al.[8] Previous to the through space/bond interaction analysis, ab initio calculations were performed on all-*trans*-polyacetylene by using this program, with an STO-3G basis set. Ten k-points in half the Brillouin zone were used, and the convergence criterion of 10^{-6} for the difference in density-matrix elements was adopted. Twice the magnitude of the lattice vector was taken as a translational vector corresponding to the unit cell of polyacetylene shown in Fig. 1.

The truncation of lattice sums in the Fock matrix given by Eq. 3 is a serious problem in obtaining the convergent energy values. Delhalle et al. have previously reported in considerable detail on the convergence properties of the long-range Coulombic contributions, using the Fourier representation technique, etc;[38–41] they have recently reported also on the behavior of exchange-energy contributions, which is important in the metallic system.[42–44] Recent data for *trans*-polyacetylene show that the difference in the band gap is less than 3kcal/cell in the region of included neighbors 4-50 C2H2- units at the HF/STO-3G level.[45] We made sure in the previous work on polynitrilometylidyne[38] that the absolute values of orbital energies are changed by a cut-off after a finite interaction range, but that the shapes of the band structures are retained, even when up to 16 CHN units are included. Therefore, in employing the through space/bond interaction analysis we used the Fock matrix elements by taking into account the contribution up to the third neighbor interaction (6 units) in the core-resonance integrals and the two-electron integrals.

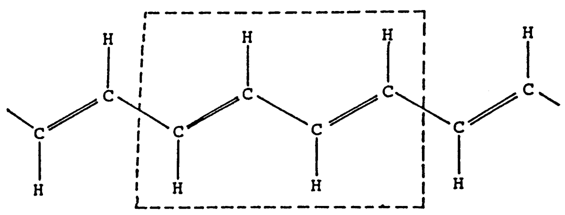

Fig. 1. Structure of all-trans polyacetylene. The unit cell is sorrounded with broken lines.

The geometries used here (Table 1) are the same as those described in Ref. 8. The band structures and the density of the states calculated indicate that the system is an insulator with a band gap of 8.12 eV, as is shown in Fig. 2. This value is, however, too large compared with the experimental value of ca. 2 eV.[46] Suhai has reported that the smaller bond alternation when correlation effects are included leads to a smaller gap (ΔE_g(HF/STO-3G)$\simeq$8.9 eV, ΔE_g (HF/6-31G**)$\simeq$5.1 eV, ΔE_g(HF+MP2/6-31G**)$\simeq$4.4 eV) at their optimal geometries) which should cover 70—75% of the valence-shell correlation energy.[11] This indicates that the correlation effects are essential for obtaining a good agreement with the experimental value in calculation including correlation effects. However, the purpose of our study is to obtain information with respect to the relationship between the orbital-energy dependence on the wavenumber vectors and the interactions of the crystal orbitals. If the nature of the material properties can be explained qualitatively from the point of view of orbital symmetry, without carrying out accurate calculations directly, it must be possible to provide easily a fundamental aspect for experimental investigation. As the first step in roughly predicting the electronic properties of polymers affected from the structural change or substitution effects, we have applied the through space/bond interaction analysis at the HF/STO-3G level to *trans*-polyacetylene.

Through Space/Bond Interaction Analysis

Method. For the analysis based on the through space/bond concept, all the Fock matrix elements and overlap integrals, which had been converged by ab initio SCF calculations, were classified into two kinds of interaction patterns. One type included those terms relating to the through-bond interactions, and the other type, the through-space interactions. The former type included the Fock matrices given by Eq. 3 and the overlap integrals given by Eq. 4 for diagonal elements and as well as off-diagonal elements between orbitals belonging to the same atom and between valence orbitals belonging only to the nearest neighboring atoms. For *trans*-polyacetylene, the valence orbitals indicate the 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals on the C atom and the 1s orbitals on the H atoms. These elements were included for all cases of analyses. The latter type includes all the terms except those for the through-bond interaction, that is, those between particular valence orbitals belonging to remote atoms, between which there are no bonds. By investigating the influence of these through-space interactions on

Table 1. Geometries of $-(CH=CH)_n-$

r(C=C)	1.35Å	Angle (C=C-C)	120°
r(C-H)	1.09Å	Angle (C=C-H)	120°
r(C-C)	1.46Å		

the former through-bond interactions, the important through-space interaction for determining the band structure can be found. The technical details of the through space/bond method have been extensively described in a previous paper.[34] In this work, first, conspicuous through-space interactions governing the band shape are found by variational analysis, and next the concrete terms that contribute to the through-space interaction are analyzed by the perturbation method.

