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Polaron-bipolaron—soliton doping in polyacetylene

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We have performed a self-consistent numerical study, which allows each CH group in a finite polyacetylene chain to relax to its equilibrium position, in order to investigate the formation of the polaron, soliton, and soliton lattice in the framework of Su-Schrieffer-Heeger model. The bond-alternation order parameter, the delocalization of the gap states, the polaron-formation energy, the soliton-formation energy, the Peierls gap, and the gap separating the valence (or conduction) band and the *impurity band* are calculated as functions of dopant level. The effect of electron-electron interaction is then examined in the Hartree approximation. Our results are compared with those derived by other authors. Although our approach simulates a doping process, further calculation based on the decaying of an electron-hole pair into a soliton-antisoliton pair gives exactly the same results as those shown in this paper. In particular, our finding clearly demonstrates the single-charge injection via polarons which subsequently combine to form soliton-antisoliton pairs, in agreement with the recent experimental discovery.

I. INTRODUCTION

Polyacetylene, $(CH)_x$, has attracted much interest from both experimentalists and theorists because of its unusual properties upon doping with a variety of donors and acceptors.[1] A number of experiments and the recent energy band calculation indicate clearly that the material is quasi one dimensional. A single neutral chain of *trans*-$(CH)_x$ exhibits the well-known Peierls distortion. As a consequence of two degenerate ground states, Rice[2] and Su, Schrieffer, and Heeger[3] (SSH) have argued that the properties of *trans*-$(CH)_x$ are dominated by neutral and charged solitons. While the SSH model is in the framework of the single-particle model, the topological feature of the soliton state prevails in more sophisticated self-consistent calculations, including the electron correlation[4–6] and the irregularity of the geometric structure of the chain.[7] In reality each $(CH)_x$ chain is of finite length with proper boundary conditions. However, the boundary conditions are ignored when one assumes a model of infinite chain. The boundary conditions turn out to be crucial[6] to the interpretation of experimental data, for example, the optical absorption.[8,9]

The continuum version of the SSH model was anlayzed by Takayama *et al.*[10] to yield the exact solution of a soliton state. Subsequently, two interacting solitons and soliton lattice were also studied.[11–13] Further theoretical studies, also in the scope of the continuum limit, revealed the polaron state, which does not have the topological stability of soliton.[14–16] For a finite cyclic chain containing at least 110 CH groups, Brédas *et al.*[17] have used the adiabatic Hückel Hamiltonian to investigate the formation of polaron. In contrast to the soliton state, the polaron is a common feature of excited states in many other conducting polymers. Nevertheless, recent results of optoelectrochemical spectroscopy[18] and electrochemical voltage spectroscopy[19] on polyacetylene suggest a fascinating phenomenon of single-charge injection via polarons which subsequently combine to form lower-lying soliton pairs.

Since the lattice deformation corresponding to a polaron is characteristically different from that corresponding to a soliton, an analytical solution of bipolaron decaying into a soliton-antisoliton pair is a very difficult task. An alternative is the self-consistent numerical solution of a finite chain of polyacetylene. Such an approach has been successfully carried out to study both the static properties[20–22] and the dynamical processes.[23–25] In this paper, we present the results of a self-consistent numerical calculation which allows a *complete relaxation of all the electrons and each individual atom* in a finite chain of polyacetylene. The chain is sufficiently long to ensure that the results obtained in this manner are almost approaching the thermodynamic limit. The computation which is similar to the method proposed by Shastry[26] simulates the doping process and illustrates the formation of polaron, the decaying of bipolaron into soliton-antisoliton pair, the structure of soliton lattice, the formation energies of polaron and soliton as functions of the dopant concentration, and the variations of the bond-alternation order parameter and optical gaps with increasing doping level. The effect of electron interaction will then be studied in the Hartree approximation. All our results will be compared to the findings of other authors.

