Gap states of charged solitons in polyacetylene

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By considering the electron interactions in polyacetylene, it is found that there exist two gap states in charged solitons of *trans*-polyacetylene: One is deep level, and the other is shallow level. The deep one shifts 0.23 eV down (for a positive soliton) or up (for a negative soliton) from the center of the gap, while the shallow one is 0.06 eV under the bottom edge of the conduction band (positive soliton) or above the top edge of the valence band (negative soliton). These results agree with the absorption spectra of *trans*-polyacetylene. Other shallow states outside the energy bands are also predicted.

I. INTRODUCTION

The most novel concept in conducting polymers is perhaps the soliton carrier with reversed relation between charge and spin, that is, the charged soliton does not have spin, but the neutral soliton has spin $\frac{1}{2}$.[1] Studying various properties of the soliton is important for a detailed understanding of many peculiar traits of conducting polymers.[2] One topic is the electron states of the soliton, in particular, the bound states trapped by the soliton. *Trans*-polyacetylene possesses twofold-degenerate dimerized ground states, phase A and phase B. When a chain of *tran*-polyacetylene contains phase A in some part of the chain and phase B in the rest, a domain wall appears between phases A and B, which is the soliton. Within phase A or phase B, atoms are arranged in a periodically dimerized lattice in which electrons move in extended states. In the region of the domain wall, however, the atomic distribution deviates from the periodic structure of the dimerization and produces a distortion potential on electrons. Then the electron can be trapped by this distortion potential to form bound states around the soliton. The levels of these bound states are located in the gap, which is the skeleton picture for the origin of gap states. The problem is to determine how many bound states can exist around the soliton and where are the locations of their levels. A simple Hamiltonian to show the soliton is the Su-Schrieffer-Heeger (SSH) model,[1] in which the electron-electron interaction is neglected. Based on the electron-lattice interaction alone (the SSH model), it is well known that there exists a midgap state in the electron spectrum of the soliton. The level of this bound state sits at the center of the gap. The question is whether there are any other gap states. We attempt to answer this question in the present paper.

The difficulty with the SSH model is that it cannot be solved analytically. In order to get a rigorous solution of the soliton, Takayama, Lin-Liu, and Maki (TLM) have introduced the continuum model[3] which can be solved analytically. For the TLM model it has been rigorously proven that the soliton has one and only one electron bound state, which is located at the middle of the gap. Since then, people have tended to think that the soliton has only one gap state. Experimentally, both the dopant-induced absorption[4] and the photoinduced absorption[5] in *trans*-polyacetylene have shown a second absorption peak whose energy is about half of that of the main peak. It provides the evidence for the gap state of a soliton produced by the dopants or the incident photons. Absorption spectra actually indicate that the energy of the second peak is not exactly equal to one half of the gap, but is about 0.25 eV smaller than half of the gap. It means that the level of the gap state is shifted from the center of the gap. Such a shift is caused by the electron-electron repulsion,[6] which has to be considered before a reliable answer can be obtained about the number and locations of bound states of the soliton.

It should also be pointed out that the TLM model is a continuum model in which the molecular structure of the polymer chain has been smeared out. However, the real polymer chain consists of discrete atoms. The continuum approximation made in the TLM model may have lost some bound states existing in the chain with discrete structure. In fact, an earlier work using the SSH model

has revealed that the discrete structure can possess some shallow electron bound states if the electron-lattice coupling is strong enough.[7] On the other hand, the photoinduced absorption spectrum demonstrates that there is a cusp on the left-hand side of the main absorption peak.[5] The separation between the cusp and the top of the main peak is about 0.06 eV. Such structure in the absorption spectrum also indicates that there is a level near the band edge. Therefore, both the theory and the experiment suggest that there are some other bound states in the gap. In order to find a definite answer, we must include both the electron-lattice and electron-electron interactions in our investigations of the electron spectrum of the soliton and consider the discrete structure of the chain.

II. THEORETICAL FORMULATION

As usual, the electron-lattice and electron-electron interactions are described by the SSH model Hamiltonian H_0 and the Hubbard term H',

$$H_0=t_0\left[-\sum_{n,s}[1+(-1)^n\phi_n]\times(C^{\dagger}_{n+1,s}C_{n,s}+C^{\dagger}_{n,s}C_{n+1,s})+\frac{1}{\lambda\pi}\sum_n\phi_n^2\right], \tag{1}$$

$$H'=(U/2)\sum_{n,s}C^{\dagger}_{n,s}C_{n,s}C^{\dagger}_{n,-s}C_{n,-s}\ , \tag{2}$$

and the total Hamiltonian is

$$H=H_0+H'\ , \tag{3}$$

where t_0 is the hopping constant, λ is the electron-lattice coupling constant, ϕ_n is the dimensionless displacement of lattice, $C^{\dagger}_{n,s}$ and $C_{n,s}$ are creation and annihilation operators, respectively, of an electron on site n with spin s, and U is the strength of the electron interactions. In the case of polyacetylene,

