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Ground state and excitations in polyacetylene chains

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While a nearest-neighbor-only Su-Schrieffer-Heeger model cannot distinguish *cis*- from *trans*-polyacetylene, a simple extension which includes a third-neighbor interaction can. This extended model gives a nondegenerate *cis* structure with a larger band gap and a smaller cohesive energy than *trans*, and yields the correct order of the total energies of the *trans*, *cis-transoid*, and *trans-cisoid* structures. It also produces bound bipolarons or excitons on doubly charged *cis* chains. All conformational excitations in both isomers are found to be repelled from the chain ends. [S0163-1829(96)03928-8]

I. INTRODUCTION

The Su, Schrieffer, and Heeger[1–4] (SSH) model has become the explanatory point of reference in almost all discussions of conjugated polymers, both experimental and theoretical. The original SSH model provides an explicit analysis of the behavior of conformational excitations on infinite *trans*-polyacetylene chains. Its ideas have been borrowed to provide qualitative explanations for finite chains, other polyacetylene isomers, and other conjugated polymers, though, in fact, the strict SSH model is not always capable of dealing with these systems.

In particular, for infinite chains, a nearest-neighbors-only version of the SSH model has identical Hamiltonians for the *trans* and both of the *cis* structures given in Fig. 1. There have been extensions of the model which incorporate the nondegeneracy of infinite *cis* chains into an external one-electron potential.[1,5] We have found that inclusion of additional coupling terms in the SSH Hamiltonian has the same effect, and does not assume nondegeneracy in advance. Specifically, the extension of the coupling terms up to *cis* third-nearest neighbors gives the *cis* ground state a larger band gap[5,6] and higher total energy[1,7,8] than *trans*-polyacetylene, as indicated by experiment. The most significant effect of this extension on fundamental excitations is that doubly charged soliton pairs, which separate freely on *trans* chains, form bipolarons on *cis* chains. These results are not new in themselves. They have long been discussed qualitatively, in a common-sense manner, in terms of the basic SSH model, and there have also been calculations based on the nondegeneracy-incorporating extensions of the model mentioned above.[1,5] What is new is that a very simple extension of the SSH model permits us to obtain these results, and to predict rather than to incorporate *cis* nondegeneracy. Thus the extension made in this paper explicitly validates SSH for *cis*-polyacetylene.

The rest of this paper is arranged as follows: Section II describes the extended SSH model, Sec. III presents the results of our calculations, and Sec. IV contains a brief summary and discussion.

II. THE EXTENDED SSH MODEL

A. Ground states

In this section we describe the SSH model for polyacetylene chains, together with the modifications needed to yield differences in behavior between the *trans* and *cis* isomers.

In the adiabatic approximation, the total energy of a chain in this model has two main components:

$$E = E_\pi + E_s . \tag{2.1}$$

E_s is a classical energy which treats all the C—C bonds as springs with a common spring constant K:

$$E_s = \sum_n \tfrac{1}{2} K (d_{i,i+1} - a)^2. \tag{2.2}$$

This term approximates any changes in energy due to the non-π electrons that occur when a carbon-carbon bond changes its length $d_{i,i+1}$ from some average value a. E_π is the total energy of the π electrons, and is the sum of the occupied single-particle energies ϵ_k:

$$E_\pi = 2 \sum_k \epsilon_k . \tag{2.3}$$

The ϵ_k are the eigenvalues of a tight-binding Hamiltonian:

$$H = -\sum_i \sum_j |i\rangle t_{i,j} \langle j|, \quad \langle i|j\rangle = \delta_{i,j} . \tag{2.4}$$

The standard SSH model contains only the nearest-neighbor interaction: $t_{i,j}$ is not zero only when i and j are nearest neighbors, that is, $j = i \pm 1$. The value of $t_{i,i+1}$ depends on the bond length $d_{i,i+1}$. We show below that nonzero $t_{i,j}$ beyond nearest neighbors are needed to obtain different band gaps and total energies for different isomers.

All the isomers of polyacetylene (Fig. 1) have dimerized ground states in which the molecules retain distinct single and double bonds with different lengths. In an undimerized chain, all C—C bond lengths have the same length a, the strain energy E_s is zero, and all $t_{i,i+1} = t_0$.

