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Interchain interactions in one-dimensional periodic systems: An analysis of second-order effects causing deformation

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The role of second-order perturbations in interchain interactions of one-dimensional electronic systems is examined. The general features of such interchain interactions are deduced from a simple two-chain model. From a perturbation-theoretic analysis, the second-order term originating from two different bands near the Fermi level leads to an important out-of-phase coupling of charge-density-waves on neighboring chains. The preferred distortion is predicted for various electron counts, using a transition-density analysis. Specific geometrical conclusions are derived for polyacene systems. © *1995 American Institute of Physics.*

INTRODUCTION

We assume that in most molecules the electrons adjust instantaneously to the nuclear positions and that the nuclei move in the average field of the rapidly moving electrons. As is well known, when an excited state lies close to the ground state in molecular systems, the Born–Oppenheimer approximation mentioned above breaks down. For degenerate electronic systems the first-order perturbation effect dominates the consequences of such a breakdown; we refer here, of course, to the familiar Jahn–Teller effect.[1,2] Nearly degenerate electronic states are also coupled vibronically and may deform, now through a second-order or pseudo-Jahn–Teller effect.[3–5] Second-order perturbation theory also provides the background for an alternative account of the well-established symmetry rules for chemical reactions.[6–8]

The Peierls distortion,[9] the indication that in a one-dimensional chain with a partially-filled band the regular chain structure is potentially unstable, is the solid state analog of the first-order Jahn–Teller effect. Distortion of one-dimensional chains takes place through coupling between an electronic state and a phonon, a normal mode of vibration of the underlying lattice which can drive the structure into an electronically more favorable configuration.[10–14] Since the late 1970s, many chemists and physicists have been concerned with the structural and electronic properties of one-dimensional systems subject to a Peierls distortion.

In real crystals there always exist three-dimensional interactions, even if their magnitude varies. Interchain interaction plays an important role in determining the macroscopic electronic properties of one-dimensional materials. This problem has been theoretically investigated from various viewpoints.[15–19] Just as for molecules, a second-order effect is also possible. Chain distortion as a consequence of interchain interactions can be classified as a second-order effect.[20] Several interesting examples of the second-order Peierls distortion are known so far.[21–23] Important qualitative discussions of interchain interactions in low-dimensional solids, analyzed in terms of orbital interactions, may be found in Whangbo's article.[20]

The purpose of this work is to investigate systematically the electronic consequences of interchain interactions on structural deformation on such one-dimensional extended systems. We will discuss second-order or pseudo-Peierls distortion in weakly-coupled chains in various charge states using a simple two-chain model.

SECOND-ORDER PERTURBATIONS IN ONE-DIMENSIONAL SOLIDS

In order to clarify the orbital interactions in the interchain problem, we expand Bader's treatment[24] of perturbation theory to one-dimensional electronic systems. We first assume an equilibrium nuclear configuration for an infinite chain. The unperturbed band orbital $|k,l\rangle$, usually given by a linear combinations of Bloch functions, and its energy $E_{k,l}$ are written as in Eq. (1),

$$H_0|k,l\rangle = E_{k,l}|k,l\rangle, \tag{1}$$

where H_0 is the original one-electron Hamiltonian, k the wave vector, and l the band index.

We are concerned with how the energy changes when a one-dimensional chain is distorted from its equilibrium configuration. The Hamiltonian may be expanded as

$$H = H_0 + (\partial H/\partial \xi_i)_0 \xi_i + \frac{1}{2}(\partial^2 H/\partial \xi_i^2)_0 \xi_i^2, \tag{2}$$

where ξ_i stands for the displacement of the atoms from the equilibrium nuclear position along the ith normal coordinate. Using second-order perturbation theory, we can write the one-electron energy of a distorted chain as a function of extension in ξ_i as in Eq. (3),

$$E_{k,l}(\xi_i) = E_{k,l} + V^i_{k,l,k,l}\xi_i + \frac{1}{2}V^{ii}_{k,l,k,l}\xi_i^2$$

$$+ \sum_m \frac{V^i_{k,l,k+Q,m}V^i_{k+Q,m,k,l}}{E_{k,l} - E_{k+Q,m}}\xi_i^2, \tag{3}$$