Variational Analysis. For performing the through-space/bond interaction variational analysis of the matrix elements, converged by the ab initio SCF calculations for Eq. 2, only the through-bond and some particular through-space components are reserved, the others are completely neglected. The eigenvalue problem for this new secular equation is solved only once, without further iterations for each wavenumber vector. By using the eigenvalue thus obtained, the effect of various through-space interactions on the band structure of the pure through-bond interaction can be investigated. The energy bands obtained by increasing the through-space components approach quantitatively to the results with full interaction, that is, the solution for Eq. 2 with full matrix elements. In this process, the most significant through-space interaction is found by comparing the changes in the band shapes. Furthermore, the relationship between band shapes and crystal orbitals for each through-space interaction can be investigated.

First, we calculated the energy bands of the pure through-bond interaction. The energy-band structure thus obtained is shown in Fig. 3. By comparing this band structure with the full interaction shown in Fig. 2, it is found that there is little difference in π and π^* bands between these two kinds of interactions. This is likely because the nature of the band structures for π-electron orbitals can be derived by a Hückel-type Hamiltonian, analogous to the pure through-bond interaction. On the other hand, it is noted that the LUMO σ^* band is greatly lowered by 0.7 au at k=0°, so that the gap between the valence and the conduction bands is extinguished. It is noteworthy that this band structure, calculated by including only the pure through-bond interactions, indicates a nearly metallic state. Therefore, we focused on this LUMO σ band and searched for the through-space interaction that elevates the LUMO σ^* energy to the insulator level.

We adopted the three kinds of through-space interactions shown in Fig 4., which exert significant effects on the band shapes of the pure through-bond interactions. The results of the analysis by various through-space interactions are shown in Figs. 5—7. Upon interaction between valence orbitals on the nonbonding C atoms (C-C interaction), no significant change in the LUMO σ^* band shape can be observed (Figs. 3 and 5). When the interaction between valence orbitals on C and the 1s orbital of H (C-H interaction) is added to the through-bond interaction, although the energy of the MO is unchanged at k=0°, it is raised by 0.5 au at k=180° (Figs. 3 and 6). Moreover, by adding the C-C and C-H interactions, the LUMO σ^* energy level at k=0° is raised and an energy gap between π and π^* bands appears (Figs. 3 and 7). The major part of the energetic destabilization at k=0° originates from the coupling of the interaction within the backbone (C-C) with the interaction between the backbone and the side chain (C-H). This concurrent effect seems to be strong enough to give rise to the appearance of the

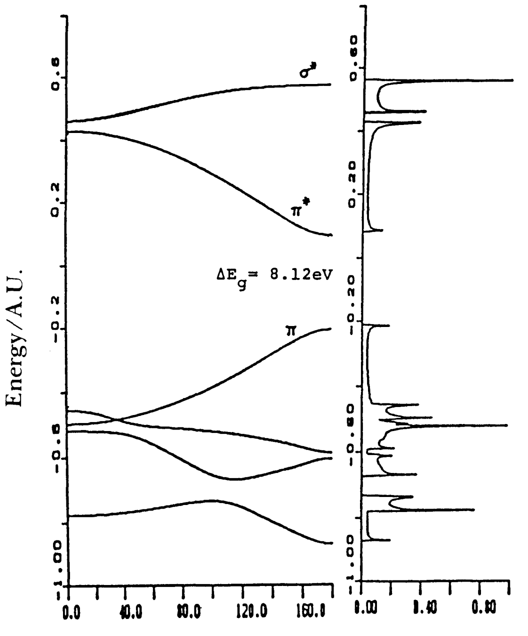

Fig. 2. Band structure and desity of states of all-*trans*-polyacetylene.

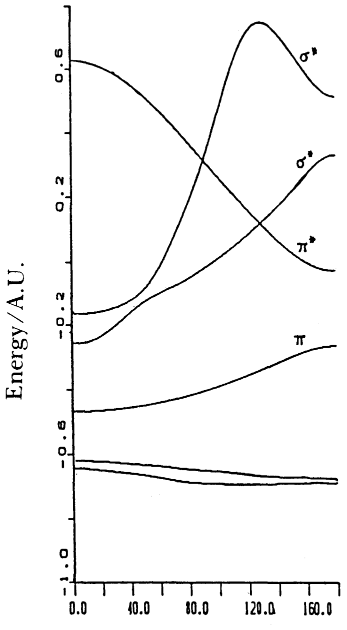

Fig. 3. Band structure for pure through bond interaction of all-*trans*-polyacetylene.