II. SELF-CONSISTENT CALCULATION SCHEME

We add the electron interaction to the SSH model[3]

$$H_0 = -\sum_{i,\sigma}[t_0+\alpha(u_i-u_{i+1})](c^\dagger_{i+1,\sigma}c_{i,\sigma}+c^\dagger_{i,\sigma}c_{i+1,\sigma}) + \frac{K}{2}\sum_i (u_i-u_{i+1}-C)^2 \tag{1}$$

and consider the Hamiltonian

$$H = H_0 + \frac{U}{2}\sum_{i,\sigma} n_{i,\sigma}n_{i,-\sigma} + \tfrac{1}{2}\sum_{i,j\sigma,\sigma'}{}' U_{ij}n_{i,\sigma}n_{j,\sigma'} \tag{2}$$

for a finite chain of N CH groups and N_e electrons in the π band. The values of the parameters are estimated[3] as $K=21$ eV/Å^2, $t_0=2.5$ eV, and $\alpha=4.1$ eV/Å, and C is determined from the condition that when $U=U_{ij}=0$ and $u_i=0$ for all i and j, H gives the ground-state energy of an undistorted neutral chain ($N_e=N$). In order to minimize the total energy in our self-consistent calculation, it is convenient to define $v_i=\alpha(u_i-u_{i+1})$ and $\gamma=\alpha^2/K$, and write (1) as

$$H_0=-\sum_{i,\sigma}(t_0+v_i)(c_{i+1,\sigma}^\dagger c_{i,\sigma}+c_{i,\sigma}^\dagger c_{i+1,\sigma})+\frac{1}{2\gamma}\sum_i(v_i-\alpha C)^2 \; . \tag{3}$$

Let $R_m=mR_0+u_m$ be the position of the mth CH group. Then the electron-interaction energies are assumed to have the form

$$\begin{aligned}U_{i,i+m}&=U\exp(-|R_i-R_{i+m}|)\\&=U\exp\left[-\left|\sum_{j=1}^{m}v_{i+j-1}/\alpha-mR_0\right|\right] \; .\end{aligned} \tag{4}$$

To solve the Hamiltonian H numerically, one must calculate the total energy $\mathscr{E}(\{v_i\})$ for given values of deformations $\{v_i\}$ and minimize $\mathscr{E}$ with respect to the whole set $\{v_i\}$. It then results in a set of N coupled equations which are difficult to solve as N gets large. Therefore, in almost all the existing works the values of $\{v_i\}$ are either fixed or approximated by a trial function which contains only a few free variational parameters. Since the self-consistent values of $\{v_i\}$ for a polaron excitation are entirely different from those for a soliton-antisoliton excitation, we must allow the whole set $\{v_i\}$ to vary freely in order to see the decay of a bipolaron into a soliton-antisoliton pair.

For given values of C and the set $\{v_i\}$, we solve the Schrödinger equation

$$H\left[\sum_j c_{j,\sigma}^\dagger B_{j,k}\right]=\epsilon_i\left[\sum_j c_{j,\sigma}^\dagger B_{j,i}\right] \; , \quad i=1,2,\ldots,N \tag{5}$$

for the eigensolutions ϵ_i and $B_{j,i}$. The electron-interaction terms are treated with the Hartree approximation. Within this approximation, for a given number of electrons N_e the total energy of the system is

$$\begin{aligned}\mathscr{E}(\{v_i\})=&-\sum_{i,\sigma}(t_0+v_i)\sum_{j\in F(\sigma)}(B_{i+1,j}^*B_{i,j}+B_{i,j}^*B_{i+1,j})+\frac{1}{2\gamma}\sum_i(v_i-\alpha C)^2\\&+\frac{U}{2}\sum_{i,\sigma}\sum_{k\in F(\sigma)}\sum_{l\in F(-\sigma)}|B_{k,i}|^2|B_{l,i}|^2+\tfrac{1}{2}\sum_{i,j,\sigma,\sigma'}\sum_{k\in F(\sigma)}\sum_{l\in F(\sigma')}U_{ij}|B_{k,i}|^2|B_{l,j}|^2 \; ,\end{aligned} \tag{6}$$

where $F(\sigma)$ is the set of all occupied σ-spin eigenstates of H. Minimizing the total energy $\mathscr{E}(\{v_i\})$ with respect to v_i, we obtain