In both isomers, under uniform dimerization, every atom site is displaced by a distance u in a direction at an angle of

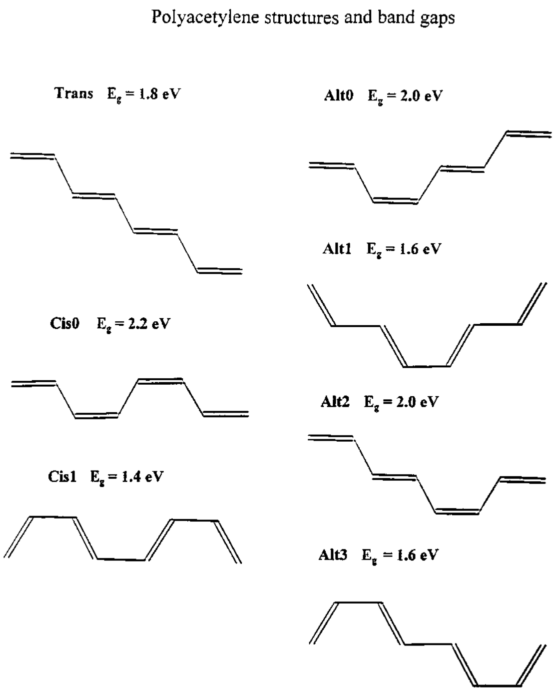

FIG. 1. Polyacetylene structures discussed in this paper for eight-carbon-atom chains. For larger chains the structures are repeated to the right. *cis*0 is generally known as the *cis-transoid* structure and *cis*1 as *trans-cisoid.*

30° to both of the neighboring bonds, in a way which creates alternating short (double) and long (single) bonds, shortened and lengthened, respectively, by $2u$ cos30°. These bonds will have π-electron coupling strengths of t_d and t_s, respectively: $t_d=t_0+2\alpha u$, $t_s=t_0-2\alpha u$. Every bond will have a spring energy of $2K'u^2\equiv 2Ku^2\cos^2 30°$, giving a total spring energy of $E_s=2(N-1)K'u^2$. The model described to this point, which includes only nearest-neighbor coupling, makes no distinction whatever between *cis* and *trans*.

There are, obviously, considerable differences between *cis*- and *trans*-polyacetylene, which need to be taken into account. *cis* has a wider band gap[5,6] and a lower cohesive energy.[1,5–8] *cis* has no internal degeneracy; the *cis-transoid* (*cis*0 in Fig. 1) structure is the actual *cis* ground state, while the *trans-cisoid* (*cis*1) structure has a much higher energy.[1,5–8]

To treat *cis*-polyacetylene, prior authors[1,5] have added a one-electron crystal potential term to the *trans* Hamiltonian. We have found that a simple extension of the π-electron interactions $t_{i,j}$ in a pure tight-binding model suffices for treating this problem. It will produce different results for *cis* and *trans* because *cis* chains contain pairs of third-nearest neighbors which are much closer together than in *trans*. More specifically, in the *cis*0 structure of Fig. 1, atoms 2 and 5, and 4 and 7, are a distance $2a$ apart, while the others, and all *trans* third-nearest neighbors, are separated by about $2.6a$. The coupling term for locally *cis* third-nearest neighbors is going to be a good deal larger than for locally *trans* pairs; in practice, we let the term for *trans* third neighbors, and higher-order terms, go to zero. While a third-nearest-neighbor interaction acting uniformly on all pairs (as does the second-neighbor coupling t_2: see below) will have no effect on the band gap or the total energy, one which acts differently across *trans* and *cis* bonds, as ours does, will have strong effects on both.

The three independent parameters of the original SSH model have the values[1–4]

$$t_0=2.5\ \text{eV},\quad \alpha=5.6\ \text{eV/Å},\quad K'=34.7\ \text{eV/Å}^2, \tag{2.5}$$

which we use throughout this paper. They yield an equilibrium dimerization[1,9,10] $u_0=0.04$ Å, an energy gap[1,10,11] $E_g=2|t_d-t_s|=8\alpha u_0=1.8$ eV, and an infinite-chain *trans* ground state with an energy 23.4 meV per atom below that of the undimerized state. We choose the value of the third-neighbor coupling $t_3=0.2$ eV to obtain the experimental *cis* band gap:[5,6] $E_g=8\alpha u_0+2t_3=2.2$ eV. We also include a second-nearest-neighbor term t_2, which is the same (as is the interatomic distance) for all second-neighbor pairs, for completeness. Its value ($t_2=0.4$ eV) was chosen to obtain a geometric progression, relative to interatomic distance, in t_0, t_2, and t_3. We have included t_2 in our calculations for *trans*- as well as for *cis*-polyacetylene. It does not change the band gaps or total energies of either isomer.