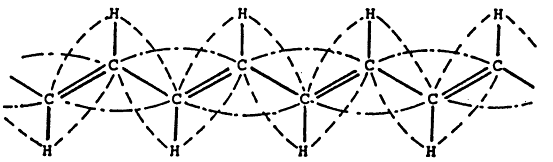

Fig. 4. The through space interactions used in this analysis. -·-·- C–C interaction, ---- C–H interaction.

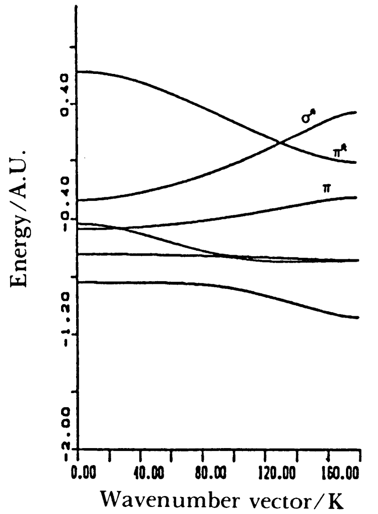

Fig. 5. The band structure for the pure through bond+C–C interaction.

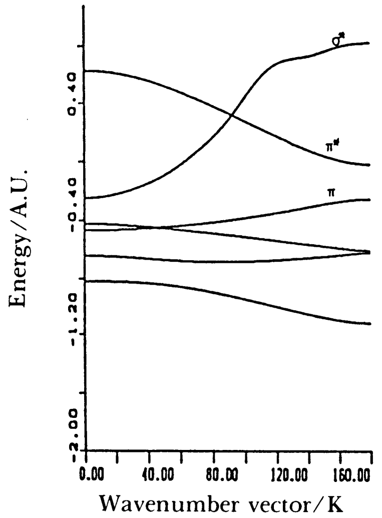

Fig. 6. The band structure for the pure through bond+C–H interaction.

gap, although each interaction (C–C) or (C–H) makes no apparent contribution. This behavior near k=0° turns out to be especially different from that at k=180° which satisfies the additivity rule for individual through-space interactions.

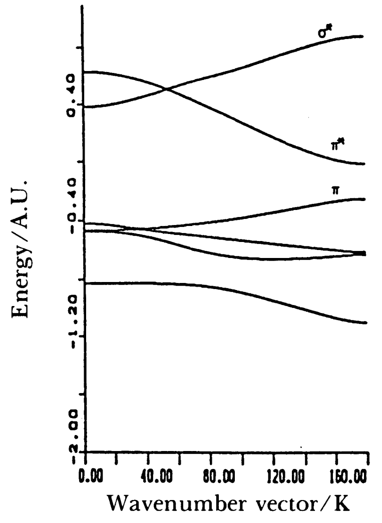

Fig. 7. The band structure for the pure through bond+(C–C+C–H) interaction.

Perturbational Analysis. In order to account for the anomalous behavior at k=0° indicated by the variational analysis, we investigated the band structure in more detail by means of a perturbative treatment. By using formula from the general perturbation theory for the extended Hückel method, which has been reported previously,[47)] the first- and the second-order terms in the energy and coefficient are given as follows:

$$C_{ti}^{(1)}=-\sum_{\substack{j\\(j\neq i)}}{}' C_{tj}^{(0)}/(E_j^{(0)}-E_i^{(0)})\sum_r\sum_s(F_{rs}^{(1)}-S_{rs}^{(1)}E_i^{(0)})C_{si}^{(0)}C_{rj}^{(0)*}$$
$$-\frac{1}{2}C_{ti}^{(0)}\sum_r\sum_s C_{ri}^{(0)*}C_{si}^{(0)}S_{rs}^{(1)} \tag{5}$$

$$E_i^{(1)}=\sum_r\sum_s(F_{rs}^{(1)}-S_{rs}^{(1)}E_i^{(0)})C_{ri}^{(0)*}C_{si}^{(0)} \tag{6}$$