where Q is a wave vector parameter, and

$$V_{k,l,k,l}^{ii} = \left\langle k,l \left| \frac{\partial^2 V(r,R)}{\partial \xi_i^2} \right| k,l \right\rangle = \int \rho_{k,l,k,l} \frac{\partial^2 V(r,R)}{\partial \xi_i^2} \, d\tau \quad (4)$$

and

$$V_{k,l,k+Q,m}^{i} = \left\langle k,l \left| \frac{\partial V(r,R)}{\partial \xi_i} \right| k+Q,m \right\rangle$$

$$= \int \rho_{k,l,k+Q,m} \frac{\partial V(r,R)}{\partial \xi_i} \, d\tau \quad (5)$$

are the perturbations. In Eqs. (4) and (5),

$$\rho_{k,l,k+Q,m} = \left\langle k,l \left| \sum_j \delta(r-r_j) \right| k+Q,m \right\rangle; \quad (6)$$

$\delta(r-r_j)$ is the operator whose expectation value is the chance of finding electron j at the point r. In these equations $V(r,R)$ is the electron–nuclear and nuclear–nuclear potential energy.

The second and third terms of Eq. (3) are first-order, and the fourth term a second-order perturbation. The second term is the usual Jahn–Teller (Peierls) term and it is significant in the degenerate case; however, we ignore this term for a while in our present development. $\rho_{k,l,k,l}$ is the electron density at wave vector k of band l for the undistorted chain. Thus, the third term of Eq. (3) describes the increase in the energy of the chain when the nuclei are displaced from their equilibrium positions and the electrons are kept fixed. The fourth term of Eq. (3) contains $V_{k,l,k+Q,m}^{i}$ which induces relaxation of the electron distribution through mixing between the occupied $|k,l\rangle$ state and unoccupied $|k+Q,m\rangle$ state. The quantity $\rho_{k,l,k+Q,m}$ appearing in $V_{k,l,k+Q,m}^{i}$ is called the *transition density*.[24,25] It is the electronic charge transferred within the one-dimensional chain as a consequence of a certain nuclear motion.

In Eq. (3) second-order perturbation theory is applied to a multiband model. If $E_{k,l}$ and $E_{k+Q,m}$ belong to two different bands, i.e., $m \neq l$, the denominator in the fourth term of Eq. (3) is large and the corresponding term in general small. We usually neglect terms of this kind; however, exactly this interband interaction will play an important role in the interchain problem about to be discussed. In molecules, the second-order effect is not negligible, if the energy difference is less than about 4 eV.[25]

The first-order wave function is

$$|k,l\rangle' = |k,l\rangle + \xi_i \sum_m \left[V_{k,l,k+Q,m}^{i}/(E_{k,l}-E_{k+Q,m}) \right]$$

$$\times \ |k+Q,m\rangle. \quad (7)$$

The transition density may contribute to the electron density of the distorted chain as

$$\rho_{k,l,k,l}' = \rho_{k,l,k,l} + 2\xi_i \sum_m \left[V_{k,l,k+Q,m}^{i}/(E_{k,l}-E_{k+Q,m}) \right]$$

$$\times \rho_{k,l,k+Q,m}. \quad (8)$$

According to Bader,[24] we can interpret the term $V_{k,l,k+Q,m}^{i}$ as the force acting on the nuclei through the re-

laxation of the electron distribution. This transition force is different from zero only if $\rho_{k,l,k+Q,m}$ and ξ_i have the same symmetry. Therefore the symmetry of favorable nuclear motion should be the same as the symmetry of $\rho_{k,l,k+Q,m}$. The following discussion of interchain interactions is based on analysis of the transition density [Eq. (6)] in one-dimensional chains.

INTERCHAIN INTERACTIONS OF ONE-DIMENSIONAL SOLIDS

Let us first consider the simplest model of interchain interaction, namely two weakly-coupled metallic chains, represented in structure 1. Here –M–M–M– stands for a linear chain of atoms, molecules, or molecular fragments, symbolized as heavy dots at right. Let us take a single unit cell, as indicated by the broken lines in structure 1, and proceed to derive the selection-rule (between electronic states and wave vector) which might drive the structure into a different, more favorable configuration.