$$v_i=\gamma\left[C'+\sum_\sigma\sum_{j\in F(\sigma)}(B_{i+1,j}^*B_{ij}+B_{ij}^*B_{i+1,j})+Z\right] \; , \tag{7}$$

where $C'=CK/\alpha$, and

$$\begin{aligned}Z=&\sum_{k,\sigma}(t_0+v_k)\sum_{j\in F(\sigma)}\frac{\partial}{\partial v_i}(B_{k+1,j}^*B_{k,j}+B_{k,j}^*B_{k+1,j})-\frac{U}{2}\sum_{p,\sigma}\sum_{k\in F(\sigma)}\sum_{l\in F(-\sigma)}\frac{\partial}{\partial v_i}(|B_{k,p}|^2|B_{l,p}|^2)\\&-\tfrac{1}{2}\sum_{p,j,\sigma,\sigma'}\sum_{k\in F(\sigma)}\sum_{l\in F(\sigma')}\frac{\partial}{\partial v_i}(U_{pj}|B_{k,p}|^2|B_{l,j}|^2) \; .\end{aligned} \tag{8}$$

Equations (4)—(8) can be solved by iteration. The explicit form of Z is very complicated. It is convenient to neglect the term Z during the iteration process. The final self-consistent solution is the same whether we neglect the term Z or not, because when the self-consistency is reached we have $Z=0$ for the system under equilibrium. Of course, when the Z term is dropped we need more iterations to achieve the same self-consistent solution.

To fix the parameters in (4), we set $R_0=1.22$ Å (from Ref. 3) and choose several values $U/W=0.06n$, where n is an integer and $W=4t_0=10$ eV is the width of the π band. We increase the range of electron interaction gradually and find that the terms $U_{i,i+m}$ for $m\geq 3$ have very little contribution and can be dropped. We also use a straight chain (with free boundary conditions) of 100 CH groups so that the chain is sufficiently long to yield reliable result. Owing to the characteristic discrete spectrum of a finite system, we found $C'=1.250\,32$ instead of $C'=4/\pi=1.273\,24$, which can be derived analytically for an infinite chain.

III. POLARON, SOLITON, AND SOLITON LATTICE

We first consider the simpler case of the SSH Hamiltonian H_0. Since in this case we set $U=U_{ij}=0$, the Hartree approximation on the electron interaction will not come in and so the results in this section are exact. For given number of electrons N_e, the self-consistent solution is obtained and the order parameter $\psi_n=-(-1)^n u_n$ is derived. Figure 1 shows 20 curves of order parameter in units of 0.05 Å for 20 values of $\mathscr{N}=N_e-N$ marked above the corresponding curves. Since $N=100$, the ratio $\mathscr{N}/N$ also represents the dopant level. The horizontal axis labels the position along the chain from $n=1$ to 100. The