$$C_{ti}^{(2)}=-\sum_{\substack{j\\(j\neq i)}}C_{tj}^{(0)}/(E_j^{(0)}-E_i^{(0)})[-\sum_r\sum_s S_{rs}^{(1)}E_i^{(1)}C_{si}^{(0)}C_{rj}^{(0)*}$$
$$+\sum_r\sum_s\{F_{rs}^{(1)}-(S_{rs}^{(0)}E_i^{(1)}+S_{rs}^{(1)}E_i^{(0)})\}C_{si}^{(1)}C_{rj}^{(0)*}]$$
$$-\frac{1}{2}C_{ti}^{(0)}\sum_r\sum_s[C_{ri}^{(1)*}C_{si}^{(1)}S_{rs}^{(0)}+(C_{ri}^{(1)*}C_{si}^{(0)}+C_{ri}^{(0)*}C_{si}^{(1)})S_{rs}^{(1)} \tag{7}$$

$$E_i^{(2)}=-\sum_r\sum_s S_{rs}^{(1)}E_i^{(1)}C_{ri}^{(0)}C_{si}^{(0)*}$$
$$+\sum_r\sum_s\{F_{rs}^{(1)}-(S_{rs}^{(0)}E_i^{(1)}+S_{rs}^{(1)}E_i^{(0)})\}C_{ri}^{(1)}C_{si}^{(0)*} \tag{8}$$

where i and j denote molecular orbitals, and r and s, atomic orbitals, and where $\sum_j{}'$ means that the summation covers all levels except i. In this study, the zero-order matrix elements $F_{rs}^{(0)}$ and $S_{rs}^{(0)}$ and the coresponding crystal orbital $C_{ti}^{(0)}$ and energy $E_i^{(0)}$ values, are the terms for the pure through-bond interaction. The first-order terms $F_{rs}^{(1)}$ and $S_{rs}^{(1)}$ are matrix elements for a selected pair of through-space components.

Equations 5 and 6 are calculated by taking a through-space interaction as a perturbation; then the concrete contribution included in the energy change obtained by solving Eq. 2 can be found. Figure 8 shows the energy bands of the LUMO σ^* orbital obtained by the first-order perturbation that is, $E^{(0)}(k)+E^{(1)}(k)$, for three kinds of through-space interactions compared with the results obtained by the variation method. By C-C interaction the energy is raised at k=0° by 0.4 au; likewise C-H interaction raises it at k=180° by 0.5 au. The first-order energies by both C-C and C-H interactions, that is, the sum of the true interactions, change the energy band in the direction of the variational result.

The change in the band structure by the first-order perturbation should be predictable from the crystal orbitals for the pure through-bond interaction, the zero-th order wave function, and the perturbed matrix elements. The crystal orbitals at k=0° and 180° are shown schematically in Fig. 9. The crystal orbitals on C atoms at k=0° are directed to the z axis, which are out-of-phase between $2p_z$ orbitals on the C1 and C3. On the other hand, those at k=180° are directed to the hydrogen atoms, which are out-of-phase between C1 and H2 or C2 and H1. The positive overlap implies bonding, and the negative one, antibonding. Therefore, C-C interaction destabilizes the MO at k=0°, as does C-H interaction at k=180°. In this manner, this behavior can reasonably be interpreted in terms of the symmetry or the phase of crystal orbitals.

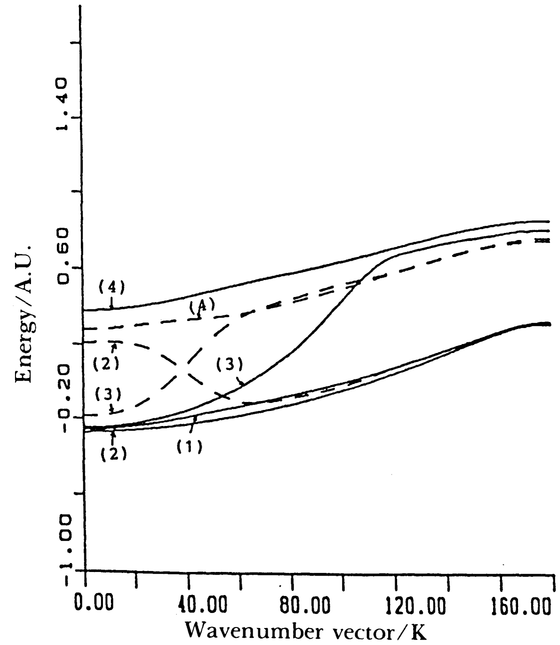

Fig. 8. The energy band of LUMO σ^* orbital by through space/bond interaction analysis. —— Variative analysis, ---- perturbative analysis (1) pure through bond interaction (2) C–C interaction (3) C–H interaction (4) (C–C+C–H) interaction.

