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Interchain order, soliton confinement, and electron-hole photogeneration in *trans*-polyacetylene

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Two neighboring *trans*-polyacetylene chains are modeled individually by the Su, Schrieffer, and Heeger Hamiltonian and coupled by an interchain electron-transfer term. Geometrical considerations show that the interchain transfer integrals alternate in size and possibly even in sign. In the latter case parallel ordering of dimerization is favored. Due to the bonding produced by the splitting of midgap levels for parallel ordering, two neutral solitons on neighboring chains are strongly bound. The binding energy is calculated in the continuum limit using the analogy to the solvable model of a diatomic polymer chain. The direct *inter*chain photoproduction of electron-hole pairs is calculated for the two orderings and for polarization perpendicular to the chain axis. It is found that not too far above threshold ($\omega=2\Delta$) this contribution is comparable to the *intra*chain optical absorption.

I. INTRODUCTION

Theoretical descriptions of conjugated polymers are often restricted to a single isolated chain. While this can yield a good approximation for certain properties like the amplitude of dimerization or the optical gap, it fails completely for describing other aspects, especially those for which the interchain electron transfer is crucial. In an earlier paper[1] we studied the effect of this interchain transfer on the relative order of dimerization on neighboring chains and concluded that the order should be out of phase (antiparallel). Through the recent synthesis of homogeneous, well-oriented samples it has become possible to address the question of interchain ordering using x-ray diffraction. In contrast to theoretical predictions, the experiments point to in-phase (parallel) alignment of the dimerization.[2] In this paper we show that the puzzle can be resolved by looking more closely at the geometrical arrangement of neighboring chains. This arrangement implies that the interchain transfer not only has different sizes on even and odd sites but can even have different signs. In this case the in-phase alignment is energetically preferred.

The question how the $(CH)_x$ chains are arranged in crystalline polyacetylene has been addressed by Baughman and Moss[3] and by Stafström[4] using semiempirical approaches. These calculations predict that neighboring chains are rotated relative to each other, in agreement with experiment.[2] However, within the accuracy of the finite chain calculations[4] the two possible alignments of dimerization are energetically degenerate. On the other hand, parallel alignment has been predicted by Jeyadev[5] on the basis of interchain Coulomb and dispersion forces. However, these effects appear to be about an order of magnitude smaller than those originating from interchain electron transfer.[1] Therefore, we neglect the interchain Coulomb effects in this paper and limit ourselves on the interchain hopping term. A similar model has been studied by Brazovskii and co-workers in a different context.[6]

A good measure for the relative sizes of intra- and interchain transfer integrals is provided by the anisotropy of electrical transport and optical absorption. Since in polyacetylene the dc conductivity is strongly influenced by sample inhomogeneities it is preferable to rely on optical data. A complication arises from the planar structure of hydrocarbon chains which implies that intrachain absorption occurs for two polarization directions, one parallel and one perpendicular to the chain.[7,8] Therefore it is not easy to separate intra- and interchain optical transitions. On the other hand, the interchain photogeneration of electron-hole pairs appears to be crucial for photoconductivity[9] and photoinduced optical absorption,[10] since carriers generated on different chains have a reduced chance to recombine compared to those generated on the same chain. The intra- and interchain contributions to the optical absorption have also been studied recently by Danielsen[11] and by Gartstein and Zakhidov,[12] however, assuming a constant interchain transfer integral.

Our generalized model for interchain coupling is introduced in Sec. II. It is shown that, depending on the relative signs of subsequent interchain transfer integrals, the dimerizations on two neighboring chains will be in phase or out of phase. Parallel ordering leads to strong binding of two solitons located on neighboring chains. This is shown in Sec. III where the two-chain problem is mapped onto two decoupled diatomic chains which can be treated exactly in the continuum limit. The confinement potential which arises from the misalignment of neighboring chains between two solitons and which increases linearly with the intersoliton distance is calculated in Sec. IV. In Sec. V both intra and interchain optical transitions are discussed for the present model of three-dimensional polyacetylene. The interchain absorption is found to depend on the relative ordering of the chains. Furthermore, near the absorption edge it is found to be of the same order as the *intra*chain absorption. Possible implications for photogeneration experiments are mentioned in Sec. VI.