1
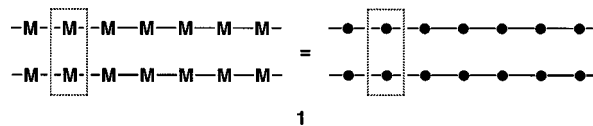
Using Bloch's theorem, the unperturbed tight-binding wave function may be written as Eq. (9),

$$|k,l\rangle = \frac{1}{\sqrt{N}} \sum_{\nu=1}^{N} \sum_{\mu=1}^{M} e^{ik\nu a} c_{k,l,\mu} \phi_{\mu}(x-\nu a), \quad (9)$$

where $\phi_{\mu}(x-\nu a)$ is the μth atomic orbital in the νth unit cell, N the total number of cells, M the number of atomic orbitals within a cell, a the lattice vector, l the band index, and $c_{k,l,\mu}$ the expansion coefficient. We assume for simplicity that each M has one electron accommodated in an atomic or molecular orbital. By symmetry,[26] the wave functions of the band 1 and 2 of the two-chain model are written as

$$|k,1\rangle = \frac{1}{\sqrt{N}} \sum_{\nu=1}^{N} e^{ik\nu a} \frac{1}{\sqrt{2+2S_{12}}}$$

$$\times [\varphi_1(x-\nu a) + \varphi_2(x-\nu a)] \quad (10)$$

and

$$|k,2\rangle = \frac{1}{\sqrt{N}} \sum_{\nu=1}^{N} e^{ik\nu a} \frac{1}{\sqrt{2-2S_{12}}}$$

$$\times [\varphi_1(x-\nu a) - \varphi_2(x-\nu a)], \quad (11)$$

respectively. $\varphi_1(x-\nu a)$ and $\varphi_2(x-\nu a)$ are atomic or molecular orbitals on chain 1 and 2 in the νth unit cell. S_{12} is the intracell overlap integral between the two orbitals. It is essential not to confuse the band index with the chain index.

Figure 1 shows schematically the band structure of the two-chain model. When the *inter*chain interaction is weak compared with the *intra*chain interaction, four Fermi wave vectors, $\pm k_{F_1}$ and $\pm k_{F_2}$ appear around $\pm \pi/2a$ in the first Brillouin zone, where a is the lattice vector. The splitting of the two bands is a measure of the strength of the interchain interaction. When the interaction is weak, the splitting
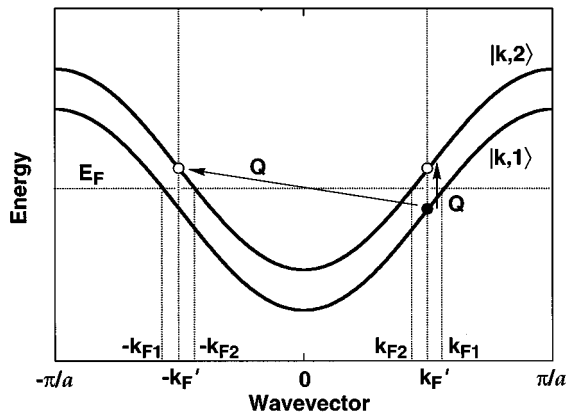
FIG. 1. Band structure of two-chain model. $k_F' = (k_{F_1} + k_{F_2})/2$ is the quasi-Fermi wave vector.

is small, and then the fourth term of Eq. (3) is important. Let us define the quasi-Fermi wave vector k_F' as $k_F' = (k_{F_1} + k_{F_2})/2$. If the two bands have the same shape, k_F' is equal to $\pi/2a$. It is quite clear from Eq. (3) and Fig. 1 that the mixing of the states near the Fermi level dominates the energy change (stabilization). It is essential in interchain interactions to take into account the second-order effect;[20] thus, we consider the case that $E_{k,l}$ and $E_{k+Q,m}$ belong to two different bands in the fourth term of Eq. (3).[27]

Let us now calculate for this interchain problem the transition density [Eq. (6)] near the Fermi level. Collecting a few terms on the assumption of a nearest neighbor approximation, we finally obtain Eq. (12),