It is noteworthy that the perturbation by the C-C interaction does not change the energy when the variational treatment is used, but it is raised at k=0° by the first-order perturbational treatment. This suggests that the terms more than first-order contribute greatly to the change in the energy band. It seems profitable to calculate the second-order energies in order to examine the concrete terms which elevate the LUMO σ band to the insulator level. The leading interaction term with the other levels in the second-order energy can be derived because, as can be seen from Eq. 8, the $E_i^{(2)}$ includes the term $C_{ri}^{(1)}$ that is given by the sum of the interactions with all the levels except i. Table 2 shows the first-order energies obtained by the three kinds of through-space interactions in comparison with the energy changes obtained by the variational treatment at k=0° and 180°.

At k=180°, the second-order energy obtained by the (C-C+C-H) interaction is almost equal to the sum of those obtained by both the C-C and C-H interactions; that is, the additivity rule holds for these interactions. The sum of the first-and the second-order energies gives values which are nearly equal to the energy changes obtained by the variational treatment. This shows that the substantial effect on the energy band of the through-space interactions may reasonably be interpreted by only the first-order term in the perturba-

Table 2. Gained Energies by Through-Space Interactions for the LUMO σ^* Orbitals (a.u.)

k=0°	Through space	C-C	C-H	C-C+C-H
	Perturbation			
	$E^{(1)}$	0.463	0.070	0.534
	$E^{(2)}$	−0.328	−0.402	0.205
	Variation	−0.015	0.008	0.635
k=180°	Through space	C-C	C-H	C-C+C-H
	Perturbation			
	$E^{(1)}$	−0.017	0.435	0.419
	$E^{(2)}$	−0.003	0.091	0.087
	Variation	−0.008	0.479	0.525

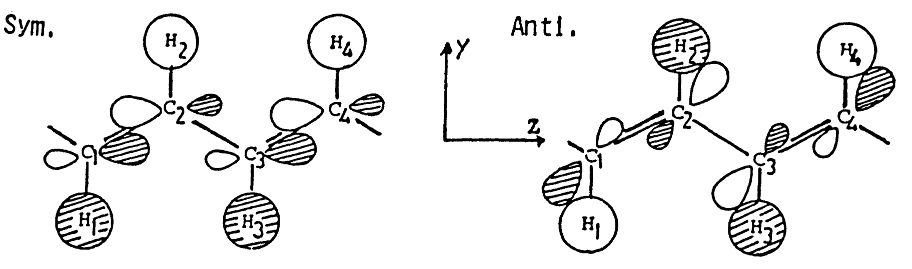

Fig. 9. Schematic representation of the magnitude of the coefficients of atomic orbitals in the crystal orbitals for the pure through bond interaction of all-*trans*-polyacetylene. Shaded areas represent positive lobes; unshaded negative. Sym. corresponds to k=0° and Anti. to k=180°.

tion expansion.

At $k=0°$, on the other hand, the second-order energy by the (C-C+C-H) interaction (0.205) is greatly different from the sum of those by both C-C and C-H interactions (−0.328, −0.402), even in sign. This behavior implies that the cross-terms included in the (C-C+C-H) interaction contribute positively to the second-order energy.

The cross-term is given by the following equation:

$$\begin{aligned} E_i^{(2)}(\text{cross}) & \\ = & -\sum_r\sum_s \{S_{rs(\text{C-C})}^{(1)} E_{i(\text{C-H})}^{(1)} + S_{rs(\text{C-H})}^{(1)} E_{i(\text{C-C})}^{(1)}\} C_{ri}^{(0)} C_{si}^{(0)*} \\ & + \sum_r\sum_s (F_{rs(\text{C-C})}^{(1)} - S_{rs(\text{C-C})}^{(1)} E_i^{(0)}) C_{ri(\text{C-H})}^{(1)} C_{si}^{(0)*} \\ & + \sum_r\sum_s (F_{rs(\text{C-H})}^{(1)} - S_{rs(\text{C-H})}^{(1)} E_i^{(0)}) C_{ri(\text{C-C})}^{(1)} C_{si}^{(0)*} \end{aligned} \tag{9}$$