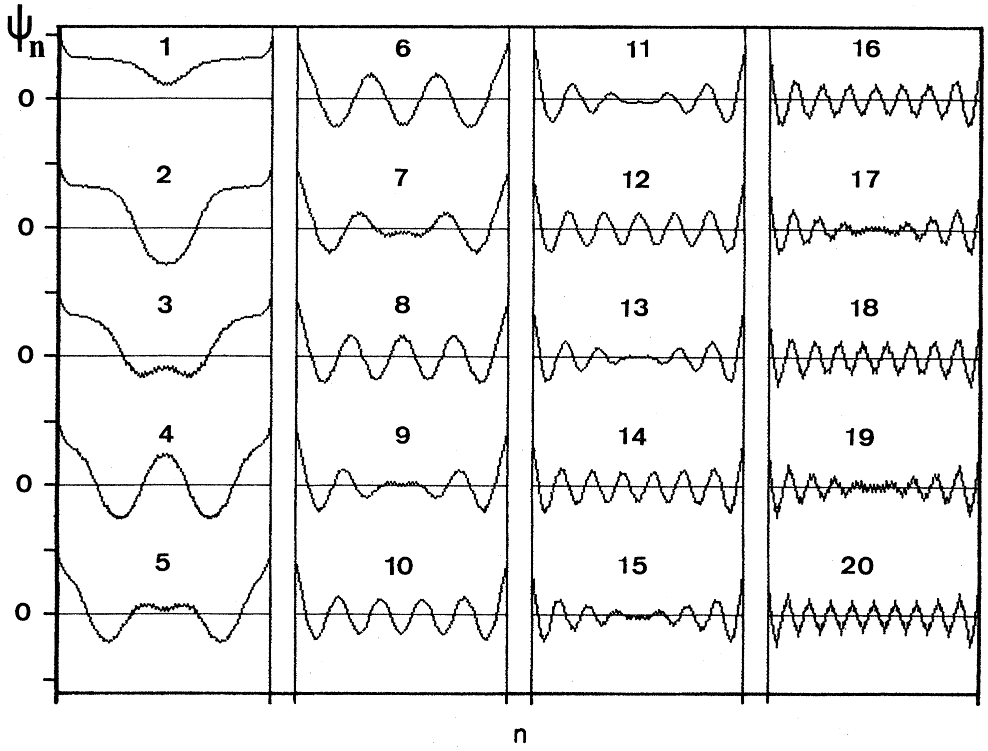

FIG. 1. Each curve represents the order parameter ψ_n as a function of the position of the CH group along the chain from $n=1$ to 100. The number above each curve is the number of electrons $\mathcal{N}$ injected into the neutral polyacetylene chain. On the vertical axis the scale is 0.05 Å for one unit (the distance between any 0 reference point to its adjacent horizontal bar). The result is for the SSH model.

four curves in each row have a common zero reference point for the vertical scale marked on the left-hand side. In units of 0.05 Å, the distance between each zero reference point and its adjacent horizontal bar on the vertical axis is 1. Therefore, the value of ψ_n for the horizontal parts of the curve $\mathcal{N}=1$ is 0.8 units, corresponding to segments of perfect Peierls distortion.

When one electron is injected into a neutral polyacetylene chain, the curve $\mathcal{N}=1$ indicates that the added electron occupies a polaron state. The polaron-formation energy is calculated to be $E_p=0.574\,58$ eV. The same energy derived from the continuum model is 0.587 15 eV. If we add a second electron to the polaron state, the bipolaron is unstable and decays into a soliton-antisoliton pair with the order parameter shown as the curve $\mathcal{N}=2$. Our calculation gives the soliton- (or antisoliton-) formation energy $E_s=0.408\,08$ eV, while from the continuum model one obtains 0.404 34 eV. The order parameters derived from the continuum model

$$\psi_n=u_0(1-[\tanh\{(x+x_0)/\sqrt{2}\xi\}-\tanh\{(x-x_0)/\sqrt{2}\xi\}]/\sqrt{2})$$

with $\xi=8$ and $u_0=0.04$ Å, and $\psi_n=-u_0\tanh[(x-x_0)/\xi]$ with $\xi=7$ and $u_0=0.04$ Å fit remarkably well to our numerical solution of ψ_n for the polaron and the soliton, respectively.

When more electrons are injected into the polyacetylene chain, a systematic evolution of the order parameter toward that of a soliton lattice is seen in Fig. 1 from $\mathcal{N}=1$ to 20. If $\mathcal{N}$ is even, there are only soliton-antisoliton pairs forming a soliton lattice. On the other hand, if $\mathcal{N}$ is odd, in addition to the soliton-antisoliton pairs, a polaron appears at the middle of the chain. Let us denote u_0 as the amplitude of the order-parameter curves when $\mathcal{N}$ is even ($u_0=0.04$ Å for $\mathcal{N}=0$ corresponding to a neutral chain). In Fig. 2, u_0 as a function of N_e (or $\mathcal{N}$) is plotted as the curve A. Mele and Rice[20] have used a trial func-