It is possible to obtain the individual π-electronic energy levels ϵ_k of a uniformly dimerized chain analytically by using a difference-equation approach.[12] This method applies equally well to any of the uniformly dimerized structures shown in Fig. 1, with or without the additional coupling terms of the extended model. For conformational excitations, however, we need to diagonalize the Hamiltonian directly to evaluate the ϵ_k.

B. Solitonic excitations

In the standard SSH model, a change in sign of the dimerization displacement u does not change the energy of an infinite *trans* chain. This makes the soliton, a gradual deformation which smoothly interchanges single and double bonds as one passes from one side to the other, a possible fundamental excitation of the system. The usual functional representation of a soliton[1–4] is

$$u(x)=u_0\tanh[(x-x_0)/w], \tag{2.6}$$

with w being the half-width and x_0 the position of the soliton. Because of the need for the displacements to be single valued with periodic boundary conditions, solitons exist in pairs in the SSH model. Natural boundary conditions, which terminate the coupling at both ends of a chain, create an energy difference between positive and negative u, as shown in curve B in Fig. 2 for a uniformly dimerized *trans* chain with 120 carbon atoms. This happens because the double bonds which exist at the ends of a chain in its ground state are replaced by single bonds with radical electrons. The difference occurs entirely near the ends of the chain; the chain interior retains its degeneracy, which we designate as internal degeneracy. This energy difference also ensures that solitons exist in pairs, to enable u to be positive at both ends of a chain. The functional representation of a pair of solitons at x_- and x_+ is

$$u(x)=u_0\{1-\tanh[(x-x_-)/w]+\tanh[(x-x_+)/w]\}. \tag{2.7}$$

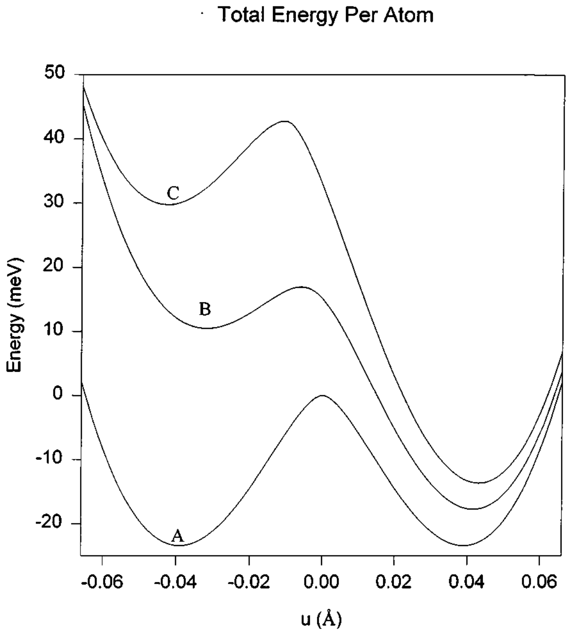

FIG. 2. Total energies per atom in meV relative to an undimerized infinite *trans* chain for *A*, an infinite *trans* chain, *B*, a uniformly dimerized *trans* chain with 120 carbon atoms, and *C*, an infinite *cis* chain.

If the solitons are widely separated, i.e., if $x_+ - x_- \gg w$, u approaches u_0 in the regions outside the solitons and $-u_0$ in the region between the solitons. A separation $x_+ - x_- = 0$ gives $u = u_0$ everywhere. This corresponds to the uniformly dimerized ground state.

The conformational excitations of both isomers are treated as forms of soliton pairs,[1–4] and are discussed in the next section.

III. RESULTS

A. Band structure and total energies

Curves *A* and *C* of Fig. 2, respectively, show the total energy per atom as a function of dimerization for infinite *trans* and *cis* chains, and curve *B* is for a *trans* chain with 120 carbon atoms ($N=120$). The positive-*u* minimum of the *cis* energy is the *cis-transoid* structure (*cis*0 in Fig. 1), which is also the lowest *cis* state, and the negative-*u* minimum the *trans-cisoid* (*cis*1) structure. Figure 1 gives the band gaps for all these isomers. As Fig. 2 shows, *cis*0 has a higher (less negative) total energy than the *trans* ground state, even though it has a wider band gap (Fig. 1).