where $S_{rs(\text{C-C})}^{(1)}$ and $F_{rs(\text{C-C})}^{(1)}$ represent the matrix elements for the through-space C-C interaction, and $S_{rs(\text{C-H})}^{(1)}$ and $F_{rs(\text{C-H})}^{(1)}$, those for the C-H interaction $E_{i(\text{C-H})}^{(1)}$ and $C_{rs(\text{C-H})}^{(1)}$ are the first-order perturbation energy and the corresponding coefficient obtained by only the C-H through-space interaction. $E_{i(\text{C-C})}^{(1)}$ and $C_{ri(\text{C-C})}^{(1)}$ have the same meaning. The cross-terms given by Eq. 9, which corresponds to the difference between $E_{i(\text{C-C+C-H})}^{(2)}$ and $E_{i(\text{C-C})}^{(2)}+E_{i(\text{C-H})}^{(2)}$, are 0.934 for $k=0°$ and 0.001 for $k=180°$. The value of the cross-term is positive enough to elevate the LUMO σ^* band to the insulator level, in spite of the negative values caused by the C-C interaction (−0.328) and the C-H interaction (−0.402). Furthermore, the $C_{ri(\text{C-C})}^{(1)}$ and $C_{ri(\text{C-H})}^{(1)}$ terms, that include interaction with the other levels, result in a dominant factor in Eq. 9. From these results it seems reasonable to assume that the conspicuous results obtained by the variational treatment can essentially be interpreted by examining the second-order term. Therefore, the cross-term included in the second-order will be analyzed in order to investigate its explicit contribution.

We attempt to represent the second-order energy explicitly by the zero-order crystal orbitals instead of the first-order crystal orbitals. We define:

$$T_{rs,i}^{(1)} = F_{rs}^{(1)} - S_{rs}^{(1)} E_i^{(0)}\ , \tag{10}$$

and substitute Eqs. 5, 6, and 10 into Eq. 8; then the second-order energy is expressed as follows:

$$\begin{aligned} E_i^{(2)} = & -\sum_r\sum_s S_{rs}^{(1)} \sum_p\sum_q T_{pq,i}^{(1)} C_{pi}^{(0)} C_{qi}^{(0)*} C_{ri}^{(0)} C_{si}^{(0)*} \\ & -\sum_r\sum_s (T_{rs,i}^{(1)} - S_{rs}^{(0)} \sum_p\sum_q T_{pq,i}^{(1)} C_{pi}^{(0)} C_{qi}^{(0)*}) \\ & \times \{ \sum_{j(\neq i)}{}' C_{rj}^{(0)} \sum_t\sum_u T_{tu,i}^{(1)} C_{ti}^{(0)} C_{uj}^{(0)*} / (E_j^{(0)} - E_i^{(0)}) \\ & + \frac{1}{2} C_{ri}^{(0)} \sum_t\sum_u C_{ti}^{(0)} C_{ui}^{(0)*} S_{tu}^{(1)} \} C_{si}^{(0)*} \end{aligned} \tag{11}$$

Neglecting the term $S_{rs}^{(0)} E_i^{(1)}$, that is, $S_{rs}^{(0)} \sum_p\sum_q T_{pq,i}^{(1)} C_{pi}^{(0)} C_{qi}^{(0)*}$ because of its small value, Eq. 11 becomes approximately:

$$\begin{aligned} E_i^{(2)} = & -\frac{3}{2} \sum_r\sum_s T_{rs,i}^{(1)} C_{ri}^{(0)} C_{si}^{(0)*} \sum_t\sum_u S_{tu}^{(1)} C_{ti}^{(0)} C_{ui}^{(0)*} \\ & -\sum_r\sum_s T_{rs,i}^{(1)} \sum_{\substack{j \\ (\neq i)}}{}' C_{rj}^{(0)} \sum_t\sum_u T_{tu,i}^{(1)} C_{ti}^{(0)} C_{uj}^{(0)*} C_{si}^{(0)*} / (E_j^{(0)} - E_i^{(0)}). \end{aligned} \tag{12}$$