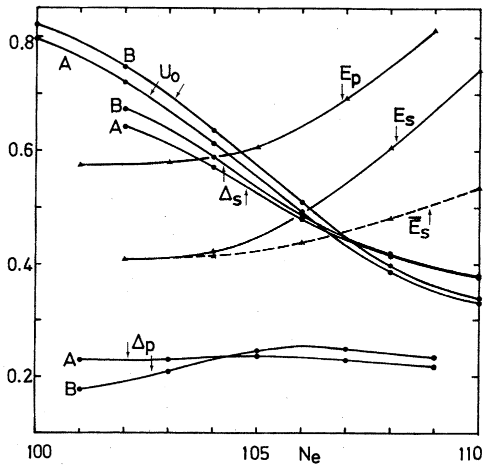

FIG. 2. The unit for the vertical scale is eV for the curves E_p, E_s, $\bar{E}_s$, Δ_s, and Δ_p, and 0.05 Å for the curve u_0. Curves marked A are from the SSH model, and curves marked B are from the full Hamiltonian (2).

tion for the order parameter in their calculation and obtained a relation between u_0 and $\mathcal{N}$. They found a rapid decrease of u_0 around $\mathcal{N} \simeq 7$ and a minimum just below $\mathcal{N}=10$. Such features disappear in our self-consistent calculation which allows each CH group to relax freely to its equilibrium position.

Let $\mathscr{E}(\mathcal{N})$ be the total energy of the ground state calculated from (6) when $\mathcal{N}$ electrons are injected into the neutral polyacetylene chain. If $\mathcal{N}$ is odd, $E_p(\mathcal{N})=\mathscr{E}(\mathcal{N})-\mathscr{E}(\mathcal{N}-1)$ is the formation energy of a polaron at the dopant level $\mathcal{N}/N$, while if $\mathcal{N}$ is even, $2E_s(\mathcal{N})=\mathscr{E}(\mathcal{N})-\mathscr{E}(\mathcal{N}-2)$ is the formation energy of a soliton-antisoliton pair at dopant level $\mathcal{N}/N$. In units of eV, the behaviors of $E_p(\mathcal{N})$ and $E_s(\mathcal{N})$ are illustrated in Fig. 2. The mean formation energy per soliton $\bar{E}_s(\mathcal{N})=[\mathscr{E}(\mathcal{N})-\mathscr{E}(0)]/\mathcal{N}$ for even $\mathcal{N}$ is also plotted in Fig. 2, which agrees very well with those obtained analytically by Horovitz[12] with the continuum model, and numerically by Albert and Jouanin[21] with an infinite chain.

After deriving all the eigenstates from (5), we can calculate the inverse participation ratio (IPR) defined as

$$\mathscr{R}_i = \left[\sum_j |B_{j,i}|^4\right] \Big/ \left[\sum_j |B_{j,i}|^2\right]^2 \tag{9}$$

of the ith eigenstate. For an infinite system with an orthonormal basis, the value of IPR varies from 0 for extremely extended states to 1 for extremely localized states. Even for a finite system, IPR has been used by many authors to estimate the degree of localization of eigenstates. Figure 3 shows the eigenenergies $\{E_i\}$ and the corresponding IPR $\{\mathscr{R}_i\}$ within an energy region $-2.2 < E_i < 2.2$ eV around the Peierls gap. There are 18 panels for 18 different values of $\mathcal{N}$ from $\mathcal{N}=3$ to 20. In each panel the position of each vertical bar marks the value of one eigenenergy and the height of the bar measures the corresponding IPR. The two eigenenergies at the ends of each spectrum are almost -2.2 and 2.2 eV. For low dopant levels (small values of $\mathcal{N}$) both the polaron and the soliton states are well localized. As $\mathcal{N}$ increases and the soliton lattice forms, the delocalization of the gap states is clearly demonstrated by Fig. 3.

