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Surface states in doped polymers

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Surface states of doped polymers are investigated by means of the Green-function technique. We consider only the particular case in which the surface is created right next to the impurity. It is shown that the surface state that resulted from cutting the double bond is qualitatively different from that created by cutting the single bond. In the former case, there is a midgap state and two localized states outside the energy bands, while in the latter case there are only two localized states, which may occur outside the energy bands or in the energy band gap depending on the sign of the impurity potential.

I. INTRODUCTION

Intensive studies of conducting polymers in recent years not only provide functional materials with significant prospects for applications,[1] but also develop concepts in low-dimensional condensed-matter physics.[2] As is well known, pure polymers are insulators. Doped polymers, however, may become good conductors. The conductivity of transpolyacetylene, for example, have overtaken that of copper. Doped polymers usually possess many other attractive properties as well. Furthermore, many polymeric devices involve the surface and interfaces. It is, therefore, important to understand surface states in undoped polymers.

The study of surface states dates back to the 1930's.[3] For a linear chain of atoms arranged at equal distances, various methods have been developed to calculate the surface states.[4–8] There are also more sophisticated methods of calculation[9–11] designed to deal with realistic features of surface states in various particular systems. Such studies may apply to semi-infinite solids of periodic structures, but cannot correctly describe one-dimensional systems such as polymers. This is because of the dimerization of polymers due to the Peierl's instability. The structure of single- and double-bond alternation is actually a remarkable characteristic of polymers, and the surface created by cutting a single or double bond can be qualitatively different from each other.

The situation is further complicated by doping impurities near the surface. We investigate in this paper surface states as well as states bound to an impurity atom in polyacetylene in which the impurity is doped at either the double or single bond. On the basis of the Su, Schrieffer, and Heeger (SSH) model,[12] the Green-function technique is employed to calculate surface states under different circumstances. Our study differs from the existing work on impurity effects in doped conducting polymers.[13] In Ref. 13, the conductivity and the phase transition between semiconducting and metallic states in doped conducting polymers are discussed, and the soliton band and gap states are calculated for polymers with a random distribution of impurities.

We first establish in Sec. II the Green-function formalism of surface states for doped polymers with a surface next to the dopant. The density of states localized next to the surface is derived in Sec. III. Energy levels are calculated for various surface localized states in Sec. IV, and a brief discussion of the results is then found in Sec. V.

II. GREEN-FUNCTION FORMALISM

We start with the SSH model[12]

$$H_0=-\sum_{m,s}J_{m+1,m}(c^\dagger_{m+1,s}c_{m,s}+c^\dagger_{m,s}c_{m+1,s})+\tfrac{1}{2}\sum_m K(u_{m+1}-u_m)^2+\tfrac{1}{2}\sum_m M\dot{u}_m^2\ , \tag{1}$$

where $J_{m+1,m}=J_0\pm J_1$ with + and − signs corresponding to the double (short) and single (long) bonds, respectively. Other symbols are standard. Since the C-C bonds are very strong, the impurity atom cannot replace a carbon atom and can only stay between chains. The carbon atoms are labeled such that the lth bond is between the atoms l and $l+1$. For simplicity, we assume that the impurity interacts only with the nearest carbon bond and denote the interaction by a parameter V_0. Thus,

$$\begin{aligned}\langle\phi_{m'}(l+1)|V|\phi_m(l)\rangle&=\langle l+1|V_0\sum_{l,s}(c^\dagger_{l+1,s}c_{l,s}+c^\dagger_{l,s}c_{l+1,s})|l\rangle\\&=V_0\quad\text{for the nearest bond}\ ,\\\langle\phi_{m'}(l+1)|V|\phi_m(l)\rangle&=0\quad\text{otherwise}\ .\end{aligned}\tag{2}$$