The first term relates only to the i-th crystal orbital, and the second term, to the other crystal orbitals belonging to all levels except i. The behavior of the energy band near $k=0°$ suggests a great contribution of the second-order term in Eq. 12. Suppose that the focused i-th crystal orbital interacts strongly with the k-th crystal orbital and weakly with the other crystal orbitals: then Eq. 12 becomes approximately:

$$E_{i(k)}^{(2)'} = -\sum_r\sum_s T_{rs,i}^{(1)} C_{si}^{(0)*} C_{rk}^{(0)} \sum_t\sum_u T_{tu,i}^{(1)} C_{ti}^{(0)} C_{uk}^{(0)*} / (E_k^{(0)} - E_i^{(0)}) \tag{13}$$

where the interactions with all levels except k are completely neglected. We write:

$$\sum_r\sum_s T_{rs,i}^{(1)} C_{si}^{(0)*} C_{rk}^{(0)} = H_{ik}^{(1)} \tag{14}$$

and using the fact that $T_{rs,i}^{(1)}$ is Hermitian, Eq. 13 is reduced to:

$$E_{i(k)}^{(2)'} = -|H_{ik}^{(1)}|^2 / (E_k^{(0)} - E_i^{(0)}) \tag{15}$$

When the $H_{ik}^{(1)}$ includes two kinds of interactions, $H_\text{A}^{(1)}$ and $H_\text{B}^{(1)}$, Eq. 15 becomes:

$$E_{i(k)}^{(2)'} = -|H_\text{A}^{(1)} + H_\text{B}^{(1)}|^2 / (E_k^{(0)} - E_i^{(0)}) \tag{16}$$

where,

$$H_\text{A}^{(1)} = \sum_r\sum_s (F_{rs}^{(1)}(\text{A}) - S_{rs}^{(1)}(\text{A}) E_i^{(0)}) C_{ri}^{(0)*} C_{sk}^{(0)} \tag{17}$$

$$H_\text{B}^{(1)} = \sum_r\sum_s (F_{rs}^{(1)}(\text{B}) - S_{rs}^{(1)}(\text{B}) E_i^{(0)}) C_{ri}^{(0)*} C_{sk}^{(0)} \tag{18}$$

This means that the i-th orbital is stabilized in the second-order energy by the interaction with the upper levels of crystal orbitals, while it is destabilized with the lower ones. We have here evidence for the well-known conclusion that the energy levels with like symmetry crystal orbitals repel each other. As is implied by Eq. 16, $E_{i(k)}^{(2)}$ is destabilized only by the interaction with the energy levels in the proximity of the i-th level. The cross-term between the A and B interactions is expressed approximately as:

$$E_i^{(2)'}(\text{cross}) = -2Re(H_\text{A}^{(1)} H_\text{B}^{(1)*}) / (E_k^{(0)} - E_i^{(0)}), \tag{19}$$

provided that only the pair of the i-th and k-th crystal orbitals interacts strongly with each other. The terms relating only to the $H_\text{A}^{(1)}$ or $H_\text{B}^{(1)}$, that is $-|H_\text{A}^{(1)}|^2/(E_k^{(0)}-E_i^{(0)})$ or $-|H_\text{B}^{(1)}|^2/(E_k^{(0)}-E_i^{(0)})$, usually give negative values. The cross-term $E_i^{(2)'}$ (cross) given by Eq. 19 is a negative values if $H_\text{A}^{(1)}$ and $H_\text{B}^{(1)}$ have the same signs and a positive value if $H_\text{A}^{(1)}$ and $H_\text{B}^{(1)}$ have different signs. By means of the formulae thus described, we can proceed to an analysis of specific cases of energy-band structures.

As can be seen from the band structure for the pure through-bond interaction, shown in Fig. 3, the LUMO σ^* band and the upper σ^* band approach each other closely at k=0°. This shows that the LUMO σ^* band is referred especially to the influence of the upper σ^* band so as to avoid the crossing with it. Therefore, it seems reasonable to apply the above-mentioned approximation given by Eq. 16 to the case at k=0°. In the present case, the value of $H^{(1)}_{\text{A}}$ corresponding to the C-C interaction and that of $H^{(1)}_{\text{B}}$ corresponding to the C-H interaction are -0.185 and 0.171, respectively. The different signs of the two terms support the idea that the cross- term between these two kinds of interactions should be positive so as to destabilize the second-order energy of the LUMO σ^*.