II. INTERCHAIN ORDER

Consider two neighboring *trans*-$(CH)_x$ chains described individually by the Su, Schrieffer, and Heeger

(SSH) Hamiltonian[1,13]

$$H_j=\tfrac{1}{2}K\sum_n (u_{j,n}-u_{j,n+1})^2 -\sum_n [t_0+\alpha(u_{j,n}-u_{j,n+1})](c^\dagger_{j,n}c_{j,n+1}+\text{H.c.})\ , \tag{1}$$

where $u_{j,n}$ and $c_{j,n}$ are, respectively, the displacement coordinate of a CH group and the annihilation operator of a π electron on the jth chain at the nth lattice site. For simplicity the spin indices have been omitted. The geometrical arrangement of chains as obtained from x-ray diffraction[2] is illustrated in Fig. 1. One notices that neighboring chains are tilted with respect to each other by a large angle of about 70°. It is well known that two-center integrals between π orbitals attached to two different sites strongly depend on the relative directions of the two orbitals and of the spatial vector connecting the two sites.[14] For an idealized arrangement with neighboring chains at right angles within a quadratic unit cell (i.e., $a=b$ and $\Phi=45°$ in Fig. 1 the interchain transfer integrals would be alternating along the chains, as illustrated in Fig. 2. Since also the distances between C atoms are alternatively longer and shorter we assume the following form for the interchain coupling:

$$H'=-\sum_n [t_1+(-1)^n t_2](c^\dagger_{1n}c_{2n}+c^\dagger_{2n}c_{1n})\ . \tag{2}$$

Introducing annihilation operators a_{jk} and b_{jk} through the relation

$$c_{jn}=\frac{1}{\sqrt{N}}\sum_k e^{ikn}[(-1)^n a_{jk}+ib_{jk}],\quad -\tfrac{1}{2}\pi<k\le\tfrac{1}{2}\pi \tag{3}$$

N being the number of sites per chain, and assuming perfect dimerization on each chain, i.e., $u_{jn}=(-1)^n u_j$, we find

$$H_j=\sum_k [\,2t_0\cos k\,(a^\dagger_{jk}a_{jk}-b^\dagger_{jk}b_{jk}) +\Delta_j\sin k\,(a^\dagger_{jk}b_{jk}+b^\dagger_{jk}a_{jk})]\ , \tag{4}$$

$$H'=-\sum_k [\,t_1(a^\dagger_{1k}a_{2k}+b^\dagger_{1k}b_{2k}) +it_2(a^\dagger_{1k}b_{2k}-b^\dagger_{1k}a_{2k})+\text{H.c.}]\ . \tag{5}$$

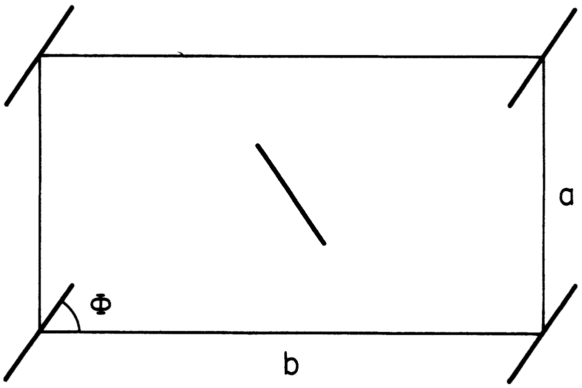

FIG. 1. Relative orientations of the planes of the (CH)$_x$ chains in *trans*-polyacetylene. According to Ref. 2 the parameter values are $a=4.18$ Å, $b=7.34$ Å, and $\Phi=57°$.

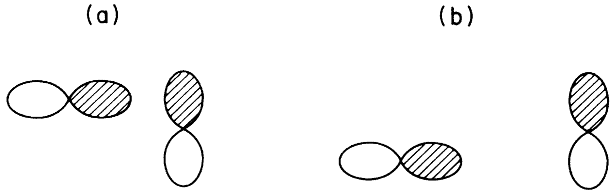

FIG. 2. Geometrical arrangement of π orbitals on neighboring chains for an idealized quadratic unit cell: (a) head-to-head on even sites, (b) head-to-tail on odd sites, or vice versa.

The gap parameters $\Delta_j=4\alpha u_j$ are assumed to have the same magnitude, $|\Delta_1|=|\Delta_2|\equiv\Delta_0$, but they are allowed to differ in sign. H_j is diagonalized by the Bogoliubov transformation

$$\begin{aligned} a_{jk}&=\cos\theta_{jk}\alpha_{jk}+\sin\theta_{jk}\beta_{jk}\ ,\\ b_{jk}&=\cos\theta_{jk}\beta_{jk}-\sin\theta_{jk}\alpha_{jk}\ , \end{aligned} \tag{6}$$

provided that

$$\tan 2\theta_{jk}=-(\Delta_j/2t_0)\tan k\ . \tag{7}$$

In terms of quasiparticle operators α_{jk} and β_{jk} the Hamiltonian H_j assumes the form