$\rho_{\pi/2a,1,\pi/2a+Q,2}$

$$
= \left\langle \frac{\pi}{2a}, 1 \left| \sum_j \delta(r - r_j) \right| \frac{\pi}{2a} + Q, 2 \right\rangle
$$

$$
= \frac{1}{2N\sqrt{1 - S_{12}^2}} \left[\sum_\nu (\alpha_1 - \alpha_2)e^{iQ\nu a} \right.
$$

$$
+ \sum_\nu [(\beta_{11} - \beta_{22})(e^{i\pi/2 + iQa} + e^{-i\pi/2})
$$

$$
\left. - (\beta_{12} - \beta_{21})(e^{i\pi/2 + iQa} - e^{-i\pi/2})]e^{iQ\nu a} \right], \quad (12)
$$

where

$$
\alpha_1 = \{\varphi_1(x - a)\}^2 \quad \text{and} \quad \alpha_2 = \{\varphi_2(x - a)\}^2
$$

are on-site (diagonal) densities;

$$
\beta_{11} = \varphi_1(x - a)\varphi_1(x - 2a)
$$

and

$$
\beta_{22} = \varphi_2(x - a)\varphi_2(x - 2a)
$$

are intercell overlap or off-diagonal densities, localized in the chain 1 and 2, respectively; and

$$
\beta_{12} = \varphi_1(x - a)\varphi_2(x - 2a)
$$

and

$$
\beta_{21} = \varphi_2(x - a)\varphi_1(x - 2a)
$$

are "cross" off-diagonal densities. The corresponding relation in a single chain may be seen in Ref. 28.

We are interested in the off-diagonal densities (β_{11} and β_{22}) rather than the on-site ones (α_1 and α_2), since the off-diagonal charge-density-wave (CDW) state corresponds to the lowest-lying eigenvalue in the so-called stability matrix used in the analysis of finite polyenes[29] and polyacetylene.[30] This means that a bond-alternating structure is favored for a single polyene chain. Incidentally, the next lowest-lying eigenvalue corresponds to the on-site CDW state. We focus our main attention on the analysis of the off-diagonal part of the transition density.

For simplicity, let us neglect the cross off-diagonal terms for a while, because they seem smaller. Equation (12) therefore becomes

$\rho_{\pi/2a,1,\pi/2a+Q,2}$

$$
= \frac{1}{2N} \left[\sum_\nu (\alpha_1 - \alpha_2)e^{iQ\nu a} + \sum_\nu (\beta_{11} - \beta_{22}) \right.
$$

$$
\left. \times (e^{i\pi/2 + iQa} + e^{-i\pi/2})e^{iQ\nu a} \right], \quad (13)
$$

where S_{12}^2 is assumed to be negligible compared with 1. Three general features of interchain interactions can be deduced from Eq. (13).

(1) The first point concerns the phase of on-site and off-diagonal densities. There is always an out-of-phase coupling of these densities *on neighboring chains*. This is important in describing the transition density of interchain interactions.

(2) When $Q = 0$, the off-diagonal part vanishes, because $\cos(\pi/2) = 0$. There is no fluctuation in the off-diagonal part of this transition density when $Q = 0$. Consequently, we can conclude that chain distortion will not occur through mixing between occupied $|\pi/2a, 1\rangle$ and unoccupied $|\pi/2a, 2\rangle$ (see Fig. 1). Although the on-site densities remain, these do not alternate in chains. Charge separation occurs between chains in this case.

