Transition between bipolaron and polaron states in doped heterocycle polymers

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On the basis of a model similar to that of Su, Schrieffer, and Heeger, we investigate transitions between bipolaron and polaron states in doped heterocycle polymers such as polypyrrole, polythiophene, and polyselenophene. The dopant impurity is assumed to be located between chains, and the interchain coupling is due to the electron hopping which is assumed to be confined to nearest-neighboring carbon groups around the counterion. The electron-electron interaction described by a Hubbard-type Hamiltonian is also included in our calculation. It is shown that the system may be in a bipolaron state or a state of a polaron pair of spin triplet (singlet) nature. We find that the interchain coupling has little influence on the stability of a bipolaron. Transitions from a bipolaron to a pair of polarons can be induced by a strong electron-electron interaction, which is also responsible for the energy difference between the singlet and triplet polarons states.

I. INTRODUCTION

Bipolarons have widely been studied as important excitations in doped conjugated polymers as well as in the interesting C_{60} materials. The bipolaron is considered to be responsible for the high conductivity of conjugated polymers as poly(p-phenylene) (PPP), polypyrrole (PPy), polythiophene (PT), and polyselenophene (PSe). In most one-dimensional conjugated polymers, the transferred charges from dopant species to the polymer do not usually reside in the band states due to the strong electron-lattice coupling in these materials. Instead, they form self-localized particlelike defects associated with quantum states deep in the energy gap.

A number of models have been proposed[1−4] to describe trans-polyacetylene (PA). It is found that there exists a solitonlike excitation, a kink-antikink pair holding one single charge with nonzero spin. However, soliton excitations are not possible in most other polymers such as PPP, PPy, PT, and PSe in which the ground state is nondegenerate. On the other hand, the transport properties of these polymers after doping can be very similar to those of trans-PA. In particular, unusually low Pauli susceptibility has been reported in the metallic regime of SbF$_5$-doped PPY,[5] and no electron-spin-resonance (ESR) signal is detected in electrochemically doped highly conducting PPY.[6]

A series of studies carried out on the Hückel theory[7] and the restricted Hartree-Fock self-consistent field *ab initio* method[8] on PPP, PPy, and PT in both the undoped and highly doped cases reveal the evidence that bipolarons are the corresponding spinless charge carriers in these polymers. It has also been shown[9] that in PSe, like in PPY and PT, bipolarons and polarons are energetically favored when charges are introduced on the polymer chain.

The deformation associated with a bipolaron is

stronger than the corresponding polaron case. But the formation of a bipolaron is energetically more favorable than that of two isolated single-charged polarons.[10] If we define the energy difference

$$\Delta\varepsilon = [E_{p\pm2} - E_0] - [E_{2p\pm1} - E_0] = \varepsilon_{p\pm2} - \varepsilon_{2p\pm1} , \tag{1}$$

where E_d and ε_d are the total energy of a system with a defect and the defect creation energy, respectively. The ground-state energy of the system is denoted E_0. If the interchain interaction is neglected, then we have

$$\Delta\varepsilon < 0 , \tag{2}$$

which implies that two polarons near each other tend to recombine into a bipolaron.

Most of the experimental measurements on chemical doping[11] and photoinduced absorptions (Refs. 5, 6, 10, 12, and 13) reveal the presence of bipolarons. In $[PT^{+y}(ClO_4)^-]$, for example, there is evidence that even in the dilute doping regime, only bipolarons are observable.[14] However, the recent modulated-absorption measurements show that the confinement parameter of bipolaron in P3HT (Ref. 15) and other polymers[16] is so small that the formation of a bipolaron becomes unfavorable.

At saturation doping, valence effective Hamiltonian results[17] indicate the possibility that a bipolaron lattice may revert to a polaron lattice under certain conditions. A major increase in the number of spins has also been observed on doping[18−20] in the *in situ* ESR measurements made on PPy. At low doping concentrations, the data yield a spin number comparable to the number of injected charges. At higher doping, on the other hand, the spin number decreases towards zero in the extrapolation. All these indicate that the polaron pairs do not always

<u>50</u> 13 364

recombine to form bipolarons. The polaron and bipolaron energies might be degenerate or the criterion (2) would no longer hold under certain conditions. Although one might infer to the presence of defects which would reduce the polaron mobility and their recombination to form bipolarons, it remains unclear whether it is the polaron-bipolaron coexistence or whether there exist conditions that prevent the reversion. If the latter is the case, one would like to find the conditions.