$$H_j=\sum_k E_k(\alpha^\dagger_{jk}\alpha_{jk}-\beta^\dagger_{jk}\beta_{jk})\ , \tag{8}$$

where the spectrum is given by

$$E_k=(4t_0^2\cos^2 k+\Delta_0^2\sin^2 k)^{1/2}\ , \tag{9}$$

whereas the interchain term becomes

$$\begin{aligned} H'=-\sum_k \{\,&[t_1\cos(\theta_{1k}-\theta_{2k})+it_2\sin(\theta_{1k}-\theta_{2k})]\\ &\times(\alpha^\dagger_{1k}\alpha_{2k}+\beta^\dagger_{1k}\beta_{2k})\\ &-[t_1\sin(\theta_{1k}-\theta_{2k})-it_2\cos(\theta_{1k}-\theta_{2k})]\\ &\times(\alpha^\dagger_{1k}\beta_{2k}-\beta^\dagger_{1k}\alpha_{2k})+\text{H.c.}\}\ . \end{aligned} \tag{10}$$

It follows already from this expression that the two transfer integrals have different effects. For in-phase alignment where $\theta_{1k}=\theta_{2k}$, t_1 connects the valence- (conduction-) band states of one chain to the valence- (conduction-) band states of the other, whereas t_2 connects the valence-band states of one chain to the conduction-band states of the other. The reverse is true for out-of-phase alignment where $\theta_{1k}=-\theta_{2k}$, at least for the states close to the Fermi energy (i.e., for $|k|\sim\frac{1}{2}\pi$). Since energy can be gained by mixing valence-band states of one chain with conduction-band states of the other we expect t_2 to favor in-phase alignment and t_1 out-of-phase alignment. This can be easily verified by diagonalizing the full Hamiltonian $H=H_1+H_2+H'$. For parallel ordering ($\theta_{1k}=\theta_{2k}$) the energy spectrum splits into

$$\tilde{E}_k=(E_k^2+t_2^2)^{1/2}\pm t_1\ , \tag{11}$$

and the energy gain amounts to

$$\Delta E^{(p)} = -4\sum_k [(E_k^2+t_2^2)^{1/2}-E_k]$$
$$\approx -(Nt_2^2/\pi t_0)\ln(8t_0/\Delta_0) \ . \qquad (12)$$

For *anti*parallel ordering ($\theta_{1k}=-\theta_{2k}$) the spectrum splits into

$$\tilde{E}_k = \{E_k^2+t_1^2+t_2^2\pm 2[\,t_1^2(4t_0^2\cos^2 k+t_2^2)+t_2^2\Delta_0^2\sin^2 k]^{1/2}\}^{1/2} \ . \qquad (13)$$

This produces an energy gain

$$\Delta E^{(a)} \approx \Delta E^{(p)} + N(t_2^2-t_1^2)/\pi t_0 \ . \qquad (14)$$

It follows that for $t_2>t_1$ in-phase alignment is favored, whereas for $t_2<t_1$ out-of-phase alignment is preferred. It is worth noticing that for the special case where $t_2=t_1$ the two orderings are energetically degenerate. Interchain hopping to more distant sites and Coulomb forces would then become crucial for deciding about the ground-state configuration.[5] Since the relative size of t_1 and t_2 is expected to depend sensitively on the angle between the C-H planes of neighboring chains (Fig. 1) the observed value of this angle may in part be determined by the competing effects of these two transfer integrals.

III. INTERACTION BETWEEN SOLITONS ON NEIGHBORING CHAINS

The interchain ordering has important consequences on the translational freedom of solitons. Consider two solitons on neighboring chains. In the antiparallel case the wave-function amplitudes of the midgap state vanish on the even site for one chain but on the odd sites for the other. Therefore, as noticed earlier in the continuum limit,[1] there is no splitting of the midgap levels. On the other hand, in the parallel case the wave-function amplitudes are finite either on even or on odd sites for both chains and therefore the two midgap states are mixed and the levels are split.[15] It follows that the two solitons are more tightly bound in the case of in-phase ordering as compared to out-of-phase alignment. On the other hand, for two solitons on the same chain there is no significant difference between the two cases.