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Consider a single impurity atom located near the lth bond. The Hamiltonian is

$$H = H_0 + V \ . \tag{3}$$

The Green function G with an impurity is given by the equation

$$G(E;m,m') = G_0(E;m,m') + G_0(E;m,l)V_0 G(E;l+1,m') \ , \tag{4}$$

where G_0 stands for the corresponding Green function for a perfect infinite chain described by H_0. It has already been shown that[12]

$$G_0(E;m,m') = \begin{cases} \dfrac{1}{N}\displaystyle\sum_k \dfrac{2E\exp[ika(m-m')]}{(E+i\delta)^2 - E_k^2} , & m-m' = \text{even} \\[2ex] -\dfrac{1}{N}\displaystyle\sum_k \dfrac{2E_k \exp[2ika(m-m')][\alpha_k + (-)^m i\beta_k]^2}{(E+i\delta)^2 - E_k^2} , & m-m' = \text{odd} \ . \end{cases} \tag{5}$$

In Eq. (5), we have defined

$$\alpha_k = \frac{1}{\sqrt{2}}\left[1 + \frac{E_0(k)}{E_k}\right]^{1/2} , \tag{6a}$$

$$\beta_k = \operatorname{sgn}(k)\left[1 - \frac{E_0(k)}{E_k}\right]^{1/2} , \tag{6b}$$

in which

$$E_k = \sqrt{E_0^2(k) + \Delta^2(k)} \ , \tag{7}$$

and

$$E_0(k) = -2J_0 \cos(2\pi k a) \ , \tag{8a}$$

$$\Delta(k) = 2J_1 \sin(2\pi k a) \ . \tag{8b}$$

Setting $m = l+1$ in Eq. (4), we have

$$G(E;l+1,m') = G_0(E;l+1,m')/[1 - V_0 G_0(E;l+1,l)] \ . \tag{9}$$

Substituting (9) back in (4), we find

$$G(E;m,m') = G_0(E;m,m') + \frac{V_0 G_0(E;m,l) G_0(E;l+1,m')}{1 - V_0 G_0(E;l+1,l)} \ . \tag{10}$$

The local density of states (LDOS) at m is given by

$$\rho(E,m) = -\frac{1}{\pi}\operatorname{Im} G^+(E;m,m) \ , \tag{11}$$

where G^+ is defined by

$$G^+(E;m,l) = G(E+i0^+;m,l) \ . \tag{12}$$

Inserting Eq. (10) in (11) and remembering (12), we find

$$\rho(E,m) = \rho_0(E,m) - \frac{1}{\pi}\operatorname{Im}\left\{\frac{V_0 G_0^+(E;m,l) G_0^+(E;l+1,m)}{1 - V_0 G_0^+(E;l+1,l)}\right\} . \tag{13}$$

At the lattice point $m = m' = l$, Eq. (10) becomes

$$G(E;l,l) = G_0(E;l,l)/[1 - V_0 G_0(E;l+1,l)] \ , \tag{14}$$

which, combined with Eqs. (11) and (12), yields

$$\rho(E;l) = \rho_0(E;l)/|1 - V_0 G_0^+(E;l+1,l)|^2 + \frac{V_0[\operatorname{Re}G_0^+(E;l+1,l)\operatorname{Im}G_0^+(E;l,l) - \operatorname{Re}G_0^+(E;l,l)\operatorname{Im}G_0^+(E;l+1,l)]}{\pi|1 - V_0 G_0^+(E;l+1,l)|^2} \ . \tag{15}$$

The LDOS is a continuum function of E in the energy band. But, at the impurity bound-state energy E_p, it exhibits the δ-function behavior. This is because the Green function has a pole at the bound-state energy $E = E_p$. Therefore, we have from Eq. (13)

$$\rho(E_p,m) = \frac{V_0 G_0(E_p;m,l) G_0(E_p;l+1,m)}{-G_0'(E_p;l+1,l)}\delta(E - E_p) \ , \tag{16}$$

where use has been made of the relation

$$\delta[f(x)] = \sum_p \frac{\delta(x - x_p)}{|f'(x_p)|} \ . \tag{17}$$

When a bond of the linear chain is cut, surfaces are created in the resulting semi-infinite chains. To represent the effects of the surface on electronic states, a surface potential U_0 is introduced to compensate the bond coupling, that is,