Since the interchain coupling and the Coulomb repulsion in the nondegenerate heterocycle systems have not been taken seriously into consideration thus far, we study the problem in this article by including in our treatment the interchain coupling as well as Coulomb confinements of the impurity counterions. On the basis of a π-electron tight-binding model which is just a generalized version of the adiabatic Su, Schrieffer, and Heeger (SSH) model,[1] we perform an energy calculation in our investigation of transitions between bipolarons and polarons in doped heterocycle polymers. The electron-electron (e-e) interactions are considered in the Hubbard model.

II. THEORY

The evolution of the optical spectra upon doping presents certain similarities among heterocycle polymers such as PPy, PT, and PSe. The structure after doping can be viewed as consisting of a backgone of sp^2 hybridized carbon atoms analogous to that of cis-$(CH)_x$, and is stabilized by a heteroatom which bonds covalently to neighboring carbons to form the heterocycle. The doping process leads to the charge transfer from dopant molecules to polymer chains within an overall electrically neutral system, leaving the counterion in the interspace between chains. Consequently, the impurity counterion plays the role of intermediate, bridging the electron hopping between neighboring chains. Therefore a proper treatment of the doped system must include both the intra- and interchain electron-lattice interactions as well as the electron-counterion interactions.

Let us consider a system of two neighboring heterocycle chains parallel to each other. Each chain is described by the Hamiltonian

$$H_j = -\sum_{n,s} \left[t_0 - \alpha(u_{j,n+1} - u_{j,n}) - t_1 \cos\left[\frac{n\pi}{2}\right] \right] (C^\dagger_{j,n+1,s} C_{j,n,s} + \mathrm{H.c.})$$

$$- \sum_{n,s} t_2 (C^\dagger_{j,4n-3,s} C_{j,4n,s} + \mathrm{H.c.}) - \sum_{n,s} t_3 (C^\dagger_{j,4n-3,s} C_{j,4n-3,s} + C^\dagger_{j,4n,s} C_{j,4n,s})$$

$$+ \frac{U}{2} \sum_{n,s} C^\dagger_{j,n,s} C_{j,n,s} C^\dagger_{j,n,-s} C_{j,n,-s} + \frac{K}{2} \sum_n (u_{j,n+1} - u_{j,n})^2 , \tag{3}$$

where $j = 1,2$ labels the chain. The operator $C^\dagger_{j,n,s}$ ($C_{j,n,s}$) creates (annihilates) a π electron with spin s at the lattice site n in the jth chain. The first term of Eq. (3) represents the electron-lattice interactions of the pseudopolyene chain. The parameter t_0 denotes the doping integral between the nearest-neighboring carbon atoms of the unpolymerized chain, and t_1 the polymerization parameter. When $t_1 = 0$, the SSH model is recovered. The electron-phonon coupling constant due to the modulation of the hopping integral is denoted by α. The symbol $u_{j,n}$ stands for the coordinate displacement of a CH group at the site n in the jth chain. The second the third terms describe the influence of the heteroatom on π electrons. It depends in general upon the coupling strength between this atom and its neighboring two carbon atoms. There are two sources of contribution. The electron hopping between lattice points $4n - 3$ and $4n$ via the heteroatom is given by the second term, and third term is the effective confinement of π electrons due to the heteroatom. Taking the carbon atom binding energy to be the zero point, the renormalized couplings are approximately represented by parameters t_2 and t_3. In the actual computation, we assume $t_2 = t_3$. The motion of the heteroatom is entirely ignored because of its much bigger mass than that of the carbon atom. The fourth term gives the electron-electron interaction of Hubbard type with U denoting the on-site coupling, and the last term represents the vibration along the chain direction with the spring constant K.