(3) On the other hand, when $Q = -2k_F' = -\pi/a$, i.e., the mixing is between occupied $|\pi/2a, 1\rangle$ and unoccupied $|-\pi/2a, 2\rangle$, the situation is quite different, as expected from Eq. (14),

$$
\rho_{\pi/2a,1,\pi/2a+Q,2} = \frac{1}{2N} \left[\sum_\nu (\alpha_1 - \alpha_2)e^{-i\nu\pi} \right.
$$

$$
\left. + 2\sum_\nu (\beta_{11} - \beta_{22})e^{-i(\nu + 1/2)\pi} \right]. \quad (14)
$$

On neighboring chains there appear out-of-phase on-site and off-diagonal CDWs which are commensurate with the lattice periodicity; the wavelength of these CDWs is $2a$. In particular, the appearance of the off-diagonal CDW is important for a certain chain distortion, as mentioned above. We can therefore predict from the fourth term of Eq. (3) (second-order perturbation; negative) that
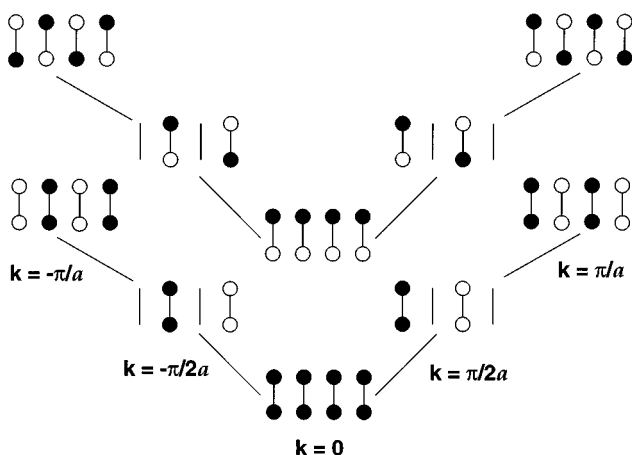
FIG. 2. Crystal orbitals of the two-chain model at $k=0$, $\pm\pi/2a$, and $\pm\pi/a$. The line-segments denote a quasimolecule in the unit cell.

a distorted chain structure is stabilized through a particular nuclear motion. This is the third important general feature of the interchain problem.

In order to obtain a more detailed and explicit picture of these general conclusions, it is convenient to use crystal orbital representations. The wave functions of band 1 and 2 at the special points, $k=0$, $\pm\pi/2a$, and $\pm\pi/a$ are shown schematically in Fig. 2.[31] The closed and open circles stand for the orbital phase "+" and "−," respectively.

We take into account $Q=0$ and $-2k_F'$, as indicated in Fig. 1. As mentioned in the previous section, the transition force operates on the nuclei or molecules when the transition density $\rho_{k,l,k+Q,m}$ and ξ_i have the same symmetry. In order to predict the distortion favored as a result of interchain interaction, let us first examine the shape of $\rho_{k,l,k+Q,m}$, where $l=1$, $m=2$, $k=\pi/2a$, and $Q = -2k_F'$. As seen in Fig. 1, $|\pi/2a,1\rangle$ is occupied and $|-\pi/2a,2\rangle$ is unoccupied.

We show in structure 2 how the transition density favors the nuclear or molecular motion with the same symmetry as $\rho_{k,l,k+Q,m}$. Here closed circles signify nuclei or molecules; and "+" and "−" represent *the sign of the product of neighboring orbitals*, or the off-diagonal density mentioned above. We do not show on-site densities, because they are less important, as discussed above. From the form of this transition density, we understand that the charge is displaced from the "−" region to the "+" region as a consequence of orbital interactions near the Fermi level. Consequently, there appears an out-of-phase coupling of the off-diagonal CDWs on neighboring chains, as shown in structure 2.


2
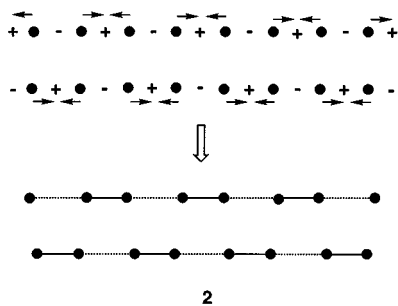
The vectors in structure 2 (upper part) show the forces

acting on the nuclei or molecules, or their preferred motion, due to the electron-distribution relaxation—it is reasonable to presume that the positively charged nuclei should move in the direction of increased electron density. Structure 2 (lower part) shows the resulting geometry. This broken-symmetry state is a direct consequence of orbital interaction near the Fermi level. This result is fully consistent, as it must be, with Whangbo's analysis, in which a doubled unit cell is assumed.[20] Since the third and fourth terms of Eq. (3) are positive and negative, respectively, the extent of the distortion would be determined by the balance of these terms. Clearly, the out-of-phase coupling of the off-diagonal CDWs minimizes the direct Coulomb repulsion between chains. This would additionally stabilize this broken-symmetry state. However, it is important to stress that this out-of-phase coupling essentially comes from orbital interactions on neighboring chains, not from a direct Coulomb effect.