The explanation for the apparent discrepancy between the behavior of the band gaps and the total energies lies in the details of the band structure: Figure 3 shows the band structure of the *trans* and *cis* ground states. In the figure, we have suppressed t_2 and exaggerated t_3 to highlight the effects of the third-nearest-neighbor interaction. The band gap for *cis* is larger than for *trans*, as experiment indicates.[5,6] The figure shows that a slight majority of the *cis-transoid* states, lying in the middle of the valence band, increase in energy, even though the states at the band edges, which determine the band gap, decrease in energy.

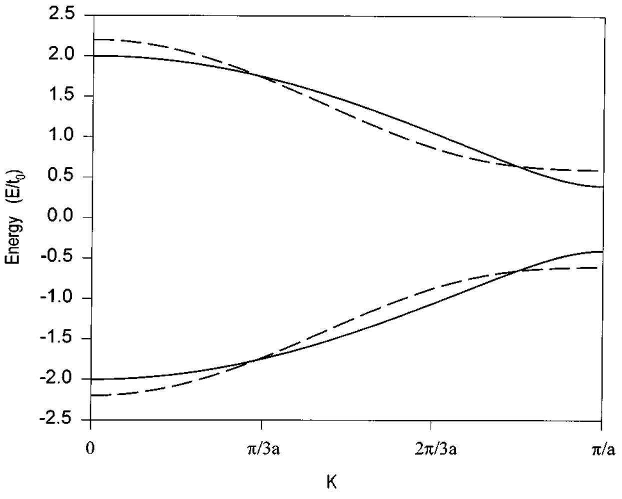

FIG. 3. Band structure of the ground states of *trans*- (solid) and *cis*- (dashed) polyacetylene, as a function of the Bloch wave number k. The second-nearest-neighbor coupling t_2 has been suppressed and the third-nearest-neighbor coupling t_3 exaggerated (to a value of 0.5 eV) to achieve greater clarity. The energy is given in units of t_0 ($=2.5$ eV).

Table I shows the energy per *cis* bond relative to *trans* for locally *cis-transoid* (*cis*0 and *alt*0 in Fig. 1) and *trans-cisoid* (*cis*1 and *alt*1) bonds on finite *cis* and *alt* chains. *Alt*2 and *alt*3 have the same energies as *alt*0 and *alt*1, respectively. For $N \geqslant 40$, the results depend very weakly on chain length, and the differences between *cis* and *alt* structures are also very small.

The trend in the total energies agrees with experimental results. Samples of polyacetylene are mostly *trans*, with some *cis*, and no *trans-cisoid*.[1,7,8] Furthermore, upon heating, a sample converts to all *trans*.[1,7,8] This indicates that the *trans* structure has the lowest energy, with a somewhat higher energy for the *cis-transoid* and a much higher energy for the *trans-cisoid* structure, as obtained in our calculations.

Our results also agree with an *ab initio* calculation.[17] The calculation in question found the energy difference between the $N=8$ *cis*1 and *alt*3 structures, which can be obtained from one another by rotating around the central single bond by 180°, converting the bond from *trans-cisoid* to *trans* in character. We obtained an energy difference of 93 meV, while the *ab initio* calculation obtained 100 meV.

B. Solitons

The energy of a neutral soliton pair for both *trans* [Fig. 4(a)] and *cis* [Fig. 5(a)] chains increases smoothly as the

TABLE I. Energy in meV per *cis* bond of various structures of polyacetylene (defined in Fig. 1) relative to *trans* as a function of chain length *N*. Per refers to periodic boundary conditions and Cont to the continuum values.

N	40	80	120	160	200	Per	Cont
*cis*0	14.9	17.5	18.5	19.1	19.3	20.0	19.4
*alt*0	15.4	18.1	19.2	19.8	20.0	20.8	
*cis*1	99.6	103.4	104.7	105.3	105.6	106.6	106.3
*alt*1	91.9	98.5	100.7	101.8	102.4	104.5	