To represent the Coulomb attraction of the counterion to π electrons, a site-impurity potential is adopted. With the interchain coupling included, the interaction due to the impurity is expressed as

$$H' = -\sum_{j,i} V_d C^\dagger_{j,4m_j+i,s} C_{j,4m_j+i,s}$$

$$- \sum_i t_1 (C^\dagger_{1,4m_1+i,s} C_{2,4m_2+i,s} + \mathrm{H.c.}) , \tag{4}$$

where the counterion is assumed to be at the middle position between the m_jth and (m_j+1)th thiophene ring as shown in Fig. 1. In Eq. (4), V_d denotes the interaction energy of π electrons with the counterion, and t_1 the interchain coupling between two nearest-neighboring chains. We have also assumed in (4) that the potential of the impurity counterion is short range in nature. There-
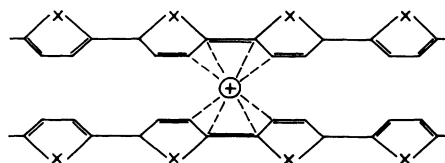

FIG. 1. Schematic diagram of a section of the heterocyclic bichain system with an impurity counterion located symmetrically between the second and third rings in the interchain space.

fore, the interchain interaction is only confined to the neighboring carbons around the counterion as illustrated in the figure. As a consequence, it appears to be much easier for interchain electron hopping in the neighborhood of the counterion than any other place. A rough estimate indicates that the final results are insensitive to the interaction range of the counterion.[21]

With a small deviation from the equilibrium configuration $\{u_n\}$, the static condition for the lattice of the bichain system can be derived by minimizing the total energy of the system which is characterized by the wave function

$$\Phi_{j,n+1}+\Phi_{j,n}=(-1)^n\frac{2\alpha}{K}\left[\sum_{\mu,s}{}'Z_{\mu,j,n,s}Z_{\mu,j,n+1,s}-\frac{1}{N}\sum_{\mu,j,n,s}{}'Z_{\mu,j,n,s}Z_{\mu,j,n+1,s}\right].\tag{5}$$

Here the prime means that we sum over the occupied states only. $Z_{\mu,j,n,s}$ stands for the electron eigenstate corresponding to the eigenvalue $\varepsilon_{\mu,s}$. It is determined by a single-particle eigenvalue equation, after the mean-field treatment of the e-e interaction,

$$-\left[t_0+\alpha(-1)^{n-1}(\Phi_{j,n}+\Phi_{j,n-1})-t_1\cos\frac{(n-1)\pi}{2}\right]Z_{\mu,j,n-1,s}$$

$$-[t_0+\alpha(-1)^n(\Phi_{j,n+1}+\Phi_{j,n})-t_1\cos(n\pi/2)]Z_{\mu,j,n+1,s}$$

$$-(t_2Z_{\mu,j,n-3,s}+t_3Z_{\mu,j,n,s})\Delta\left[\frac{n}{4},\text{int}\right]-(t_2Z_{\mu,j,n+3,s}+t_3Z_{\mu,j,n,s})\Delta\left[\frac{n+3}{4},\text{int}\right]$$

$$-t_\perp\sum_i Z_{\mu,2,4m_2+i,s}\delta_{j,1}-t_\perp\sum_i Z_{\mu,1,4m_1+i,s}\delta_{j,2}-V_d\sum_i Z_{\mu,j,4m_j+i,s}+UX_{j,n,-s}Z_{\mu,j,n,s}=\varepsilon_{\mu,s}Z_{\mu,j,n,s},\tag{6}$$

where we have ignored particle number fluctuation terms and imposed the periodic boundary conditions

$$Z_{\mu,j,n+N_j,s}=Z_{\mu,j,n,s}\ ;\tag{7a}$$

$$u_{j,n+N_j}=u_{j,n}\tag{7b}$$

on both the electronic and lattice systems for each chain. Aside from the Kroniker delta, we have also introduced the function

$$\Delta(i,\text{int})=\begin{cases}1, & i=\text{integer} , \\ 0, & \text{otherwise}.\end{cases}\tag{8}$$

Other notation in (6) is as follows. $X_{j,n,-s}$ represents the electronic charge distribution with spin $-s$ and

$$X_{j,n,-s}=\sum_\mu{}'|Z_{\mu,j,n,-s}|^2\ ,\tag{9}$$

N_j is the total number of $(\text{CH})_x$ group in the jth chain, and $N=N_1+N_2$. Since the spin degeneracy is lifted due to the e-e interaction, the electronic wave function Z depends explicitly on s as has been indicated in (6). As our interest in this research is focused on the static nonlinear defects which usually extend over four heterocycle rings in space, it is reasonable to treat the electron-electron interactions in the self-consistent field Hartree-Fock method.