$$U_0=\langle \phi_{m'}(1)|H_0|\phi_m(0)\rangle ,$$

$$\begin{aligned} U_0&=\langle \phi_{m'}(1)|-\sum_{m,s} J_{m+1,m}(c^\dagger_{m+1,s}c_{m,s} \\ &\qquad +c^\dagger_{m,s}c_{m+1,s})|\phi_m(0)\rangle \qquad (18) \\ &=-(J_0\pm J_1) , \end{aligned}$$

in which the second term is positive for a double bond and negative for a single bond. For definiteness, we assume that the surface is located at $m=0$ if the double bond is cut and at $m=1$ if the single bond is cut.

It is important to note that the process of creating a surface will, in general, modify bonds near the surface as the lattice is not rigid. Therefore, the chain length will change accordingly due to the lattice relaxation. In the SSH model, this may be determined by minimizing the energy. On the other hand, it is not difficult to see in the SSH model that the lattice relaxation may change the gap-state wave function appreciably, but not the energy level that remains at the gap center. This suggests that the lattice relaxation can change the wave function of a defect but not its energy. Since we are mainly discussing the energy levels in the gap due to the surface and impurity near the surface, the effect of lattice relaxation is not important. Hence, the electron-lattice interaction is neglected in our consideration.

In terms of G the Green function G^s describing the impurity-doped semi-infinite chain satisfies the equation

$$G^s=G+GU_0G^s . \qquad (19)$$

It is understood that the condition $G^s(E;m,m')=0$ is implied whenever $m=0$ or $m'=0$. Solving Eq. (19) for $G^s(E;1,m)$ and substituting back into (19), we obtain immediately

$$G^s(E;m,m')=G(E;m,m') +\frac{U_0G(E;m,0)}{1-U_0G(E;1,0)}G(E;1,m') . \qquad (20)$$

The diagonal matrix elements of G^s can be found after some algebra. The results are expressed in terms of G_0 as follows:

$$\begin{aligned} G^s(E;1,1)&=\frac{G(E;1,1)}{1-U_0G(E;1,0)} \\ &=\frac{G_0(E;1,1)[1-V_0G_0(E;l+1,l)]+V_0G_0(E;1,l)G_0(E;l+1,1)}{[1-U_0G_0(E;1,0)][1-V_0G_0(E;l+1,l)]-V_0U_0G_0(E;1,l)G_0(E;l+1,0)} , \end{aligned} \qquad (21)$$

$$\begin{aligned} G^s(E;m,m)=G_0(E;m,m)+\{&V_0[1-U_0G_0(E;1,0)]G_0(E;m,l)G_0(E;l+1,m) \\ &+U_0[1-V_0G_0(E;l+1,l)]G_0(E;m,0)G_0(E;1,m) \\ &+U_0V_0[G_0(E;m,0)G_0(E;1,l)G_0(E;l+1,m) \\ &+G_0(E;m,l)G_0(E;l+1,0)G_0(E,1,m)]\} \\ &\times\{[1-V_0G_0(E;l+1,l)][1-U_0G_0(E;1,0)] \\ &-V_0U_0G_0(E;1,l)G_0(E;l+1,0)\}^{-1} . \end{aligned} \qquad (22)$$

III. SURFACE LOCALIZED DENSITY OF STATES

There exist two types of electronic states in a semi-infinite linear chain, in general. The extended states appear within certain ranges of energy. They form the energy bands and are characterized by step functions. The surface states, on the other hand, are localized on the surface with amplitudes decaying exponentially as they extend into the bulk. Surface states appear outside the energy bands at singular points of the Green function $G^s(E;m,m)$, and hence are characterized by the δ function. We are mainly concerned in this paper with the surface states in the presence of an impurity doped near the open end of the chain.