It is convenient to consider first two solitons centered at the same site as illustrated in Fig. 3. We assume that they are described by the same inhomogeneous order parameter $\Delta_{1,n}=\Delta_{2,n}\equiv\Delta_n$, where $\Delta_{j,n}=2\alpha(-1)^n\times(u_{j,n}-u_{j,n+1})$. Transforming to bonding and antibonding operators

$$b_n=2^{-1/2}(c_{1n}+c_{2n}) \text{ and } a_n=2^{-1/2}(c_{1n}-c_{2n}) \ ,$$

respectively, we obtain the following form for the electronic part of the Hamiltonian $H=H_1+H_2+H'$:

$$H_e=\sum_n \{\,[t_1+(-1)^n t_2](a_n^\dagger a_n-b_n^\dagger b_n) - [t_0+\tfrac{1}{2}(-1)^n\Delta_n] \times(a_n^\dagger a_{n+1}+b_n^\dagger b_{n+1}+\text{H.c.})\} \ . \qquad (15)$$

This represents the Hamiltonian of two uncoupled hypothetic a and b chains. For $t_1=0$ the individual chains correspond to the *AB* polymer introduced by Rice and Mele.[16] The different sign of the local energy on the two chains implies that if Δ_n represents an A soliton on the a chain it corresponds to a B soliton on the b chain (and vice versa). The continuum approach of Rice and Mele[16] is easily generalized to include a finite t_1. The electronic structure of the two solitons is illustrated in Fig. 4. It is the same as for the A and B soliton of the *AB* polymer except for rigid shifts by $\pm t_1$. The energy of this complex (as compared to the homogeneous ground state) is found to be

$$\Delta E = 2E_{S0}-(4/\pi)(t_1+t_2)\tan^{-1}(\Delta_0/t_2) \ , \qquad (16)$$

where $E_{S0}=(2/\pi)\Delta_0$ is the soliton energy[17] in the absence of interchain coupling. Notice that the configuration of Figs. 3 and 4 is not unique. Shifting single and double bonds in Fig. 3 by one lattice constant would be the same as replacing the kinks by antikinks or Δ_n by $-\Delta_{n+1}$ in Eq. (15). A simple transformation $a_n\to b_{n+1}$, $b_n\to a_{n+1}$ brings H_e back to its original form except that t_1 is replaced by $-t_1$. This implies that the electronic structure of the A soliton which was shifted upwards by t_1 previously is now shifted downwards by $-t_1$, and correspondingly for the B soliton. The energy of a pair of antikinks is given by Eq. (16) with t_1 replaced by $-t_1$. The binding energy induced by interchain coupling (for two neutral solitons on neighboring chains) is therefore

$$E_b=(4/\pi)(t_2\pm t_1)\tan^{-1}(\Delta_0/t_2) \ , \qquad (17)$$

where the plus sign refers to two kinks and the minus sign to antikinks. If t_2 is much smaller than Δ_0 the binding energy becomes

$$E_b\approx 2(t_2\pm t_1) \ , \qquad (18)$$

which is simply the bonding energy provided by the splitting of the midgap levels. For two positively or two negatively charged solitons both levels in the gap are empty or doubly occupied and there is no net binding. The same is true for a positively and a negatively charged soliton. Therefore, this interaction energy between two solitons on neighboring chains does not enhance the recombination of charged solitons generated optically on different chains.

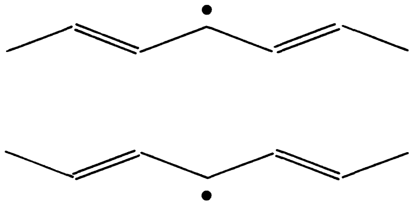

FIG. 3. Bound pair of solitons in the case of parallel ordering.

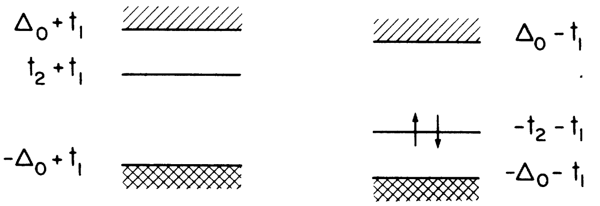

FIG. 4. Electronic structure for a bound pair of kinks.

IV. SOLITON CONFINEMENT

We have shown in the previous section that the splitting of the midgap levels leads to a strong binding of neutral solitons on adjacent chains. This is the main mechanism if the solitons are close to each other, namely for $l \lesssim \xi = v_F/\Delta_0$. For larger distances the overlap of the localized wave functions becomes exponentially small and the bonding mechanism is ineffective. However, as realized by several authors,[1,3,15] in this case the energy of the soliton pair increases linearly with distance due to the misalignment of the chains between the two solitons.