$$t_0=2.5\text{ eV},\quad \lambda=0.2,\quad U=5\text{ eV}\ . \tag{4}$$

In the Hartree-Fock approximation, the eigenequation of Hamiltonian (3) is

$$\varepsilon^s_\mu Z^s_{n,\mu}=-t_0[1+(-1)^n(\phi_n+\phi_{n+1})]Z^s_{n+1,\mu}-t_0[1+(-1)^{n-1}(\phi_n+\phi_{n-1})]Z^s_{n-1,\mu}+UX_{n,s}Z^s_{n,\mu}\ , \tag{5}$$

where ε^s_μ and $Z^s_{n,\mu}$ are the eigenenergy and wave function of the electron in the eigenstate μ with spin s, and

$$X_{n,s}=\langle C^{\dagger}_{n,-s}C_{n,-s}\rangle \tag{6}$$

is the self-consistent ground-state average of the electron occupation at site n with spin $-s$. The lattice displacement ϕ_n is determined by minimizing the total energy,

$$\phi_n+\phi_{n+1}=\pi\lambda(-1)^n\left[\sum_{\substack{\mu,s\\(\text{occ})}}Z^s_{n,\mu}S^s_{n+1,\mu}-\frac{1}{N}\sum_n\sum_{\substack{\mu,s\\(\text{occ})}}Z^s_{n,\mu}Z^s_{n+1,\mu}\right]. \tag{7}$$

Combining Eqs. (5), (6), and (7), the energy spectrum ε^s_μ and wave function $Z^s_{n,\mu}$ of the electron can be obtained by solving these closed equations numerically. In our calculation, we take a chain with 201 atoms. For charged solitons, each level is either doubly occupied or empty. In this case, the electron states are spin independent:

$$Z^s_{n,\mu}=Z^{-s}_{n,\mu}\quad\text{and}\quad\varepsilon^s_\mu=\varepsilon^{-s}_\mu\ . \tag{8}$$

III. RESULTS AND DISCUSSION

The energy spectra of positive and negative solitons are shown in Figs. 1 and 2, respectively. There are two gap states: deep level ε_d and shallow level ε_s. The deep level does not sit at the center of the gap, but shifts 0.23 eV down (positive soliton) or up (negative soliton) from the center of the gap. The shallow level is 0.06 eV beneath the bottom edge of conduction band (positive soliton) or above the top edge of valence band (negative soliton).

For the case of a positive soliton (Fig. 1), both deep and shallow levels are empty, and the electrons in the valence band can be excited into higher levels. There are three ways to make a transition: (1) going to the conduction band, which corresponds to the main absorption peak; (2) going to the deep level ε_d, which is the second absorption peak, whose energy is 0.23 eV smaller than half of the gap, and which agrees with the dopant and photoinduced absorption; and (3) going to the shallow level ε_s, forming a cusp which is separated by 0.06 eV from the top of the main peak. The photoinduced absorption[3] has shown evidence of such a cusp.

For the case of a negative soliton (Fig. 2), both deep and shallow levels are occupied. There are also three transitions: (1) from the valence band to the conduction band, which is the main absorption peak; (2) from a deep level ε_d to the conduction band, which is the second absorption peak; and (3) from a shallow level ε_s to the conduction band, which is the cusp. The frequencies of these three transitions are exactly the same as those of a positive soliton.

The wave functions $Z_{n,s}$ and $Z_{n,d}$ of the shallow and deep levels are shown in Fig. 3. As expected, the width of the wave function $Z_{n,d}$ of the deep level is smaller than that of the wave function $Z_{n,s}$ of the shallow level.

Based on the above results, we can theoretically give a schematic absorption spectrum for the charged solitons shown in Fig. 4, where three features appear: (1) the main peaks, (2), the second peak, and (3) the shoulder. These features correspond to three absorption lines with some uncertain broadenings. The strength and broaden-

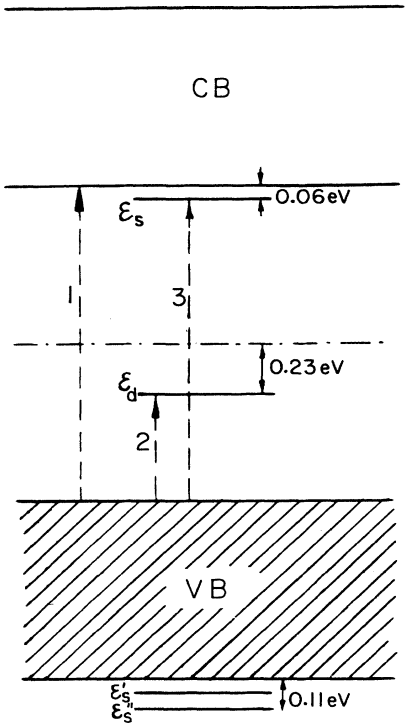

FIG. 1. Energy spectrum of an electron in a positive soliton.