Two different kinds of surfaces can be created in a linear chain by cutting the double or single bond. We consider the following two cases in our discussion of surface states: (a) The surface is created by cutting the double bond and an impurity is located at the next single bond, and (b) the single bond is cut to form the surface with an impurity sitting at the next double bond. The situation is illustrated in Fig. 1.

To find the Green function for surface states, we look for singular points of G^s in Eq. (21), which correspond to the surface-state energy levels. We denote the denominator of G^s by

$$F_s(E;1,1)=[1-U_0G_0(E;l,0)][1-V_0G_0(E;l+1,l)]-U_0V_0G_0(E;1,l)G_0(E;l+1,0) , \qquad (23)$$

and then expand the function F_s around $E=E_0$. Thus, Eq. (21) can be written as

$$G^s(E;1,1)=\frac{G_0(E;1,1)[1-V_0G_0(E;l+1,l)]+V_0G_0(E;1,l)G(E;l+1,1)}{F_s(E_0;1,1)+(E-E_0)F_s(E_0;1,1)} . \qquad (24)$$

At the surface-state energy or when $E_0 = E_s$, we have $F_s(E_s;1,1)=0$. The LDOS for surface states can be written down directly from Eqs. (11), (12), and (24). The result is

$$\begin{aligned}\rho^s(E;1,1) &= -\frac{1}{\pi}\operatorname{Im}G^s(E+i0^+;1,1)\\ &= \{G_0^+(E_s+i0^+;1,1)[1-V_0G_0^+(E_s;l+1,l)]+V_0G_0^+(E_s;1,l)G_0^+(E_s;l+1,1)\}\delta(E-E_s)\\ &\quad\times\{-U_0G_0'(E_s;1,0)[1-V_0G_0(E_s;l+1,l)]-V_0G_0'(E_s;l+1,l)[1-U_0G_0(E_s;1,0)]\\ &\qquad -U_0V_0[G_0'(E_s;1,l)G_0(E_s;l+1,0)+G_0(E_s;1,l)G_0'(E_s;l+1,0)]\}^{-1}\,. \end{aligned} \tag{25}$$

IV. ENERGY LEVELS OF SURFACE STATES

In the following discussion of surface states, we take the midpoint of the energy gap to be the zero relative to which surface-state energies are measured. Consider first the case in which the surface is created by cutting the short bond. The Green function is given by Eq. (22), and the surface-state energy is determined by setting the denominator to zero. As is shown in Fig. 1, there are two distinct cases. If we consider, for definiteness, the case illustrated in Fig. 1(a), we can write the Green function simply be setting the $l=1$ in Eq. (22), that is,

$$\begin{aligned}G^s(E;m,m) = G_0(E;m,m)+\{&V_0[1-U_0G_0(E;1,0)]G_0(E;m,1)G_0(E;2,m)\\ &+U_0[1-V_0G_0(E;2,1)]G_0(E;m,0)G_0(E;1,m)\\ &+U_0V_0[G_0(E;m,0)G_0(E;1,1)G_0(E;2,m)+G_0(E;m,1)G_0(E;2,0)G_0(E;1,m)]\}\\ &\times\{[1-V_0G_0(E;2,1)][1-U_0G_0(E;1,0)]-U_0V_0G_0(E;1,1)G_0(E;2,0)\}^{-1}\,. \end{aligned} \tag{26}$$

Various Green functions that appeared in (26) are found as follows. Since all the Green functions depend explicitly on the energy, we omit E in the following just for simplicity in notation. Thus, we find from Eq. (5), by using the residue theorem,

$$G_0(1,0)=\frac{1}{2(J_0^2-J_1^2)}\left[(J_0-J_1)-J_0\left[\frac{4J_1^2-E^2}{4J_0^2-E^2}\right]^{1/2}+J_1\left[\frac{4J_0^2-E^2}{4J_1^2-E^2}\right]^{1/2}\right], \tag{27}$$