The ground state and possible defect states of the bichain system can be obtained numerically by means of a self-consistent iterative method from Eqs. (5) and (6). We begin the process of iteration with two different initial conditions. One is that extra electronic charges go into the first ($j=1$) chain, leaving the second chain neutral, and the other is that each chain possess one single extra charge. There are two possible states in the latter case, namely, the triplet state with the two electron spins parallel and the singlet state with electron spins antiparallel. The criteria for terminating the optimization are set as follows. When the change in the dimensionless order parameter $(\alpha/t_0)(\Phi_{j,n+1}+\Phi_{j,n})<10^{-4}$ and in the total energy (in the unit of t_0) is less than 10^{-5}, the iteration process stops.

III. RESULTS AND DISCUSSION

In our numerical work, the geometry optimization is preformed in a system containing $N_1=N_2=80$ sites in the donor-impurity case with parameters $t_0=2.5$ eV, $t_1=0.27t_0$, $t_2=0.05t_0$, $V_d=0.4t_0$, and $t_\perp=0.05t_0$. To fit the calculated results to certain experimental data of neutral heterocycle materials, we take the electron-lattice coupling $\lambda=2\alpha^2/\pi Kt_0=0.24$ for PT or PSe, and $\lambda=0.30$ for PPy.

In order to check the validity of the model proposed here, a simulation has been made on one single PT chain in impurity-free case for which $t_\perp=0$ and $V_d=0$. Two nondegenerate ground states are found. The length of the quinoid ring is $0.025t_0$ lower than that of the benzoid structure. The length change of the bond between two successive quinoid rings is found to be about 2.1 times that of the short bond in the ring. This is somewhat larger than what is reported in Ref. 9. The energy band gap calculated in this simulation is 2.15 eV, which is very close to 2.0 eV for PT and 2.1 eV for PSe observed from the absorption spectrum of the undoped state.[13] Furthermore, it is noted that each ring contains four carbon atoms and hence corresponds to a $4a$ periodic structure, the conduction band (CB) and valence band (VB) split

into subbands separately. Our calculation yields the subgap of 1.78 eV for the VB and 1.93 eV for the CB.

The electron-hole symmetry has already been destroyed due to the presence of the heteroatom even without considering the e-e interaction. When there is a polaron or bipolaron state in the chain, shallow energy levels will emerge near each side of the energy band (or subband) in addition to the defect energy levels localized in the gap.[8,13] Therefore all the corresponding electronic states are localized, a fact that is generally considered as characteristic for a discrete lattice structure. In Fig. 2, we display energy bands calculated for three cases: an isolated chain with $U=0$ and $U=0.4$, and a bichain system with $t_1=0.05$, $V_d=0.4$, and $U=0.4$. Three groups of bands are presented for every case. They are the band structure of a neutral system, a negative-charge-doped system with a bipolaron, and a negative-charge-doped system with a pair of polarons.

Because of the influence of heteroatoms, the creation energy ε of an electronic excitation is found to be generally different from that of a hole exciton. For example, $\varepsilon_{p-1}=0.88$ eV for an electronic polaron and $\varepsilon_{p-2}=1.30$ eV for an electronic bipolaron. On the contrary, $\varepsilon_{p+1}=1.03$ eV for a hole polaron and $\varepsilon_{p+2}=1.60$ eV for a hole bipolaron. These results are apparently consistent with the criterion (2) which, as we should have emphasized, holds in the isolated PT chain with both the impurity potential and interchain couplings being absent. Moreover, they are also consistent with the conclusion
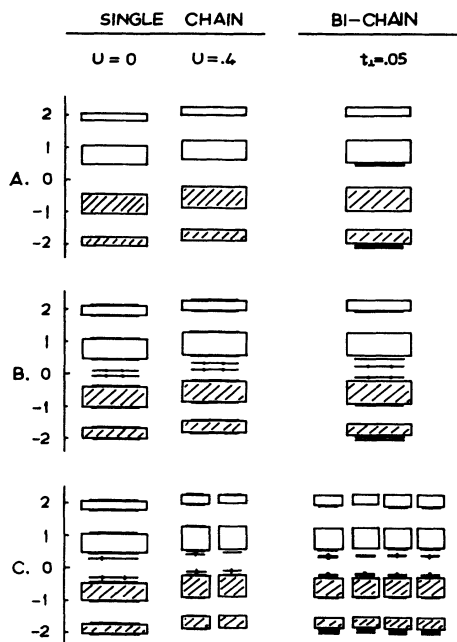
obtained in the Peierls-Hubbard approach.[8,9] Hence our Hamiltonian does yield a reasonable description of heterocycle chains and is qualitatively valid.

