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GAP STATES OF CHARGED SOLITON IN POLYACETYLENE *

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ABSTRACT

By considering the electron interaction in polyacetylene, it is found that there exist two gap states in charged solitons of trans-polyacetylene: one is deep level, another is shallow level. The deep one shifts 0.23 ev down (for positive soliton) or up (for negative soliton) from the center of the gap; while shallow one is 0.06 ev under the bottom of conduction band (positive soliton) or above the top of valence band (negative soliton). These results agree with the absorption spectra of trans-polyacetylene.

Based on the electron-lattice interaction alone, it is well known that there is a mid-gap state in the electronic spectrum of soliton of trans-polyacetylene [1]. Both the dopant induced [2] and photo-induced absorptions [3] in trans-polyacetylene showed a second peak appearing about half way of the main peak, which is the evidence of the gap state of soliton produced by the dopants or incident photons. The absorption spectra indicate that the gap state is not in the middle of the gap, but it is about 0.25 ev below the centre of the gap. Such a shift is believed to be caused by electron interaction [4]. So far, people commonly think that the soliton only has one gap-state. However, our recent studies reveal that the SSH (Su, Schrieffer, Heeger) model [1] may also possess several shallow electronic bound states trapped by soliton [5]. This means that, besides the mid-gap state, there exist some other discrete levels in the gap of soliton. These discrete levels are quite close to the band edges. On the other hand, the photo-induced absorption demonstrates that there is a cusp sitting in the left side of the main absorption peak, the separation between the cusp and the top of the main peak is avout 0.06 ev [3]. This structure of absorption can be understood by assuming a shallow level near the band edges. Therefore both theory and experiment indicate that there are some other gap states in soliton. Our earlier work [5] could not give the final conclusion, since the electron interaction was neglected there. In order to get a definite answer, we should include electron correlation and, then, investigate how many gap states can exist in the soliton.

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

$$H_0 = t_0\Big(-\sum_{n,s}(1+(-1)^n\phi_n)(C^+_{n+1,s}C_{n,s} + \text{h.c.}) + \frac{1}{\lambda N}\sum_n \phi_n^2\Big) \qquad (1)$$

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

and the total Hamiltonian is

$$H = H_0 + H', \qquad (3)$$

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

$$t_0 = 2.5 \text{ ev}, \quad \lambda = 0.2, \quad U = 5 \text{ ev} \qquad (4)$$

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

$$\epsilon^s_\mu Z^s_{n,\mu} = -t_0[1 + (-1)^n(\phi_n + \phi_{n+1})]\ Z^s_{n+1,\mu}$$

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

where ϵ^s_μ and $Z^s_{n,\mu}$ are the energy spectrum and wave function of electron with spin s, and

$$X_{n,s} = \langle C^+_{n,-s}\ C_{n,-s}\rangle_{HF} \quad . \qquad (6)$$

The lattice displacement ϕ_n is determined by minimizing the total energy,

$$\phi_n + \phi_{n+1} = 2\pi\lambda(-1)^n\Big[\sum_{\substack{\mu,s\\(occ.)}} Z^s_{n,\mu}\ Z^s_{n+1,\mu} - \frac{1}{N}\sum_n\sum_{\substack{\mu,s\\(occ.)}} Z^s_{n,\mu}\ Z^s_{n+1,\mu}\Big] \quad . \qquad (7)$$

Combining Eqs.(5), (6) and (7), the electronic states ϵ^s_μ, $Z^s_{n,\mu}$ and lattice configuration ϕ_n can be solved numerically by iteration. In our calculation, we take a chain with 201 atoms.

For charged solitons, each level is either doubly occupied or empty, then the electron states are spin independent

$$Z^s_{n,\mu} = Z^{-s}_{n,\mu} \quad \text{and} \quad \epsilon^s_\mu = \epsilon^{-s}_\mu \quad . \qquad (8)$$

The energy spectra of positive and negative solitons are shown in Figs. 1 and 2. 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, it shifts 0.23 ev down (positive soliton) or up (negative soliton) from the center of gap. The shallow level is 0.06 ev beneath the bottom of conduction band (positive soliton) or above the top of valence band (negative soliton).