$$G_0(2,0)=G_0(0,0)z_1^2,\quad G_0(0,2)=G_0(0,0)z_1^2\,, \tag{28}$$

where z_1 is defined by

$$z_1=\begin{cases} i\left[\left[\dfrac{4J_0^2-E^2}{4J_0^2-4J_1^2}\right]^{1/2}-\left[\dfrac{4J_1^2-E^2}{4J_0^2-4J_1^2}\right]^{1/2}\right] & \text{in the gap}\\ -\left[\left[\dfrac{E^2-4J_1^2}{4J_0^2-4J_1^2}\right]^{1/2}+i\left[\dfrac{4J_0^2-E^2}{4J_0^2-4J_1^2}\right]^{1/2}\right] & \text{in the band}\,. \end{cases} \tag{29}$$

In a similar fashion we can, by applying the residue theorem to perform the integral over k, work out the relations

$$\begin{aligned} &G_0(m,0)G_0(1,m)=G_0(0,0)G_0(1,0)z_1^{2(m-1)},\quad m\ge 1,\ \text{for odd } m\,,\\ &G_0(m,0)G_0(1,m)=G_0(0,0)G_0(2,1)z_1^{2(m-1)},\quad m\ge 2,\ \text{for even } m\,. \end{aligned} \tag{30}$$

$$\begin{aligned} &G_0(m,1)G_0(2,m)=G_0(0,0)G_0(1,0)z_1^{2(m-2)},\quad m\ge 3,\ \text{for odd } m\,,\\ &G_0(m,1)G_0(2,m)=G_0(0,0)G_0(2,1)z_1^{2(m-2)},\quad m\ge 2,\ \text{for even } m\,. \end{aligned} \tag{31}$$

$$\begin{aligned} &G_0(m,0)G_0(1,1)G_0(2,m)=G_0(0,0)G_0^2(1,0)z_1^{2(m-2)},\quad m\ge 3,\ \text{for odd } m\,,\\ &G_0(m,0)G_0(1,1)G_0(2,m)=G_0^3(0,0)z_1^{2(m-2)},\quad m\ge 2,\ \text{for even } m\,. \end{aligned} \tag{32}$$

$$\begin{aligned} &G_0(m,1)G_0(2,0)G_0(1,m)=G_0^3(0,0)z_1^{2m},\quad m\ge 3,\ \text{for odd } m\,,\\ &G_0(m,1)G_0(2,0)G_0(1,m)=G_0(0,0)G_0^2(2,1)z_1^{2(m-1)},\quad m\ge 2,\ \text{for even } m\,. \end{aligned} \tag{33}$$

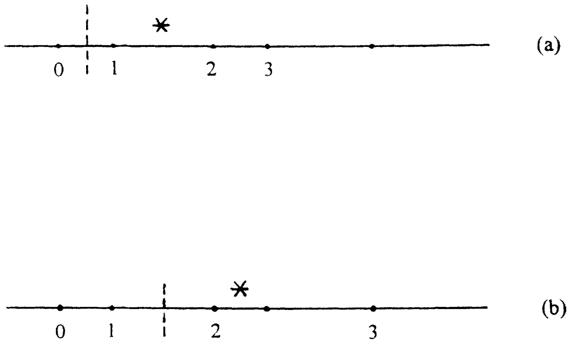

FIG. 1. Schematic diagram showing the surface created by cutting (a) the double (short) bond and (b) the single (long) bond. The position of a doped impurity is indicated by an asterisk.

It is easy to see that when J_1 is replaced by $-J_1$, Eq. (27) becomes $G_0(2,1)$. Hence, we have

$$G_0(2,1)=G_0(1,0)|_{J_0\to -J_1} . \tag{34}$$

Also it can be shown that[12]

$$\begin{aligned} G_0(E;m,m)&=\frac{-iE}{[(4J_0^2-E^2)(E^2-\Delta^2)]^{1/2}}, \quad \Delta\le|E|\le 2J_0 ,\\ G_0(E;m,m)&=\frac{-E}{[(4J_0^2-E^2)(\Delta^2-E^2)]^{1/2}}, \quad 0<|E|<\Delta ,\\ G_0(E;m,m)&=\frac{E}{[(E^2-4J_0^2)(E^2-\Delta^2)]^{1/2}}, \quad |E|>2J_0 , \end{aligned} \tag{35}$$