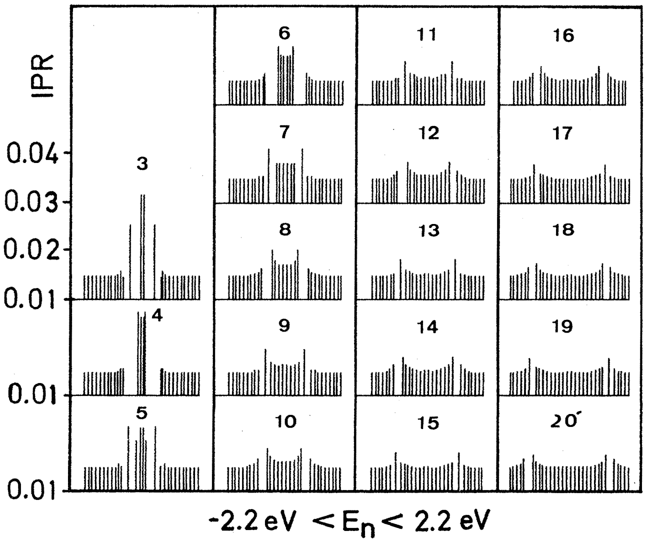

FIG. 3. The inverse participation ratio (measured by the height of each vertical bar) of the eigenstates with eigenenergies $\{E_i\}$ in a region around the Peierls gap. The number above each plot is the number of injected electrons $\mathcal{N}$.

To avoid ambiguity let us call the aggregate of states in the Peierls gap the *impurity states* or *impurity band.* The impurity states are split off from the valence and the conduction bands. Therefore, when more states are pulled from the valence and the conduction bands into the gap, the Peierls gap gets wider, as illustrated in Fig. 3. In the next section we will return to this for a quantitative analysis. For even $\mathcal{N}$, in each spectrum of Fig. 3 there is a well-defined gap between the top (or bottom) of the valence (or conduction) band and the bottom (or top) of the impurity band. This gap is denoted by Δ_s. On the other hand, for odd $\mathcal{N}$, we also learn from Fig. 3 that in each of the two Δ_s gaps there is a polaron state. Let Δ_p be the energy which separates the lower (or upper) polaron state and the top (or bottom) of the valence (or conduction) band. The variations of Δ_s and Δ_p with $\mathcal{N}$ are shown in Fig. 2 by the two curves marked as A. Qualitatively, similar Δ_s-vs-$\mathcal{N}$ relations are obtained by Mele and Rice,[20] Nakahara and Maki,[13] and Albert and Jouanin.[21] The result of Mele and Rice also agrees with ours fairly well quantitatively, but the other two results do not. We should point out that in contrast to Δ_s, Δ_p is rather insensitive to the dopant levels.

IV. ELECTRON-ELECTRON INTERACTION

Several attempts have been made to examine the electron correlation effect on the electronic states in polyacetylene. In these works either the ground state[27,28] (without polaron or soliton) or only the on-site[29,30] (Hubbard-type) correlation effect on soliton was considered. Hence the conclusions derived in this manner are still far from the final answer. Since the electron-electron interaction was treated in Sec. II with the Hartree approximation, the results discussed in this section should be judged as a simplified estimation. After we have obtained the self-consistent solution of the full Hamiltonian H of (2), it is discovered that the dominating terms are U_{ij} with $|i-j| \leq 2$. Therefore, the results shown in this section are obtained from a calculation retaining only U_{ij} with $|i-j|=0,1$ and 2. We remind the reader that the U in (4) is treated as a varying parameter in units of the π band width $W=10$ eV.

The order parameter ψ_n is shown in Fig. 4 in four parts marked with the corresponding numbers of electrons $N_e=101$, 103, 105, and 107. Each part consists of three columns for $U/W=0.06$ (left column), 0.24 (middle column), and 0.42 (right column), and three rows for nonzero U_{ij} with $|i-j|=0$ (bottom row), ≤ 1 (middle row), and ≤ 2 (top row). The labels for both the horizontal and the vertical axes are the same as in Fig. 1. We see that the characteristic feature of ψ_n is preserved even when the electron-electron interaction is taken into account within the Hartree approximation. This is because in our self-consistent calculation each CH group adjusts to a new equilibrium position under the influence of the electron-electron, electron-ion, and ion-ion interaction.