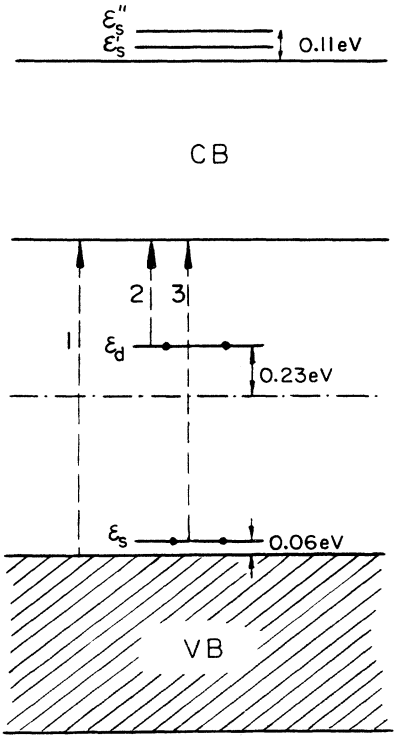

FIG. 2. Energy spectrum of an electron in a negative soliton.

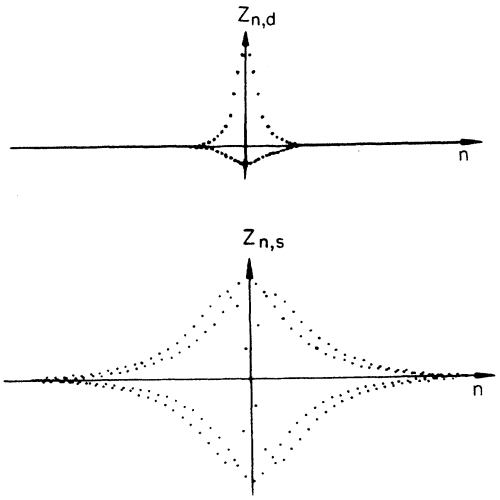

FIG. 3. Electron wave functions of a deep gap state $Z_{n,d}$ and shallow gap state $Z_{n,s}$.

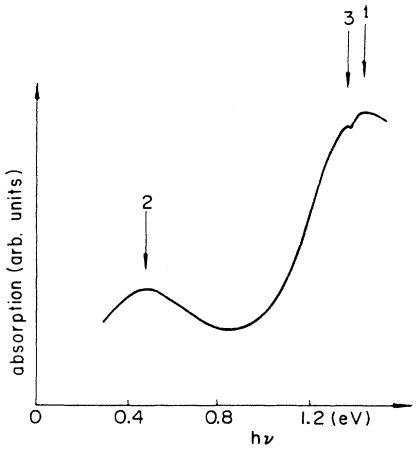

FIG. 4. Schematic absorption spectrum for the charged solitons.

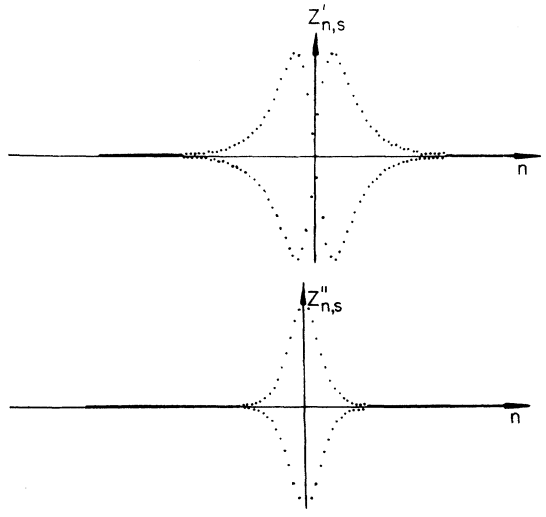

FIG. 5. Electron wave functions of two outside shallow states $Z_{n,s}'$ and $Z_{n,s}''$.

ing of these absorption lines depend on the density of solitons and the interaction between the solitons and the surroundings. Further study is needed in order to obtain more details. Apparently, the skeleton features of our theoretical absorption spectrum are in accord with the photoinduced absorption.[5] In the dopant absorption, besides the main peak and the second peak, there also appears a shoulder near the main peak.[4]

It should be mentioned that there are two more shallow levels ε_s' and ε_s'' sitting outside the bands. For a positive soliton, these two shallow levels are underneath the bottom edge of the valence band (see Fig. 1). For a negative soliton, they are above the top edge of the conduction band (see Fig. 2). The wave functions of these two shallow levels are shown in Fig. 5. These two shallow levels will give more features of the absorption spectrum in the energy region of 5–6 eV. It is therefore of great interest to carry out experiments to observe the absorption spectrum in that energy region.

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