where Δ stands for the energy gap between the conduction and valence bands, and it is given by

$$\Delta=4J_1 . \tag{36}$$

We first look for the midgap state by taking the limit $E\to 0^+$. From Eqs. (27)–(29) and (34), we find

$$G_0(1,0)|_{E\to 0^+}\approx\frac{1}{J_0+J_1}+\frac{J_0+J_1}{16J_0^2J_1^2}(E+i0^+)^2 , \tag{37a}$$

$$G_0(2,1)|_{E\to 0^+}\approx -\frac{J_0-J_1}{16J_0^2J_1^2}(E+i0^+)^2 , \tag{37b}$$

$$G_0(2,0)|_{E\to 0^+}\approx\frac{J_0-J_1}{4J_0J_1(J_0+J_1)}(E+i0^+) , \tag{37c}$$

$$G_0(0,0)|_{E\to 0^+}=G_0(1,1)|_{E\to 0^+}\approx -\frac{(E+i0^+)}{4J_0J_1} , \tag{37d}$$

and

$$[1-(J_0+J_1)G_0(1,0)]_{E\to 0^+}=\frac{(J_0+J_1)^2}{16J_0^2J_1^2}(E+i0^+)^2 . \tag{38}$$

Inserting the limiting results in Eq. (37) into Eqs. (30)–(33) and remembering Eq. (34), we obtain

$$G_0(m,0)G_0(1,m)\approx\begin{cases} -\dfrac{1}{4J_0J_1(J_0+J_1)}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-1}(E+i0^+) & \text{for odd } m\\ -\dfrac{J_0-J_1}{64J_0^3J_1^3}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-1}(E+i0^+)^3 & \text{for even } m , \end{cases} \tag{39a}$$

$$G_0(m,1)G_0(2,m)\approx\begin{cases} -\dfrac{1}{4J_0J_1(J_0+J_1)}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-2}(E+i0^+) & \text{for odd } m\\ \dfrac{J_0-J_1}{64J_0^3J_1^3}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-2}(E+i0^+)^3 & \text{for even } m . \end{cases} \tag{39b}$$

$$G_0(m,0)G_0(1,1)G_0(2,m)\approx\begin{cases} -\dfrac{(J_0-J_1)^2}{1024J_0^5J_1^5}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-2}(E+i0^+)^5 & \text{for odd } m\\ \dfrac{1}{64J_0^3J_1^3}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-1}(E+i0^+)^3 & \text{for even } m , \end{cases} \tag{40a}$$

$$G_0(m,1)G_0(2,0)G_0(1,m)\approx\begin{cases} \dfrac{1}{64J_0^3J_1^3}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m}(E+i0^+)^3 & \text{for odd } m\\ \dfrac{(J_0-J_1)^2}{1024J_0^5J_1^5}\left[\dfrac{J_0-J_1}{J_0+J_1}\right]^{m-1}(E+i0^+)^5 & \text{for even } m . \end{cases} \tag{40b}$$

Substituting Eqs. (37)–(40) into (26) and making use of the limit $G_0(m,m)|_{E\to 0^+}\to 0$ for $m>0$, we find after some algebra the surface Green function

$$
\begin{aligned}
&G^s(E+i0^+;m,m)=\frac{4J_0J_1}{(J_0+J_1)^2-(J_0-J_1)V_0}\left[\frac{J_0-J_1}{J_0+J_1}\right]^{m-1}(E+i0^+)^{-1}\quad\text{for odd } m\ ,\\
&G^s(E+i0^+;m,m)=0,\quad\text{for even } m\ ,
\end{aligned}
\tag{41}
$$

and the LDOS

$$
\begin{aligned}
&\rho^s(E;m,m)=\frac{4J_0J_1}{(J_0+J_1)^2-(J_0-J_1)V_0}\left[\frac{J_0-J_1}{J_0+J_1}\right]^{m-1}\delta(E)\quad\text{for odd } m\ ,\\
&\rho^s(E;m,m)=0,\quad\text{for even } m\ .
\end{aligned}
\tag{42}
$$

In reaching the resulting surface Green function (41), we have made use of the fact that $G_0(m,m)|_{E\to 0^+}\to 0$, which follows from Eq. (35).