Next, we will attempt to predict readily the contribution of the cross-term to the second-order energy in terms of the phase of the zero-order crystal orbitals without calculating the term $E^{(2)}_{i(k)}$ (cross). Equations 17 and 18 imply that whether or not the signs of the $H^{(1)}_{\text{C-C}}$ and the $H^{(1)}_{\text{C-H}}$ are the same can be elucidated by means of the i-th and the k-th zero-order crystal orbitals. The crystal orbitals for the pure through-bond interaction are shown schematically in Fig. 10 for the i-th LUMO σ^* orbital and the upper k-th σ^* orbital. The 2p orbital on Cl of the i-th orbital and that on C3 of the k-th orbital, for example, are in-phase along the direction of the z-axis, as are the 2p orbital on Cl of the k-th orbital and that on C3 of the i-th orbital, so that the $H^{(1)}_{\text{C-C}}$ become negative. The ls orbital on H1 of the i-th orbital and the 2p orbital on C2 of the k-th orbital are out-of-phase along the direction of the y-axis, as are the 1s orbital on H1 of the k-th orbital and the 2p orbital on C2 of the i-th orbital, so that the $H^{(1)}_{\text{C-H}}$ is positive. This explication is consistent with the results obtained by calculating the $H^{(1)}_{\text{C-C}}$ and $H^{(1)}_{\text{C-H}}$ terms. This shows that the effect of the cross-term on the band shape should be predictable from the phase of the crystal orbitals with only the pure through-bond interaction. As a result of the perturbative analysis, it was found that the large positive cross term (0.934) between the $H^{(1)}_{\text{C-C}}$ and the $H^{(1)}_{\text{C-H}}$ terms governs the LUMO σ^*-band shape near k=0° for the full interaction and is responsible for the appearance of the gap between the π and π^* bands. This method seems useful for investigating the relationship between the structural problem of a polymer and its band structure, which plays an important role in the conducting mechanism. Henceforth, we intend to apply this approach to the estimation of the structures of various polymers which are favorable for a high conductivity.

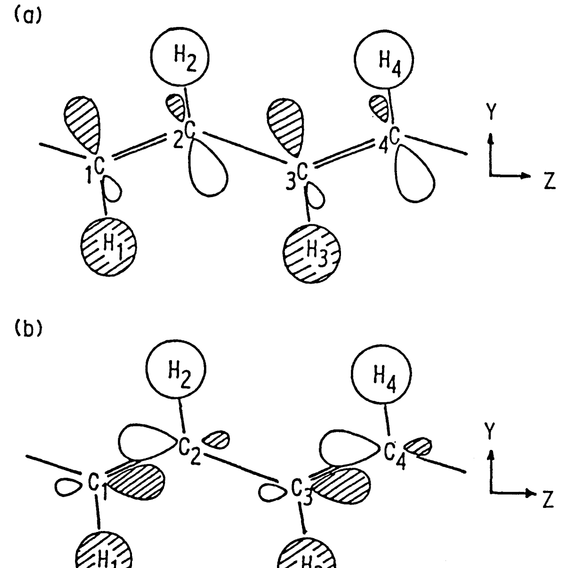

Fig. 10. Schematic representation of the magnitude of the coefficients of atomic orbitals in the crystal orbitals at k=0° for the pure through bond interaction of all-*trans*-polyacetylene. Shaded areas represent positive lobes; unshaded negative. (a) k-th and (b) i-th levels in Eqs. 13—18.

Conclusion

In this article we discuss the features of the band structure of all-*trans* polyacetylene as obtained by the use of through space/bond interaction analysis. The band structure for the pure through-bond interaction shows that the LUMO σ^* orbital is greatly lowered at k=0° and extinguishes the gap between the π and π^* bands. The results obtained by the variational analysis for the LUMO σ^* orbital at k=0° are different from those obtained at k=180° with regard to the dependences of the band structure on through-space interactions. The most interesting feature is that there is a large coupling between two interactions; one is the interaction between C atoms belonging to the neighboring cells, and the other is that between the C atom and the H atom bonded to the neighboring C atom. It is this coupling term that is responsible for the band shape near k=0°. This fact suggests an important rule of the cross term between these two kinds of interactions. With the aid of the perturbation method, a simple formula for the cross-term is derived when two particular energy levels interact very strongly so as to avoid crossing. This formula enabled us to predict, though in a somewhat rough way, the behavior of the σ orbital near the gap in the band structure of all-*trans*-polyacetylene.

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