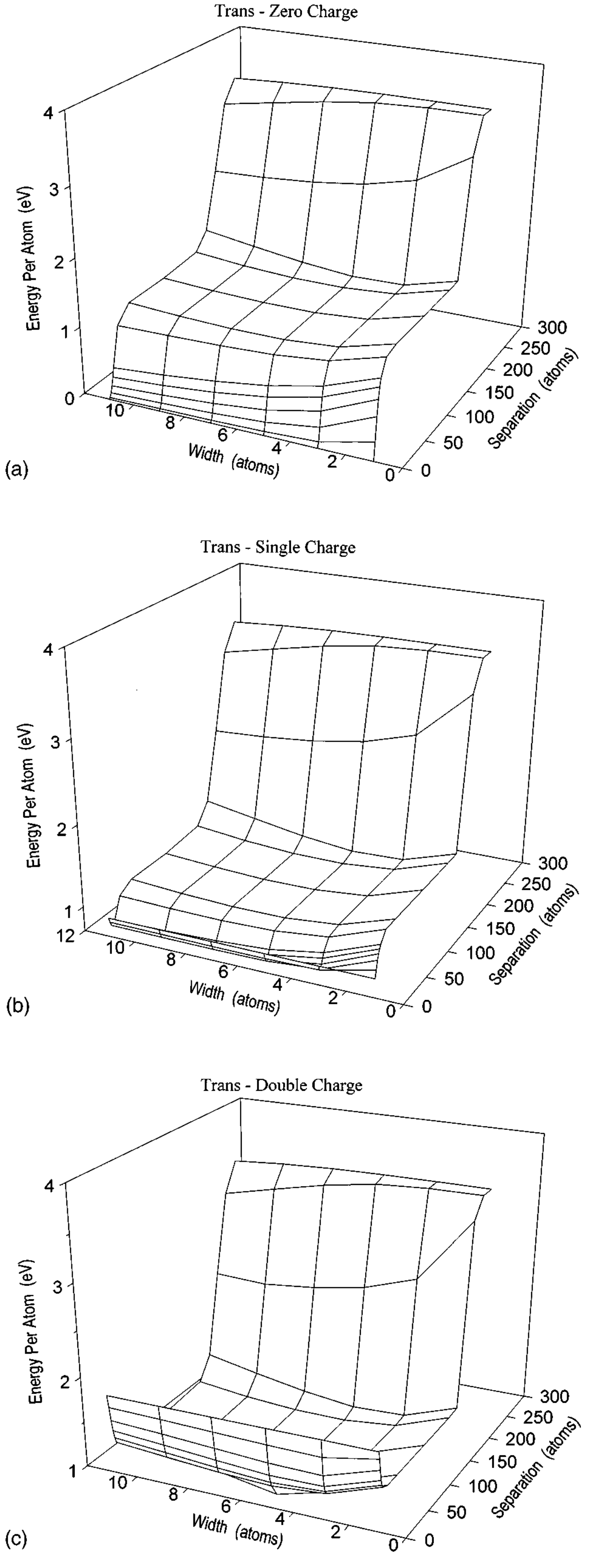

FIG. 4. Energy of a soliton-pair-bearing *trans*-polyacetylene chain of length $N=200$ as a function of the half-width w of the individual solitons and the pair separation y for the zero charge (ground), singly charged, and doubly charged (including electron-hole pairs) electronic configurations. Zero separation corresponds to the absence of solitons.