Equations (41) and (42) clearly indicate that there exists, for odd m, a midgap state at $E=0$, which is localized at the surface. Its LDOS decays into the bulk of the chain. Furthermore, the DOS of this state vanishes at even sites. This feature is the signature of a soliton. Thus, a broken double bond creates an edge soliton, which represents the surface state at the midgap.

There are additional discrete states localized near the surface. They are determined by the singular points of Eq. (26), or by the equation

$$
[1-U_0G_0(E;1,0)][1-V_0G_0(E;2,1)]-U_0V_0G_0(E;1,1)G_0(E;2,0)=0\ . \tag{43}
$$

To find the energy for these states, we introduce the new variable y such that

$$
y^2=(4J_0^2-E^2)/(4J_1^2-E^2)\ . \tag{44}
$$

Equation (44), together with Eqs. (27)–(29) transforms Eq. (43) to

$$
J_1[V_0-(J_0+J_1)]y^2-(J_0+J_1)[V_0-(J-J_1)]y+J_0(V_0+J_0+J_1)=0\ , \tag{45}
$$

which is then solved numerically. We find that there are two localized states. One sits above the conduction band and the other below the valence band. These states also decay towards inside of the chain. In fact, they can be identified as the electronic bound states around the impurity,[14] which is located next to the surface. The results are illustrated in Fig. 2 in which the dependence of the surface-state energy on the parameter V_0 is shown.

Similarly, if we set $l=2$ in Eq. (22), we find the Green function for the case of a broken long bond shown in Fig. 1(b) as

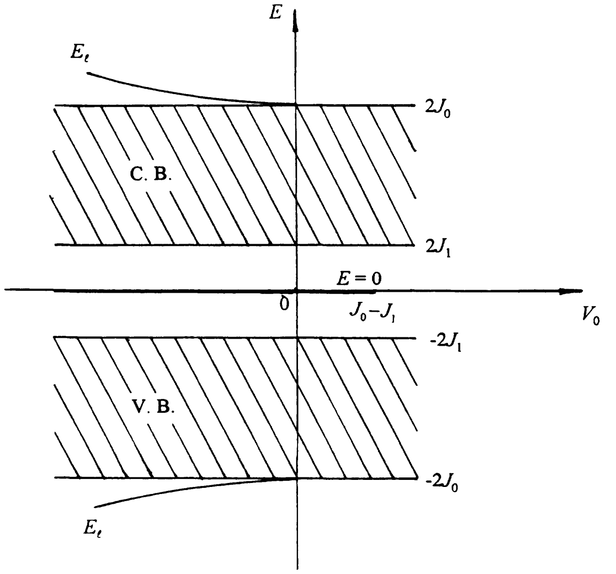

FIG. 2. Energy levels of surface states for the case of a broken short bond. The midgap state exists for the impurity potential energy $V_0<J_0-J_1$ only.