In Ref. 1 we have calculated this confinement potential for antiparallel ordering and $t_2 = 0$. It is straightforward to extend this analysis to finite t_2 and to the case of parallel ordering. We introduce spinor fields

$$\psi_j(x) = \begin{bmatrix} u_j(x) \\ v_j(x) \end{bmatrix} \tag{19}$$

to describe the right- and left-moving electrons on the jth chain. The continuum version of the Hamiltonian (1) becomes

$$H_j = (2\pi\lambda v_F)^{-1} \int dx\, \Delta_j^2(x) + \int dx\, \psi_j^\dagger(x)[-iv_F \partial_x \sigma_3 + \Delta_j(x)\sigma_1]\psi_j(x) \,, \tag{20}$$

where $\lambda = 2\alpha^2/(\pi K t_0)$, $v_F = 2t_0 a_0$ (a_0 being the lattice constant), and σ_1, σ_3 are Pauli matrices. Similarly the interchain coupling, Eq. (2), becomes

$$H' = \int dx\, \psi_1^\dagger(x)(-t_1 + t_2\sigma_2)\psi_2(x) + \text{H.c.} \tag{21}$$

For large enough distances between the solitons the overlap between the wave functions of the midgap states is negligible and we can use nondegenerate perturbation theory. To lowest order in H' we obtain a correction in energy,

$$\Delta E = -2i \int dx \int dx' \int \frac{d\omega}{2\pi} \operatorname{tr}[(t_1 - \sigma_2 t_2)G_1(x,x',\omega) \times (t_1 - \sigma_2 t_2) \times G_2(x',x,\omega)] \,, \tag{22}$$

where the factor 2 results from the spin summation and $G_j(x,x',\omega)$ is the Green's-function matrix associated with the two-component fields $\psi_j(x)$ and $\psi_j^\dagger(x)$.

Performing the trace and the spatial integrations we find

$$\Delta E = -4 \left[\sum_{k,k'} |M_{k,k'}|^2/(E_k + E_{k'}) + \sum_k |M_k|^2/E_k \right] , \tag{23}$$

where the first term represents interband transitions and the second term involves transitions between the midgap state and conduction and valence bands. The matrix elements M_k and $M_{kk'}$ are calculated in the Appendix where also the remaining integrations are performed. We find for $l \gg \xi$,

$$\Delta E = (\pi v_F)^{-1}[-L(t_2^2/\lambda) + 2l \coth(l/\xi)(t_2^2 - t_1^2)] \,. \tag{24}$$

In view of the gap equation relating λ to Δ_0 this result is consistent with Eqs. (12) and (14) of Sec. II.

V. INTERCHAIN CONDUCTIVITY

Due to the zig-zag structure of a *trans*-polyacetylene chain there are two contributions to the *intra*chain conductivity, one for an electric field polarized parallel to the chain axis, the other for a polarization perpendicular to the chain axis but still within the planar structure. These two contributions have been calculated for the SSH model[7] and identified experimentally.[8] Here we calculate only the *inter*chain contributions. We consider two chains separated by a distance d and described by the Hamiltonian of Sec. II, Eqs. (1) and (2). For perfect dimerization the electron transfer between the chains occurs exactly perpendicular to the chain axes in the case of in-phase alignment, but slightly oblique if the two dimerization patterns are out of phase. It follows that for a field polarized parallel to the chains there is no interchain conductivity in the case of in-phase alignment whereas out-of-phase ordering allows for a small contribution of order $(u/d)^2$. In fact, for parallel polarization the current operator is given by

$$j_\parallel = \begin{cases} 0 \text{ for in-phase ordering} \\ -2ieu_0 \sum_n [(-1)^n t_1 + t_2] c_{1n}^\dagger c_{2n} + \text{H.c.} \\ \qquad\qquad \text{for out-of-phase ordering} \,, \end{cases} \tag{25}$$

whereas for perpendicular polarization the current is

$$j_\perp = -ied \sum_n [t_1 + (-1)^n t_2] c_{1n}^\dagger c_{2n} + \text{H.c.} \,, \tag{26}$$

both for parallel and antiparallel ordering. (For simplicity, we consider an idealized quadratic unit cell and neglect the small variations in distances between C atoms on neighboring chains.) In the following we treat only the case of perpendicular polarization. Using Eqs. (3) and (6) we write $j_\perp$ as

$$j_\perp = -ied \sum_k \{ [t_1 \cos(\theta_{1k} - \theta_{2k}) + it_2 \sin(\theta_{1k} - \theta_{2k})](\alpha_{1k}^\dagger \alpha_{2k} + \beta_{1k}^\dagger \beta_{2k}) + i[t_2 \cos(\theta_{1k} - \theta_{2k}) + it_1 \sin(\theta_{1k} - \theta_{2k})](\alpha_{1k}^\dagger \beta_{2k} - \beta_{1k}^\dagger \alpha_{2k}) \} + \text{H.c.} \tag{27}$$

We discuss the two cases of parallel and antiparallel ordering separately.