Let us now introduce the impurity potential and interchain coupling. In the presence of these interactions, electron transfer between chains is expected to take place in the neighborhood of the heteroatom which serves as a bridge. If the simulation is processed with the initial condition that two impurity-electrons exist in the first chain, leaving the second chain neutral, then a steady bipolaron state located on the double-charged chain will be obtained. The static configuration $\bar{\phi}_n=\frac{1}{4}\sum_{i\in R(n)}\phi_i$ with $\phi_i=(-1)^n(\alpha/t_0)u_i$ and the corresponding net charge distribution $\bar{Q}_n=\bar{Q}_{n,\uparrow}+\bar{Q}_{n,\downarrow}$ calculated for this case is shown in Fig. 3, where we have defined the net charge distribution in the ring n as $\bar{Q}_{ns}=\sum_{i\in R(n)}Q_{i,s}$ $=\sum_{i\in R(n)}(X_{i,s}-0.5)$.

In the absence of the impurity $V_d=0$, the static configuration and the corresponding charge distribution for a bipolaron and a polaron state are plotted in (a) and (b), respectively. When $V_d\neq0$, they are depicted in (c). It is observed that the bipolaron width decreases appreciably because of the impurity attraction. Thus the bipolaron is more strongly localized and the charge density more concentrated in the neighborhood of the counterion. It is also seen from Fig. 3(c) that the lattice in the second chain shows little distortion. On the other hand, the charge distribution is no longer uniform and shows a kind of oscillatory behavior, although it remains to be

FIG. 2. Diagram of energy bands for an isolated chain with an without the e-e interaction, and a bichain system. The energy bands shown are for (a) a neutral system, (b) a negative charge doped system with a bipolaron, and (c) a negative-charge-doped system with a pair of polarons. Open (shaded) rectangles represent conduction (valence) bands and the lines indicate localized energy levels.
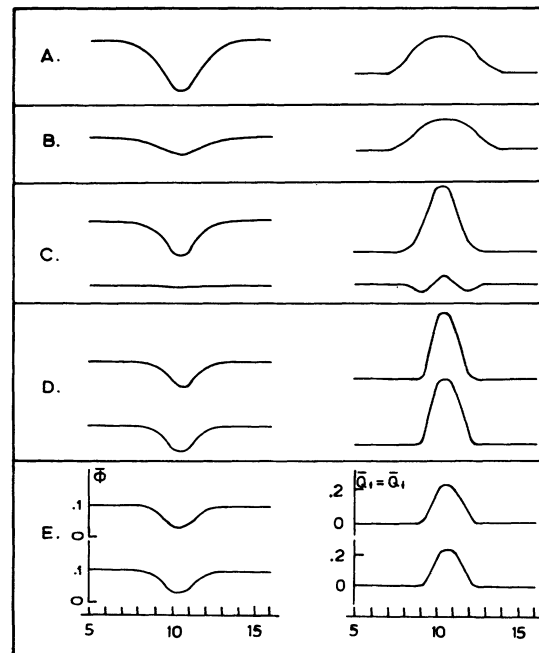

FIG. 3. The static configuration $\bar{\phi}$ and corresponding charge distribution $\bar{Q}$ of different excitations at a heterocyclic ring arbitrarily labeled between 10 and 11: (a) a bipolaron state in an isolated chain, (b) a polaron state in an isolated chain, (c) a bipolaron state in one chain of a bichain system, (d) a triplet state, and (e) a singlet state of a pair of polarons with one on each chain of a bichain system.

neutral and extra charges in the first chain have not transferred. This means that the bipolaron state created is stable even if there exists the interchain coupling. The situation may change, however, if the coupling strength changes. It has been pointed out in a recent study of trans-PA bichain system[22] that the polaron-bipolaron stability does not change continuously with the coupling strength and there exists a critical value of the coupling. We note that the e-e interaction is not considered in Ref. 22, and their results are spin independent.