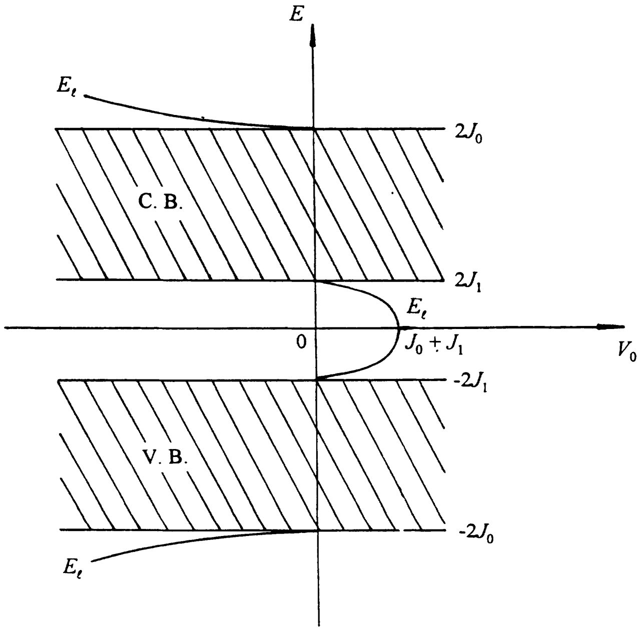

FIG. 3. Energy levels of surface states for the case of a broken long bond. The midgap state appears only when $V_0=J_0+J_1$.

$$\begin{aligned}G^s(E;m,m)=G_0(E;m,m)+\{&V_0[1-U_0G_0(E;1,0)]G_0(E;m,2)G_0(E;3,m)\\&+U_0[1-V_0G_0(E;3,2)]G_0(E;m,1)G_0(E;2,m)\\&+U_0V_0[G_0(E;m,1)G_0(E;2,2)G_0(E;3,m)+G_0(E;m,2)G_0(E;3,1)G_0(E;2,m)]\}\\&\times\{[1-V_0G_0(E;3,2)][1-U_0G_0(E;2,1)]-U_0V_0G_0(E;2,2)G_0(E;3,1)\}^{-1}\ .\end{aligned}\tag{46}$$

If we take the limit $E \to 0^+$, we find instead of Eq. (38)

$$[1-(J_0-J_1)G_0(2,1)]_{E\to 0^+} \approx 1+\frac{(J_0-J_1)^2}{16J_0^2J_1^2}(E+i0^+)^2\ .\tag{47}$$

There is no singularity at $E=0$, and hence the surface at a broken single bond does not possess a midgap state. Consequently, there is no edge soliton in the case shown in Fig. 1(b).

Because of the impurity, however, there still exist localized bound states. They can be found by solving the equation

$$[1-U_0G_0(E;2,1)][1-V_0G_0(E;3,2)] -U_0V_0G_0(E;2,2)G_0(E;3,1)=0\ .\tag{48}$$

In terms of the variable y defined in (44), Eq. (48) becomes

$$J_1(J_0-J_1-V_0)y^2+(J_0-J_1)(J_0+J_1-V_0)y +J_0(J_0-J_1+V_0)=0\ .\tag{49}$$

Numerical calculation shows that there are two sets of solutions corresponding to the ± signs of the potential parameter V_0. They are the localized states bound to the impurity. The results are shown in Fig. 3. For positive V_0, these states fall inside the energy gap; and for negative V_0, they appear outside the energy bands.

V. CONCLUSION

We have shown that two different kinds of surfaces can be created in a polymer chain due to the dimerization. When an impurity atom is doped next to the surface, we have found qualitatively different surface states as well as states bound to the impurity. For the case shown in Fig.1 (a), the surface is formed by cutting the short band and the impurity is located at the long bond. There occurs an edge soliton represented by the midgap surface state, as indicated by the thick line in Fig. 2, for $V_0<J_0-J_1$. This state disappears when $V_0=J_0-J_1$, because of the cancellation of the impurity potential energy by the hopping energy $-(J_0-J_1)$ in the long bond. The result of this cancellation is equivalent to a broken long bond, and hence the edge soliton disappears. In addition, there are also impurity-bound states with energies outside the energy bands.

For the other case of a surface at the broken long bond as in Fig. 1(b), the edge soliton does not appear unless $V_0=J_0+J_1$. This is because the impurity potential energy is completely canceled by the hopping energy $-(J_0-J_1)$ in the short bond. The result is, therefore, equivalent to a broken short bond and hence the appearance of the midgap state as discussed above. Other impurity-bound states are depicted in Fig. 3. There are localized states in the energy gap as well as outside the bands.

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