In the case of positive soliton (Fig. 1), both deep and shallow levels are empty, the electrons in the valence band can be excited into higher levels. There are three ways to transit: 1) going to conduction band, it corresponds to the main absorption peak. 2) going to the deep level ϵ_d, it is the second absorption peak, which energy is 0.23 ev smaller than half of the gap, it agrees with the dopant and photo-induced absorption. 3) going to the shallow level ϵ_s, it forms the cusp, which separates 0.06 ev from the top of the main peak. The photo-induced absorption [3] has shown evidence of such a cusp.

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

The wave functions $Z_{n,s}$ and $Z_{n,d}$ of shallow level and deep level are shown in Fig. 3. As it is expected the wave function $Z_{n,d}$ of deep level has better localization than $Z_{n,s}$ of shallow level.

It should be mentioned that there are two more shallow levels ε_s' and ε_s'' sitting outside the bands. For positive soliton, these two shallow levels are underneath the bottom of valence band; for negative soliton, they are above the top of conduction band. The wave functions of these two shallow levels are shown in Fig. 4.

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FIGURE CAPTION

Fig. 1 The energy spectrum of electron in positive soliton.

Fig. 2 The energy spectrum of electron in negative soliton.

Fig. 3 The electron wave functions of deep gap state $Z_{n,d}$ and shallow gap state $Z_{n,s}$.

Fig. 4 The electron wave functions of outside shallow states $Z_{n,s}'$ and $Z_{n,s}''$.

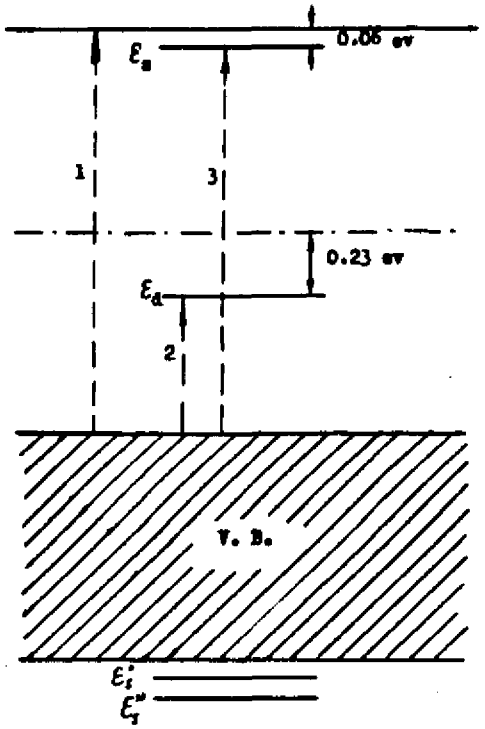
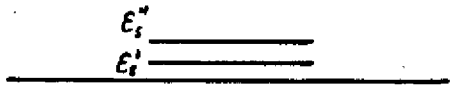


Fig. 1


$\mathcal{E}_s''$
$\mathcal{E}_s'$

C. B.

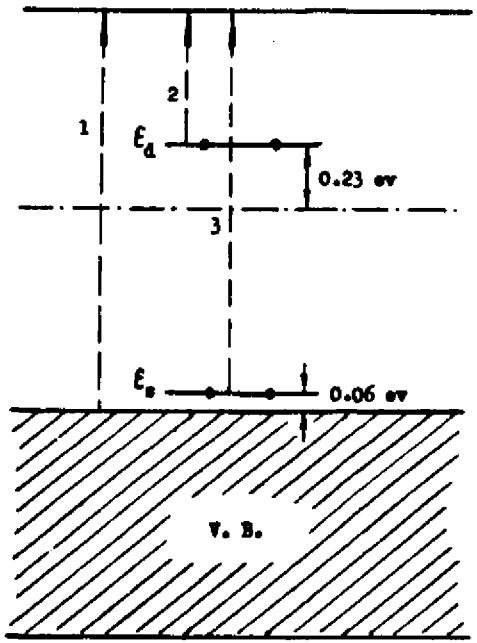
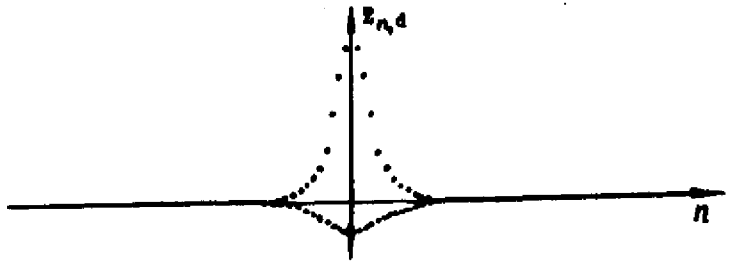

1
2
3
$\mathcal{E}_d$
0.23 ev
$\mathcal{E}_s$
0.06 ev
V. B.