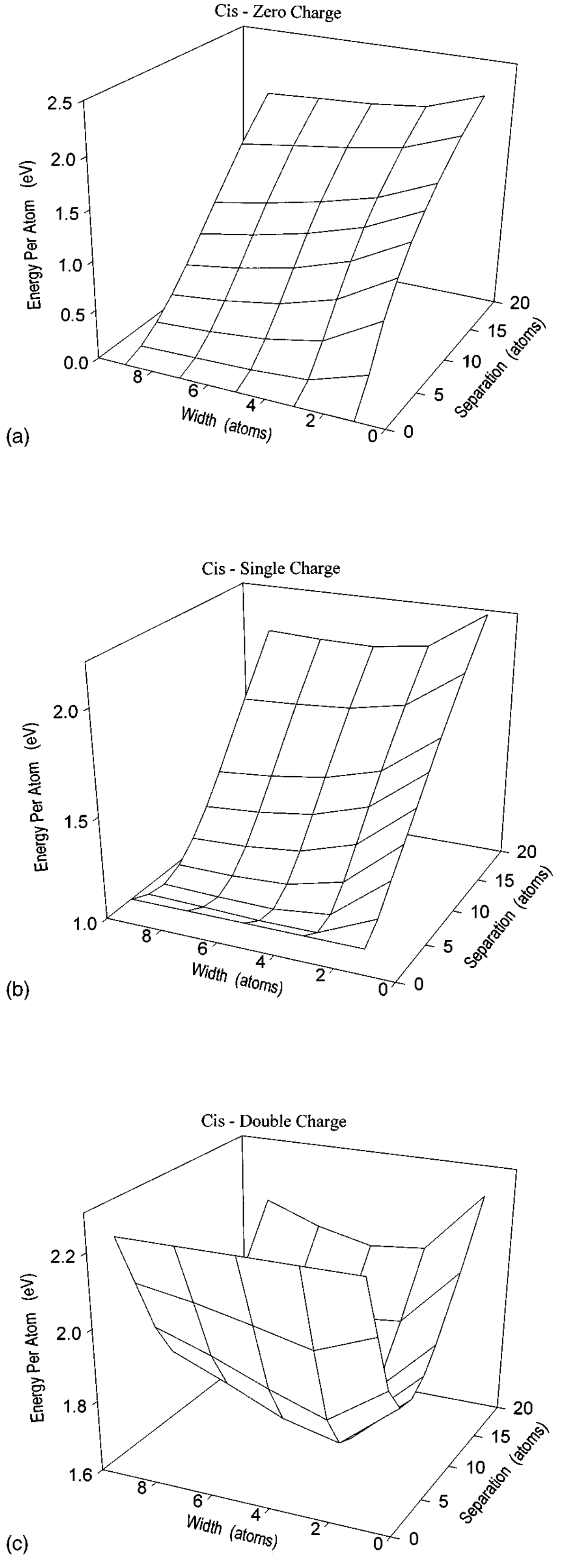

FIG. 5. Energy of a soliton-pair-bearing *cis*-polyacetylene chain of length $N=200$ as a function of the half-width w of the individual solitons and the pair separation y for the zero charge (ground), singly charged, and doubly charged (including electron-hole pairs) electronic configurations. Zero separation corresponds to the absence of solitons.

soliton pair separation $y = x_+ - x_-$ increases over the entire range from the ground state to full separation. Doubly charged excitations (including electron-hole pairs) in *trans* chains form fully separable soliton pairs, while their *cis* counterparts, because of the nondegeneracy of the *cis* ground state, form bound soliton pairs called bipolarons for like charges and excitons for electron-hole pairs. In both isomers, singly charged excitations form very closely associated pairs called polarons, which behave as single particles.

While the ground state of an even-numbered chain of either isomer is uniformly dimerized, the ground state of an odd-numbered *trans* chain contains a single soliton, which can be neutral or singly charged. This result is similar to those obtained for semi-infinite *trans* chains,[2,13] and has substantial experimental support.[1,2,8,13–16] Our calculations for odd-numbered *cis* chains have single-soliton ground states where the soliton is trapped near one end, as would be expected from the nondegeneracy of the infinite-chain ground state.

C. Polarons

The energies of singly charged excitations on both *trans* [Fig. 4(b)] and *cis* [Fig. 5(b)] even-numbered chains have very well-defined minima at small separations. The *cis* energy has a minimum at $w=5$ and $y=4$, with an energy 0.04 eV below that for $y=0$ (uniform dimerization), while *trans* has a minimum at $w=9$ and $y=6$, 0.13 eV below the value at $y=0$. In both cases, the separation is smaller than the half-width w, and u does not change sign. It therefore makes sense to treat the single-charge excitation in either isomer as a single particle called a polaron.[1,2,18–22]

In both isomers, the polaron as a whole is free to move in the interior of a chain, but is repelled from the ends, gaining considerably in energy when closer than 20 atoms from a chain end. Our calculated wave functions suggest an effective full width of 40 atoms for a *trans* polaron and slightly less for a *cis* polaron.

D. Bipolarons and excitons

cis-polyacetylene's lack of internal degeneracy should have a strong effect on the form of the fundamental excitations.[1–4] The region between two separated solitons would contain energetically unfavorable *trans-cisoid* bonds, which implies that soliton pairs are bound. These bound pairs are called bipolarons when the two solitons have the same charge and excitons when they have opposite charges.

Our calculations confirm this expectation. The *cis* double-charge energy surface in Fig. 5(c) has a well-defined global minimum at $w=3$ and $y=8$, at an energy about 0.5 eV below that for $y=0$ (uniform dimerization), in contrast to the case for *trans* [Fig. 4(c)], where the energy is almost constant over the region $40<y<160$ and $5<w<9$, with a value about 0.7 eV below that for $y=0$. Given the total chain size of 200 in the figures, this means that individual *trans* solitons on a doubly charged chain can move independently anywhere except within 20 atoms of the chain ends or 40 atoms of each other, and can thus be treated as independent singly charged particles with a full width of 40 atoms. The doubly charged *cis* soliton pair, on the other hand, is definitely bound, though not as closely as a polaron, forming a bipolaron or exciton.