A. Parallel ordering ($\theta_{1k}=\theta_{2k}$)

The matrix elements connecting valence and conduction bands of the two chains are readily deduced from Eq. (27),

$$\langle k_{1c} \,|\, j_\perp \,|\, k_{2v} \rangle = \langle k_{2c} \,|\, j_\perp \,|\, k_{1v} \rangle = edt_2 \ . \tag{28}$$

This yields an interchain conductivity

$$\begin{aligned} \sigma^\perp_{\text{inter}}(\omega) &= 2(2\pi/\omega d^2)(edt_2)^2 L^{-1} \sum_k \delta(\omega - 2E_k) \\ &= \frac{4e^2}{a_0} t_2^2 F(\omega) \ , \end{aligned} \tag{29}$$

where

$$F(\omega) = \begin{cases} [(16t_0^2-\omega^2)(\omega^2-4\Delta_0^2)]^{-1/2} \ , & 2\Delta_0 < |\,\omega\,| < 4t_0 \\ 0, \ \text{otherwise} \ . \end{cases} \tag{30}$$

There are two square-root singularities, one at $2\Delta_0$ the other at $4t_0$. It is noteworthy that in the case of parallel ordering the interchain conductivity depends only on t_2 (but not on t_1).

B. Antiparallel ordering ($\theta_{1k}=-\theta_{2k}$)

In this case Eq. (27) implies

$$\begin{aligned} \langle k_{1c} \,|\, j_\perp \,|\, k_{2v} \rangle &= \langle k_{2c} \,|\, j_\perp \,|\, k_{1v} \rangle^* \\ &= ed\,(2t_0 t_1 \cos k + i\Delta_0 t_2 \sin k)/E_k \ , \end{aligned} \tag{31}$$

giving rise to an interchain conductivity

$$\begin{aligned} \sigma^\perp_{\text{inter}}(\omega) &= 2(2\pi/\omega d^2)(ed)^2 L^{-1} \sum_k [(2t_0 t_1 \cos k)^2 + (\Delta_0 t_2 \sin k)^2] E_k^{-2} \delta(\omega - 2E_k) \\ &= \frac{4e^2}{a_0} F(\omega) \{ 4t_0^2 [t_2^2 + (t_1^2 - t_2^2)(2\Delta_0/\omega)^2] - \Delta_0^2 t_1^2 \} / (4t_0^2 - \Delta_0^2) \ . \end{aligned} \tag{32}$$

The limiting form for the particular case $t_2=0$,

$$\sigma^\perp_{\text{inter}}(\omega) = \frac{4e^2}{a_0} F(\omega) t_1^2 (\Delta_0/\omega)^2 (16t_0^2 - \omega^2)/(4t_0^2 - \Delta_0^2) \ , \tag{33}$$

agrees with an earlier calculation by Danielsen.[11] As t_2 increases towards t_1 Eq. (32) smoothly approaches Eq. (29). Therefore, if t_1 and t_2 are approximately equal it would be difficult to deduce the interchain ordering from observed optical absorption spectra.

It is instructive to compare the *inter*chain conductivities given by Eqs. (29) and (32) with the *intra*chain contribution[7]

$$\sigma^\perp_{\text{intra}}(\omega) = \frac{1}{6} \frac{e^2 a_0}{d^2} \omega^2 F(\omega) \ . \tag{34}$$

For ω close to $2\Delta_0$ Eq. (32) becomes essentially equal to Eq. (29) with t_2 replaced by t_1. Thus at threshold

$$\frac{\sigma^\perp_{\text{inter}}(\omega)}{\sigma^\perp_{\text{inter}}(\omega)} \approx 6(d/a_0)^2 (t_\perp/\Delta_0)^2 \ , \tag{35}$$

where $t_\perp = \max(t_1, t_2)$. With parameter values appropriate for polyacetylene, $\Delta_0 \approx 0.9$ eV, $t_\perp \approx 0.1$ eV, and $d/a_0 \approx 3.5$, this ratio is about 1. Therefore the two contributions are comparable at threshold. However, for larger ω the *intra*chain transitions clearly dominate, as shown in Fig. 5.