If each chain has an extra electron initially, then a single-charged polaron state will be formed on each chain separately. Our calculation yields the following two possible states. One is a single polaron state of charge 1 and spin $\frac{1}{2}$. This is the familiar state which is the same as in an isolated chain. The other is a single polaron of charge 1 and spin 0. This is a new type of excited state corresponding to the case of two electrons with opposite spins. Physically this represents one kind of the interchain coupling in which two electrons of opposite spins hop back and forth between the two chains in the neighborhood of the impurity atom, so that each chain shares one electron with spin zero on the average. Two polarons of this type form an interchain trapping state which will be referred to as a "singlet state." When the two electrons hopping between chains have parallel spins, the electron hopping between chains will result in a different kind of interchain coupling. Each chain shares in this case a single-charged polaron with spin $\frac{1}{2}$ on the average, and hence we have a "triplet state."

The lattice configuration and charge distribution for the triplet and singlet states of the interchain coupling are shown in Figs. 3(d) and 3(e), respectively. It is observed that the lattice configuration is about the same in these cases of different kinds of polarons. The charge distribution, however, is apparently different in the two cases. In the triplet state, there is a polaron with spin $\frac{1}{2}$ in each chain and contributes effectively to the polaron charge. The charge of the opposite spin, not shown in Fig. 3(d), remains a uniform distribution in both chains. In the singlet state, on the other hand, a spinless single-charge polaron forms in each chain, and both contribute equally to the charge distribution of the polaron. The singlet and triplet states of two polarons confined to two phenyls of a trans-stilbene chain have been investigated recently[23] on the basis of the combined exact solutions of the Pariser-Parr-Pople model[24] and the semiclassical Parametric Method 3 (Ref. 25) for the π electrons. It was found in Ref. 23 that the bipolaron energy depends on both the charge and spin. Because both the Hückel and SSH theories consider only the linear electron-phonon coupling without e-e interactions, the energy is the same for singlet and triplet states. We find in this work that when the e-e interaction is included, the singlet state has different energy from the triplet states and they are both higher than the bipolaron state.

As a matter of fact, our calculation shows that the two types of polaron states are degenerate if e-e interactions are neglected. The degeneracy is lifted when the e-e interaction is switched on. It is found that the singlet state has a little higher energy than the triplet states. For example, if we take the interchain coupling $t_\perp = 0.05t_0$, the e-e interaction energy $U = 0.4t_0$ and the impurity potential energy $V_d = 0.4t_0$,[26] the energy required to create a triplet state is found to be $\varepsilon^t_{p-1} = 1.90$ eV, or 0.95 eV for each spin-$\frac{1}{2}$ polaron on average. For a singlet state, the required energy is $\varepsilon^s_{p-1} = 1.95$ eV, or 0.98 eV for each spin-0 polaron.

We have also found from our numerical study that the singlet state behaves qualitatively different from the triplet state. It is always energetically higher than the triplet state, and becomes unstable for sufficiently strong e-e interactions, e.g., $U > 1.2t_0$. On the other hand, we find that it required less energy to create a bipolaron state. With the same parameters, we find $\varepsilon_{p-2} = 1.70$ eV. Hence a bipolaron is energetically more favorable than two polarons for either singlet or triplet states. The situation remains unchanged whether or not the interchain coupling is included in the consideration.

The energy difference $\Delta\varepsilon$ required for a bipolaron and a pair of polarons in a bichain system with and without the interchain coupling is computed as a function of the Hubbard U. The results are plotted in Fig. 4 for three cases. The dot-dashed curve represents $\Delta\varepsilon$ when there is no impurity and no interchain coupling. We find $\Delta\varepsilon < 0$ for the e-e interchain $U < U_c = 1.9t_0$, and $\Delta\varepsilon > 0$ for $U > 1.9t_0$. Thus, the processes of bipolaron and polaron creation in an isolated chain will be competing when the e-e interaction energy is in the neighborhood of $1.9t_0$, and the bipolaron-polaron transition can take place when $U = U_c$. In other words, the bipolaron can decompose to two polarons when $U \geq U_c$.