The *cis* bipolaron as a whole is free to move inside a chain but repelled from the ends, much like individual solitons in *trans*-polyacetylene and polarons in both isomers. As with neutral soliton pairs, the doubly charged excitations have a smooth transition from a bipolaron (*cis*) or soliton pair (*trans*) to a pure dimerized state. In this case, however, it is the solitonic states which have the lower energy. The effective size of a *cis* bipolaron is about the same as that of a single *trans* soliton or a polaron—around 40 atoms.

IV. CONCLUSIONS

We have extended the SSH model to perform calculations on *cis* chains of the same quality as those which the original model allows for infinite *trans* chains. The modification involved is the inclusion of second- and third-nearest-neighbor coupling terms which enable us to obtain different results for *cis* than for *trans*.

On choosing a value of the third-neighbor term which gives the correct widening of the band gap of *cis*-polyacetylene,[5,6] we also obtain the ordering of the total energies of the different structures of polyacetylene (*trans* <*cis-transoid*<*trans-cisoid*) suggested by experiment[1,7,8] and an *ab initio* calculation.[17] Excitations behave in a way which reflects the lack of internal degeneracy in *cis*-polyacetylene; in particular, doubly charged soliton pairs form bound bipolarons and excitons.

Thus a simple and modest extension of the SSH model allows us to perform quantitative calculations for the ground state and fundamental excitations of chains for both isomers of polyacetylene. The extended model is, in principle, also applicable, without further alterations, to linear and planar conjugate polymers whose electronic structure is dominated by perpendicular π electrons.

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[1] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, Rev. Mod. Phys. **60**, 781 (1988), and references cited therein.

[2] W.-P. Su, in *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2, pp. 757–794.

[3] W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[4] W.-P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979).

[5] S. A. Brazovskii and N. Kirova, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 6 (1981) [JETP Lett. **33**, 4 (1981)].

[6] L. Lauchlan, S. Etemad, T.-C. Chung, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. B **24**, 3701 (1981).

[7] H. Shirikawa and S. Ikeda, Synth. Met. **1**, 175 (1979).

[8] P. Bernier, M. Rolland, C. Linaya, and M. Disi, Polymer **21**, 7 (1980).

[9] C. R. Fincher, C. E. Chen, A. J. Heeger, A. G. MacDiarmid, and J. B. Hastings, Phys. Rev. Lett. **48**, 100 (1982).

[10] C. S. Yannoni and T. C. Clarke, Phys. Rev. Lett. **51**, 1191 (1983).

[11] H. Suzuki, M. Ozaki, S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. **45**, 1209 (1980); **45**, 1483(E) (1980).

[12] A.-B. Chen, Y.-M. Lai-Hsu, and W. Chen, Phys. Rev. B **39**, 923 (1989).

[13] W.-P. Su, Solid State Commun. **35**, 899 (1980).

[14] P. Bernier, in *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2, pp. 1099–1125.

[15] M. Mehring, H. Seidel, W. Müller, and G. Wegner, Solid State Commun. **45**, 1075 (1983).

[16] M. Nechtschein, F. Devreux, R. L. Greene, T. C. Clark, and G. B. Street, Phys. Rev. Lett. **44**, 356 (1980).

[17] B. K. Rao, J. A. Dorsey, and N. R. Kestner, Phys. Rev. B **31**, 1187 (1985).

[18] J. Kroschwitz, *Electrical and Electronic Properties of Polymers* (Wiley, New York, 1988), pp. 84–101.

[19] J. L. Brédas, R. R. Chance, and R. Silbey, Phys. Rev. B **26**, 5843 (1982).

[20] J. L. Brédas, R. R. Chance, and R. Silbey, Mol. Cryst. Liq. Cryst. **77**, 319 (1982).

[21] J. L. Brédas, J. C. Scott, K. Yakushi, and G. B. Street, Phys. Rev. B **30**, 1023 (1984).

[22] R. R. Chance, J. L. Brédas, and R. Silbey, Phys. Rev. B **29**, 4491 (1984).