VI. CONCLUDING REMARKS

We have studied a two-chain model for *trans*-polyacetylene and shown that the relative ordering of the two dimerization patterns depends essentially on the variation of the interchain resonance integrals along the chains. In view of the three-dimensional packing of the chains deduced from x-ray diffraction[2] it is plausible that the resonance integrals vary strongly and possibly even change sign between neighboring sites. In this case parallel ordering is preferred. Furthermore, solitons on neighboring chains form a tightly bound pair with a binding energy of the order of $2\,|\,t_\perp\,| \approx 0.2$ eV. This is true for two neutral solitons or for a neutral soliton on one chain and a charged soliton on the other chain, which can gain energy from the splitting of the midgap levels, however not for two positively or two negatively charged solitons,

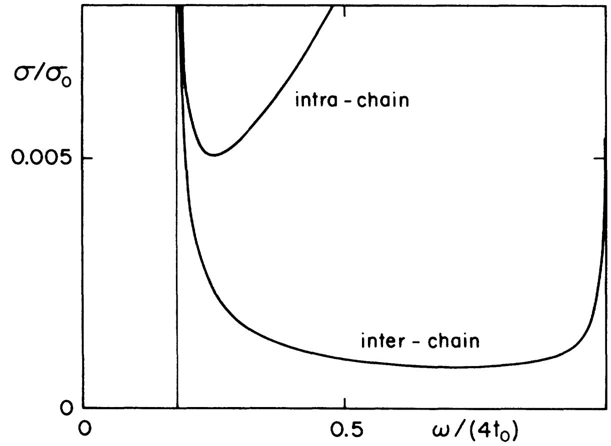

FIG. 5. Real part of the conductivity for polarization perpendicular to the chain axis in the case of parallel alignment of neighboring chains. The parameters are $(d/a_0)=3.5$, $\Delta_0=0.9$ eV, $t_2=0.1$ eV, $t_0=2.5$ eV, and $\sigma_0=e^2/(\hbar a_0)=2.1\times10^4$ $(\Omega\,\text{cm})^{-1}$.

where it is the linear increase of the energy as a function of the intersoliton distance which produces confinement.

This qualitative difference between parallel and antiparallel ordering is expected to be appreciably modified if (intrachain) electron-electron interactions are included. It is well established that in contrast to the case of the SSH model where the wave-function amplitudes of the midgap state vanish on even or odd sites, models including Coulomb interactions lead to more uniformly distributed amplitudes.[18] Therefore, one may expect level splittings due to interchain electron tunneling and consequently a strong binding of solitons both for parallel and antiparallel ordering.

We have also calculated the *inter*chain conductivity and found that it is negligible for polarization parallel to the chain, but of the same order at threshold as the *intra*chain contribution for polarization perpendicular to the chain. Since one expects that an electron-hole pair has a better chance to escape geminate recombination when created on two different chains (as compared to intrachain photogeneration), it is conceivable that the yield both for photocarriers and for photoinduced defects is relatively large for polarization perpendicular to the chain axis. This expectation is borne out by recent experiments.[9,10]

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APPENDIX: CONFINEMENT ENERGY FOR PARALLEL ORDERING

A kink on a single chain of the form

$$\Delta(x)=\Delta_0\tanh[(x-l)/\xi]\ , \tag{A1}$$

where $\xi=v_F/\Delta_0$, produces a midgap state with wave function[17]

$$\psi_b(x)=\tfrac{1}{2}\xi^{-1/2}\operatorname{sech}(x/\xi)\begin{bmatrix}1\\ -i\end{bmatrix}\ . \tag{A2}$$

The extended states are given by

$$\psi_k^{\pm}(x)=\tfrac{1}{2}(A_k/E_k)e^{ikx}\begin{bmatrix}E_k\pm[v_Fk+i\Delta(x)]\\ iE_k\mp i[v_Fk+i\Delta(x)]\end{bmatrix}\ , \tag{A3}$$

where

$$E_k=(v_F^2k^2+\Delta_0^2)^{1/2}\ , \tag{A4}$$

$$A_k=(L-\xi\cos^2\phi_k)^{1/2}\ \text{ with }\cos\phi_k=\Delta_0/E_k\ , \tag{A5}$$

and the plus and minus signs refer to the conduction and valence bands, respectively. Consider a situation with two kinks centered at 0 and l on neighboring chains 1 and 2, respectively. The matrix elements determining the interchain contribution to the energy are

$$M_b=\int dx\ \psi_{b1}^{*}(x)(t_1-t_2\sigma_2)\psi_{b2}(x)=(t_1+t_2)(l/\xi)(\sinh l/\xi)^{-1}\ , \tag{A6}$$

$$\begin{aligned}M_k&=\int dx\ \psi_{1k}^{\pm *}(x)(t_1-t_2\sigma_2)\psi_{2b}(x)\\ &=\pm\tfrac{1}{2}\pi A_k(t_1+t_2)\xi^{1/2}\operatorname{sech}(\tfrac{1}{2}\pi k\xi)\{e^{-ikl}\sin\phi_k+i[1-e^{-ikl}\cosh(l/\xi)]\cos\phi_k(\sinh l/\xi)^{-1}\}\ ,\end{aligned} \tag{A7}$$