When effects of the impurity pinning and interchain coupling are considered as they are usually present in real polymers, our calculation indicates that $|\Delta\varepsilon|$ reduces in general. The dashed line in Fig. 4 represents the energy difference between a bipolaron and a pair of polarons in the singlet state, and the solid line is that for a bipolaron and polarons in triplet states. It is seen that the two curves start from the same point when $U = 0$ and split as the e-e interaction increases. In other words, the degeneracy of singlet and triplet states is effectively lifted by
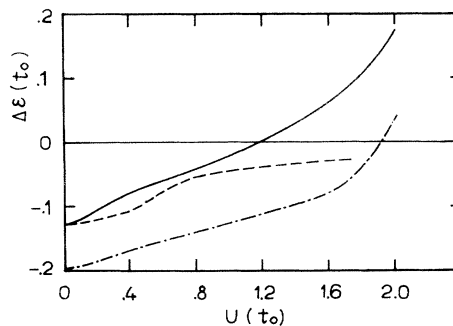

FIG. 4. The creation energy difference $\Delta\varepsilon$ vs e-e interaction U. For a bichain system with $V_d = 0.4$ eV, the solid line represents the triplet-polaron and bipolaron energy difference, the dashed line the singlet-polaron and bipolaron energy difference. The dot-dashed line is the bipolaron-polaron energy difference for an isolated chain.

the *e-e* interaction. The singlet state has always higher energy than the triplet states. It is seen that the dashed line does not seem to intersect the U axis, implying that $\Delta\varepsilon$ remains negative for this case. This is because the strength of electron-electron correlation is nearly the same for bipolaron and singlet polaron states, both are stronger than the *e-e* correlation for triplet polaron states, as is found from the electron-density distribution of these elementary excitations. When the *e-e* interaction increases, the singlet polaron and bipolaron states are no longer stable, but the *e-e* correlation is much weaker in the triplet polaron states which remains stable as U increases indefinitely.

It is also observed that due to the presence of interchain coupling, the critical value U_c decreases from 1.9 to 1.2 eV with increasing V_d and t_1, i.e., the interchain coupling is favorable for the transfer from bipolaron states to polaron states. The situation may be understood in the following fashion. The impurity pinning effect can only increase the localization of either polaron or bipolaron, and at the same time decrease its creation energy. On the other hand, the *e-e* repulsion inside the excitation increases as well because of the localization. This repulsion is particularly strong in a bipolaron compared to the polaron pair. Hence $|\Delta\varepsilon|$ defined in Eq. (1) decreases in size when the impurity potential is included.

It has been pointed out[27] that as the bipolaron is excited in polythiophene by impurity doping, the electron-electron repulsion inside the bipolaron approximately cancels the attraction due to the impurity counter cations. This implies that the stability of bipolarons depends very little on U and V_d. The situation is more complicated than this in realistic case. The present study indicates that under certain conditions, bipolaron and polarons can coexist in the system. Such coexistence has already been confirmed experimentally in ESR measurements of doped PT (Ref. 18) and PSe.[19] Our results can qualitatively account for these observations.

IV. SUMMARY

We have investigated numerically the ground states, the stability of bipolaron and polarons in doped heterocycle polymers by taking into account effects of the interchain coupling, impurity confinement, and *e-e* interactions within the framework for the SSH model. It is found that two single-charged polarons located on neighboring chains interact via the interchain coupling, and lead to the singlet and triplet states. A new type of excitation, a spinless polaron with one unit of charge can exist on one chain due to the interchain coupling when the *e-e* interaction is weak.

Although the Coulomb attraction of the impurity counterion on electrons may bond the bipolaron more tightly, the energy difference $|\Delta\varepsilon|$ between a double-charged bipolaron and two single-charged polarons decreases with increasing U and V_d. Under certain conditions, this energy difference may vanish, so that bipolaron-polaron transitions become possible and bipolaron and polarons can coexist.

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chosen from the following considerations. Generally speaking, t_0 is around 2–2.5 eV according to the tight-binding model. The band width along the chain is $W = 4t_0$ or 8–10 eV. Because of the weak interchain coupling, the transverse band width is of the order of 0.1 eV. Hence we take $t_\perp \sim 0.05 t_0$. For the impurity potential energy, we assume it to be a half of the maximum screened Coulomb energy or $0.4 t_0$, which is also taken as the e-e interaction energy U.

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