On the other hand, there exist no off-diagonal CDWs in the transition density at $Q=0$, as seen from Fig. 2. Thus in this case the transition force does not operate on the nuclei or molecules. Consequently, the mixing between occupied $|\pi/2a,1\rangle$ and unoccupied $|\pi/2a,2\rangle$ does not induce effective nuclear distortion. In this case only on-site CDWs appear through the orbital mixing.

Although we have neglected the cross off-diagonal terms (β_{12} and β_{21}) of Eq. (12), these terms may play an important role in some interchain distortions. Let us now consider this intriguing possibility, distortion driven by the cross off-diagonal densities. We can see from Eq. (12) that the cross off-diagonal densities appear when $Q=0$, in remarkable contrast to the off-diagonal densities which appear at $Q=-2k_F'$. These interactions will cause a kind of "parallelogram" distortion, as indicated schematically in structure 3. This theoretical possibility has not, to our knowledge, been considered so far.

3
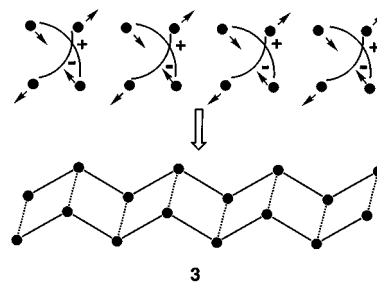
Having described the interchain coupling of the two metallic chains whose repeat unit M has one electron, let us next examine how doping (a common experimental perturbation) might affect the interchain interaction. Suppose that electrons are removed from the system by doping the material with electron-acceptors. For simplicity, consider that the quasi-Fermi wave vector k_F' is shifted from $\pm\pi/2a$ to $\pm\pi/4a$, due to a specific (and substantial) decrease in the number of electrons. In this case, $|\pi/4a,1\rangle$ and $|-\pi/4a,2\rangle$ are occupied and unoccupied, respectively. The transition density may be written as Eq. (15),
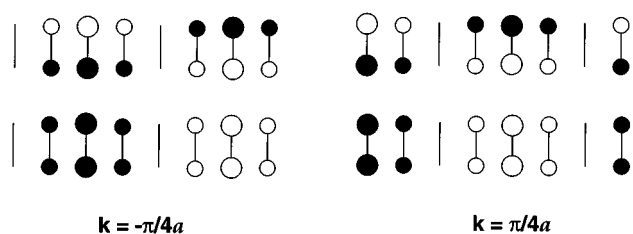
k = -π/4a   **k = π/4a**

FIG. 3. Crystal orbitals of the two-chain model at $k = \pm \pi/4a$. The line-segments indicate a quasimolecule in the unit cell.

$$\rho_{\pi/4a,1,\pi/4a+Q,2} = \frac{1}{2N}\left[\sum_{\nu} (\alpha_1 - \alpha_2)e^{-i\nu/2\pi} + 2\sum_{\nu} (\beta_{11} - \beta_{22})e^{-i(\nu/2+1/4)\pi}\right],\qquad(15)$$

where $Q = -2k_F' = -\pi/2a$. Clearly, this generates another type of out-of-phase CDW coupling on neighboring chains. The wavelength of these CDWs (4a) is twice as large as in the former case.

Figure 3 depicts the wave functions of the band 1 and 2 at $k = \pm \pi/4a$.[31] We show in structure 4 the schematic transition density $\rho_{k,l,k+Q,m}$, where $l=1$, $m=2$, $k=\pi/4a$, and $Q = -2k_F'$. Charge is displaced from the "−" region to the "+" region as a consequence of orbital interaction near the Fermi level. The nuclear motion favored is indicated with the vectors. In the resulting structure 4 (lower), bond alternation would be weak compared to structure 2.