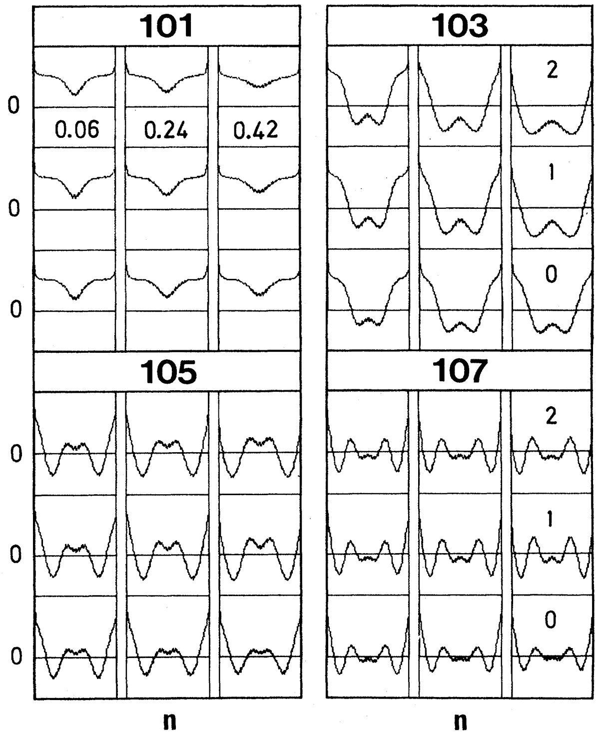

FIG. 4. Same plots as in Fig. 1 but for the full Hamiltonian (2). See the text for details.

To clarify the point, in Fig. 5 we compare the order parameter for the case $U=0$ (left part of each panel) and the order parameter for the case of nonzero U_{ij} with $|i-j|\leq 2$ and $U/W=0.42$ (right part of each panel). The number of electrons for each panel is written at the top. Because of the symmetry property, in each panel only half of the order parameter curve is plotted. The arrows at the right part of each panel mark the positions where $\psi_n=0$ if $U=0$. From the change of the order parameter we examine the relaxation of each CH group and found that the whole chain stretches out to a new equilibrium configuration under the driving force of electron-electron interaction.

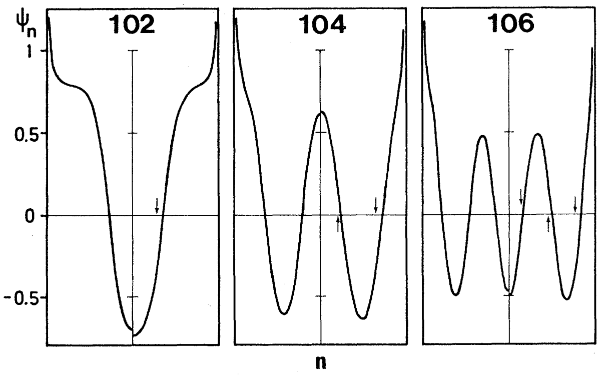

FIG. 5. The left part of each panel is the order parameter derived from the SSH model, and the right part of each panel is the order parameter derived from the full Hamiltonian (2) with $U/W=0.42$ and including as far as the next-nearest-neighbor interaction. The horizontal axis labels the position of the CH group along the chain ($1\leq n\leq 100$), and the vertical axis is in units 0.05 Å. The number at the top of each panel is the number of electrons $\mathcal{N}$ injected into the neutral chain.

Assuming nonzero U_{ij} with $|i-j|\leq 2$ and $U/W=0.42$, the computed amplitudes u_0 of the order-parameter curves for even $\mathcal{N}$, as well as the Δ_s and Δ_p are shown in Fig. 2 as curves B.

We have mentioned in the preceding section that the Peierls gap gets wider with increasing dopant level. Table I gives the Peierls gap in units of eV for various cases specified by the number of electrons N_e, the value of U/W, and the range of U_{ij} ($|i-j|$ less than or equal to the number of interacting neighbors). The general feature of the Peierls gap is that for both even and odd $\mathcal{N}$, it monotonically increases with increasing N_e, but decreases with increasing U/W. Only for $N_e=101$ is the Peierls gap a monotonically decreasing function of the number of interacting neighbors. For all other values of N_e the

TABLE I. Peierls gap in units of eV for various numbers of electrons N_e, electron-electron interaction strength U/W, and the range of electron interaction including only the on-site (0), the nearest-neighbor (1), or the next-nearest-neighbor (2) interaction.