Fig. 2


$\Sigma_{n,d}$
n

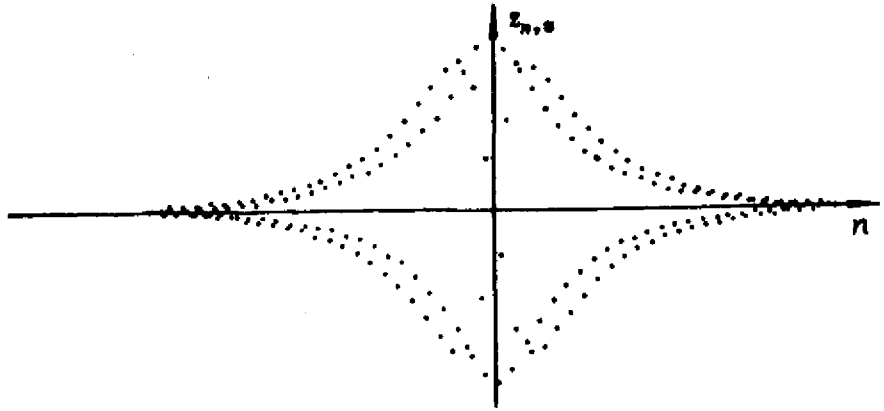

$\Sigma_{n,s}$
n

Fig. 3

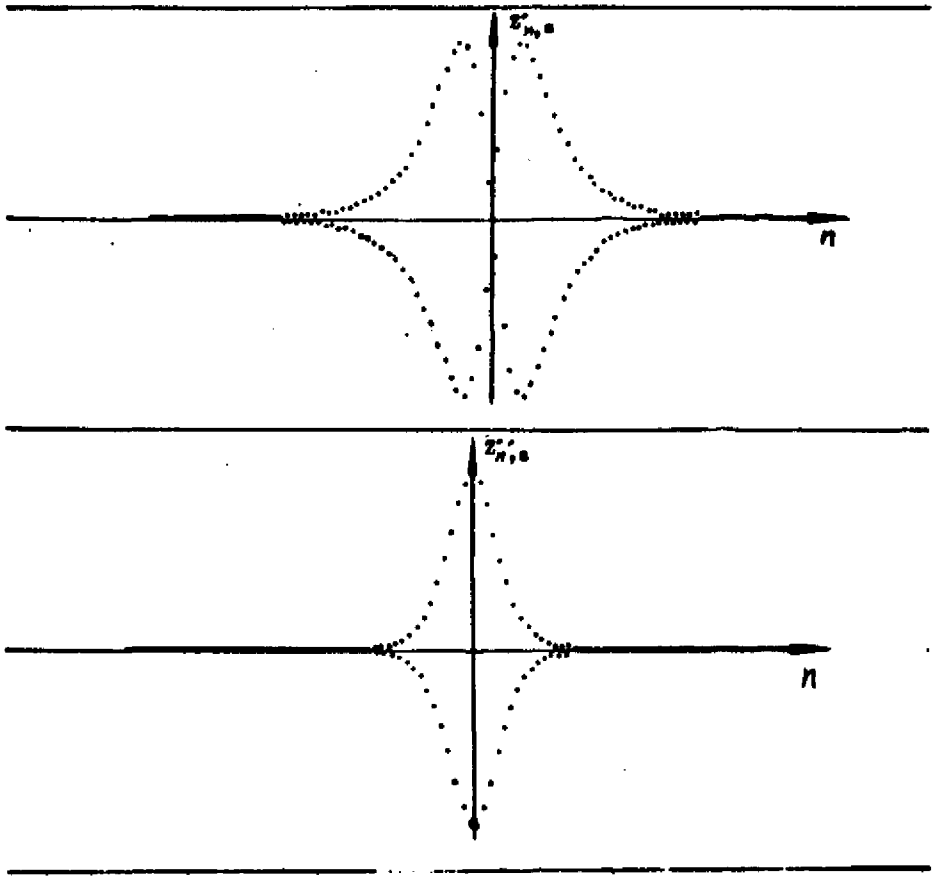


Fig. 4