$$\begin{aligned}M_{kk'}&=\int dx\ \psi_{1k}^{+*}(x)(t_1-t_2\sigma_2)\psi_{2k'}^{-}(x)\\ &=A_kA_{k'}\{e^{-ikl}t_2L\delta_{k,k'}+\tfrac{1}{2}\pi\xi(t_1+t_2)[\sin\phi_k\cos\phi_{k'}e^{-ikl}-\cos\phi_k\sin\phi_{k'}e^{-ik'l}\\ &\qquad +i\cos\phi_k\cos\phi_{k'}(e^{-ik'l}-e^{-ikl})\coth(l/\xi)][\sinh\tfrac{1}{2}\pi(k-k')\xi]^{-1}\}\ ,\end{aligned} \tag{A8}$$

where $\sin\phi_k=v_Fk/E_k$. These expressions agree with the results of Danielsen and Ball[15] in the limit $t_2=0$. (Notice, however, that for parallel alignment on which the present analysis is based t_2 has to be larger than t_1.) For $l\gg\xi$ the contribution of M_b is negligible and the second term in Eq. (23) becomes

$$\sum_k |M_k|^2/E_k=(\pi\xi/8)(t_1+t_2)^2\int_{-\infty}^{\infty}dk\ \operatorname{sech}^2(\pi k\xi/2)/E_k+O(e^{-l/\xi})\ . \tag{A9}$$

The interband contribution in Eq. (23) consists of three terms,

$$\sum_{k,k'}|M_{kk'}|^2/(E_k+E_{k'})=I_a+I_b+I_c\ , \tag{A10}$$

where

$$I_a=t_2^2\sum_k L^2A_k^4/(2E_k)\ , \tag{A11}$$

$$I_b=-t_2(t_1+t_2)\Delta_0^2(l/L)\sum_k E_k^{-3}[\coth(l/\xi)-v_Fk/\Delta_0]\ , \tag{A12}$$

$$I_c=(t_1+t_2)^2(\pi v_F/2L)^2\sum_{k,k'}(E_k+E_{k'})^{-1}E_k^{-2}E_{k'}^{-2}$$
$$\times\,|\,v_F(ke^{-ikl}-k'e^{-ik'l})+i\Delta_0(e^{-ik'l}-e^{-ikl})\coth(l/\xi)\,|^2[\sinh\tfrac{1}{2}\pi(k-k')\xi]^{-2}\ . \qquad \text{(A13)}$$

In view of the gap equation

$$\int dk\,E_k^{-1}=(v_F\lambda)^{-1}\ , \qquad \text{(A14)}$$

we find

$$I_a=Lt_2^2/(4\pi v_F\lambda)+t_2^2/(\pi\Delta_0)\ . \qquad \text{(A15)}$$

Furthermore,

$$I_b=-(\pi v_F)^{-1}t_2(t_1+t_2)l\coth(l/\xi)\ . \qquad \text{(A16)}$$

Introducing the variables $K=\frac{1}{2}(k+k')$ and $\kappa=k-k'$, we write the third interband term as

$$I_c=(t_1+t_2)^2(v_F/4)^2\int_{-\infty}^{\infty}d\kappa(\sinh\tfrac{1}{2}\pi\xi\kappa)^{-2}$$
$$\times\int_{-\infty}^{\infty}dK\,(E_k+E_{k'})^{-1}E_k^{-2}E_{k'}^{-2}[\,2(E_k^2+E_{k'}^2)\sin^2(\tfrac{1}{2}\kappa l)+v_F\kappa(v_F\kappa\cos\kappa l-2\Delta_0\sin\kappa l)]\ . \qquad \text{(A17)}$$

Neglecting the contributions from rapidly oscillating terms and expanding the integrand in powers of κ we obtain to leading order in l/ξ

$$I_c\approx\tfrac{1}{2}(t_1+t_2)^2v_F^2\int_0^{\infty}d\kappa\sin^2(\tfrac{1}{2}\kappa l)/\sinh^2(\tfrac{1}{2}\pi\xi\kappa)\int_0^{\infty}dK\,E_K^{-3}$$
$$=(2\pi v_F)^{-1}(t_1+t_2)^2[l\coth(l/\xi)-\xi]\ . \qquad \text{(A18)}$$

Adding Eqs. (A9), (A15), (A16), (A18), and neglecting constant terms of order 1 we finally obtain Eq. (24).

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