N_e	U/W	NUMBER OF INTERACTING NEIGHBORS		
		0	1	2
101	0.06	1.346239	1.344552	1.341812
	0.18	1.334433	1.328469	1.319419
	0.30	1.325094	1.307628	1.291919
	0.42	1.316027	1.283755	1.260494
103	0.06	1.354781	1.358031	1.351273
	0.18	1.326394	1.342358	1.325177
	0.30	1.310170	1.329512	1.309125
	0.42	1.296032	1.322481	1.301964
105	0.06	1.454022	1.460259	1.453453
	0.18	1.422700	1.441918	1.415292
	0.30	1.401587	1.428213	1.381438
	0.42	1.385141	1.422270	1.358898
107	0.06	1.659231	1.665650	1.657999
	0.18	1.631455	1.649596	1.620081
	0.30	1.614156	1.638894	1.587518
	0.42	1.601392	1.635340	1.564186
109	0.06	1.912630	1.918050	1.910040
	0.18	1.888278	1.903413	1.873991
	0.30	1.873597	1.895611	1.844523
	0.42	1.862919	1.894826	1.823928
102	0.06	1.335082	1.335418	1.333436
	0.18	1.325401	1.324063	1.317524
	0.30	1.312694	1.312772	1.301141
	0.42	1.302261	1.301798	1.285054
104	0.06	1.379416	1.382649	1.380026
	0.18	1.360225	1.371502	1.361132
	0.30	1.345421	1.361038	1.342539
	0.42	1.332179	1.351004	1.324958
106	0.06	1.520249	1.526095	1.522479
	0.18	1.496153	1.517304	1.502840
	0.30	1.478726	1.508917	1.483025
	0.42	1.463633	1.501021	1.463974
108	0.06	1.733176	1.739369	1.734674
	0.18	1.707155	1.731832	1.714903
	0.30	1.689253	1.724956	1.694854
	0.42	1.674306	1.719265	1.676111
110	0.06	1.981052	1.987793	1.982839
	0.18	1.955670	1.980724	1.963216
	0.30	1.938080	1.974813	1.943105
	0.42	1.923839	1.970636	1.925480

Peierls gap has a maximum when the range of interaction is the nearest neighbor. The reason for this peculiarity lies in the fact that soliton states have finite amplitude only at every second CH group. If $N_e = 101$, there is no soliton state in the polyacetylene chain.

The variation of the Peierls gap with the dopant level has been calculated by Nakahara and Maki[13] using the continuum model without electron-electron interaction. Their result agrees with ours at low dopant levels. At high dopant levels their value is about 20% larger than ours.

V. FINAL REMARKS

The random field due to the charged impurities and the interchain coupling are not included in our calculation. Their significant influence on the electronic properties of polyacetylene have been demonstrated by many authors.[20,31–33]

Although our calculation was performed with electrons added to the system, simulating a doping process, we have done a similar calculation to study the generation of soliton-antisoliton from electron-hole pairs. The result is exactly the same as what we have shown in this paper. The dopant-level-dependent formation energies of soliton and polaron, Peierls gap, as well as Δ_s, certainly make the optical absorption a complicated process. The optical absorption from polarons has been investigated recently by Fesser *et al.*,[34] where the authors consider a single electron (or hole) polaron in the polyacetylene chain. In this paper we have shown that the gap Δ_p is almost independent of the dopant levels. Therefore, the conclusion reached by Fesser *et al.*[34] regarding the $\alpha_p^{(2)}$ polaron optical-absorption process should remain valid even for higher dopant levels.

Finally, we should emphasize that the Hartree approximation for the electron-electron interaction is too rough. For the case of a neutral polyacetylene chain, more rigorous results have been obtained by Hirsch using the Monte Carlo method.[35] Hirsch has demonstrated that as the intra-atomic Coulomb U increases, the dimerization increases first and then decreases. On the other hand, the nearest-neighbor Coulomb repulsion always enhances the ground-state dimerization. Such features are not found in our simple Hartree results.

ACKNOWLEDGMENT

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