4
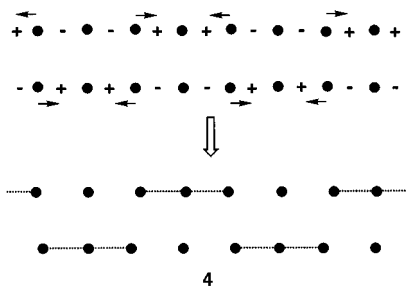
Consider next a more realistic problem, the bond-alternation of polyacene. The undeformed organic polymer is shown in structure 5; structures 6 and 7 are two possible ways of localizing bonds in the polymer. Extended Hückel band calculations[32] indicate that structure 7 is energetically favored for this one-dimensional organic polymer. The single and double line-segments in these structures stand for long and short C–C bonds, respectively. Let us consider the preferred nuclear distortion implied by a transition-density analysis.


5   **6**

7
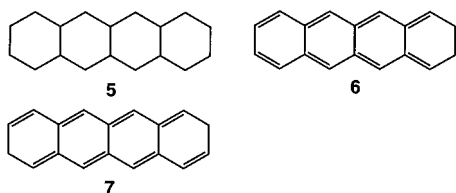
One way to view polyacene is as two interacting *trans*-polyacetylene chains. Since the electronic states around the

Fermi level are important for this perturbational treatment, we consider just the π electrons. Although polyacene and the two-chain model 1 are topologically different and hence it is impossible to take a unit cell of the type we drew in structure 1, we nevertheless find it useful to formulate analysis of the system in this way. The σ system certainly is far from the ideal one, but the π band-structure near the Fermi level is likely to be similar to that of the two-chain model (Fig. 1).

An analysis of the transition density points to the preferred nuclear distortion indicated in structure 8. There is a clear ordering of CDW modulations on neighboring chains. This indeed suggests a preference for structure 7, a result consistent with the analysis of the orbital interactions by Kertesz and Hoffmann.[21]

8
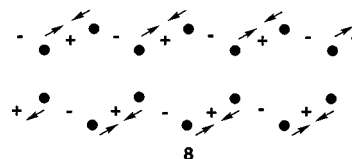
Doping should modify the structure of polyacene. Imagine that electrons are removed from the system by *p*-type doping. We assume here that the quasi-Fermi wave vector k_F' is shifted to $\pi/4a$ as a result of the lowered electron count. We show in structure 9 the transition density $\rho_{k,l,k+Q,m}$, where $l=1$, $m=2$, $k=\pi/4a$, and $Q = -2k_F'$. There is now a different out-of-phase coupling of CDWs between chains.

9
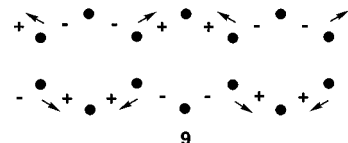
The preferred nuclear motion is also indicated with the arrows. This analysis predicts structure 10 as the favored geometry of *p*-type doped polyacene (for the particular electron count specified). The broken line-segments indicate incremental bonding. This structure clearly suggests a relaxation of the bond alternation, which indeed is what happens in doped polyacetylene.[33]

10
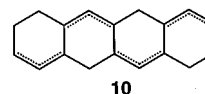
The detailed geometrical structure of neutral and doped polyacene is not known experimentally, because crystalline polyacene has so far eluded synthesis. It will be very interesting to see the geometry of the system when it is made, as it surely will be.

CONCLUSIONS

The first-order perturbation effect is dominant in degenerate electronic states, and in one-dimensional extended systems the usual Peierls distortion occurs to remove that de-

generacy. In this paper, we have discussed nondegenerate cases, i.e., second-order or pseudo-Peierls distortion. We have examined from a quantum chemical viewpoint the way the second-order perturbation functions, specifically in controlling interchain interactions. The second-order term which derives from two different bands near the Fermi level plays an important role in such interactions. As a consequence, there appears an out-of-phase coupling of CDWs on neighboring chains. The preferred distortions which arise from interchain interactions were predicted as a function of electron count, using an analysis of the transition-density near the Fermi level. We believe that our approach will be useful for the understanding of the role of orbital interactions in interchain coupling of one-dimensional materials.

ACKNOWLEDGMENTS

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