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Energetic study of polarons and bipolarons in polythiophene: Importance of Coulomb effects

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We study the effect of Coulomb interactions on the formation of polarons and bipolarons in polythiophene. First, the interaction of an ionized dopant is considered and these defects are found to be always energetically favored upon doping, bipolarons being the lowest-lying charged excitations. The influence of the Coulomb repulsion associated with the double occupation of the gap levels that occurs in bipolarons is then investigated within a phenomenological model. This interaction leads to a modification of the different equilibrium parameters and reduces appreciably the difference between the creation energy of a pair of polarons and that of a bipolaron. However, this contribution is not strong enough to destabilize bipolarons that remain the most stable excitation. Implications of these results for the existence of polarons are discussed depending on whether the excitations are photogenerated or created by doping.

I. INTRODUCTION

The organic conducting polymers have attracted considerable attention and many studies$^{1-18}$ have demonstrated that kinks such as solitons, polarons, and bipolarons play a fundamental role in determining their electronic properties. Recently, polythiophene (PT) has been the focus of considerable research interest because of its chemical stability. PT consists of chains of successive heterocycles formed by a sulfur atom covalently bound to carbon atoms [Fig. 1(a)]. This structure appears to be rather similar to a polyacetylene chain weakly interacting with the sulfur atoms. As shown in Fig. 1(b), a resonance structure can be derived for PT by permutation of single and double bonds between the carbon atoms, and the configuration 1(a) is energetically more stable than the configuration 1(b). Unlike *transpolyacetylene*, PT does not have a degenerate ground state, and elementary excitations as topological solitons cannot exist. Thus the large coupling between the lattice deformation and the elementary excitations will lead to the formation of defects like polarons and bipolarons [Fig. 1(c)], which are the dominant charged species. The existence of localized lattice deformation affects markedly the electronic structure of the polymer chain. For polymers with nondegenerate ground state, the main effect lies in the appearance of two localized electronic states associated with kinks. As the total number of electronic states in π bands is conserved, each one of the conduction and the valence bands have a deficit of a state for each spin. Since the valence band is always fully occupied both with and without kink, it follows that in a neutral polaron, two electrons are missed by the valence band and are going to occupy the lowest state in the gap, the highest one being empty. However, such a neutral defect cannot be stable apart from particular circumstances as, for instance, chemical impurities or structural imperfections. In the case of p-type doping (similar arguments can also be held for n-type doping), an acceptor impurity removes one electron from the chain and the presence of the hole created in this way stabilize the lattice deformation giving a hole polaron P^+. The lost electron comes from the highest occupied energy level. Therefore the lower gap level has only one electron, as shown in Fig. 2(a). As the valence band remains spin paired, while this electron is unpaired, the polaron has a spin of one-half. When this electron is removed in turn from the chain, a hole bipolaron that is a doubly charged defect is formed and the lowest level is then empty [Fig. 2(b)]. The bipolaron has zero spin and no resonance can be associated with this excitation. Also, magnetic experiments may be used to obtain direct evidence for the existence of polarons on polymer chains. Bipolarons can be also accomplished by recombination of two polarons according to the reaction $P^+ + P^+ \longrightarrow (\mathrm{BP})^{2+}$. The hole polaron states in the

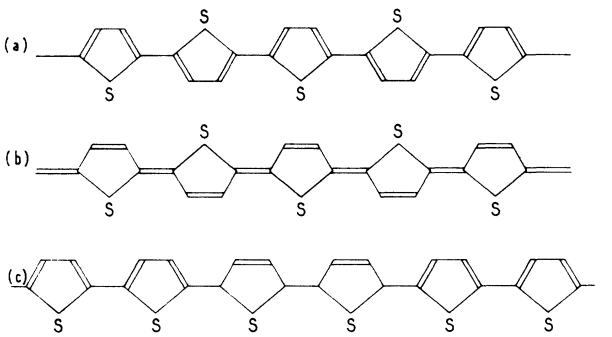

FIG. 1. Schematic diagram of chain structure (a) for perfect polythiophene, (b) for the resonance form of higher energy, and (c) for a chain with a defect as polaron or bipolaron. In the last case, the alternated orientation of two adjacent rings is not shown.

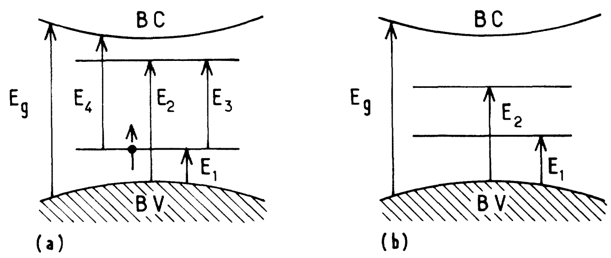

FIG. 2. Energy level diagram showing allowed optical transitions and occupation of localized energy levels for polythiophene chain with a (a) hole polaron and (b) a hole bipolaron.

gap may be at the origin of four transitions in the optical spectra from the valence band and the lower gap level to the conduction band and the upper level. For a chain with bipolarons, transitions from the lowest level cannot exist because it is empty and only the two transitions originating from the valence band remain possible. Thus polarons and bipolarons are excitations which differ in their optical and magnetic properties because the existence of the unpaired electron of the polaron gives rise at the same time to two additional transitions in the gap and to a spin resonance.

The creation of charged defects upon doping is experimentally attested by some recent studies of the optical and magnetic properties. The evolution of the optical absorption spectra of PT during electrochemical doping process has been studied for a large range of doping concentrations and for two sorts of dopant molecules.[3-8] All the spectra show important modification of absorption features which are interpreted as a charge storage by formation of kinks. Except at dilute concentrations where changes in optical spectra might be attributed to polarons, the absorption data are consistent with the concept of charge storage in bipolarons.[4-7] On the other hand, several electron-spin resonance (ESR) studies[5,9-11] have been performed on PT in order to identify the nature of the charge states induced by the doping. However, the experimental situation is somewhat complex and the results differ about the presence of mobile spins at dilute regimes. Recent photogenerated ESR data reported by Vardeny *et al.*[12] indicate no spin in the low concentration regime and the authors conclude that the dominant photocarriers in PT are bipolarons. From the detailed study of the spectra, they show the influence of the Coulomb contributions on the creation energy of the defects according to whether these are induced by doping or by photogeneration. In the first case, for doping-induced polarons and bipolarons, the attraction of the dopant ion as well as the Coulomb repulsion associated with the double occupancy of the gap states must be taken into account. The impurity potential lowers creation energy of the defects by an amount which is denoted V_P for a pinned polaron and V_B for a pinned bipolaron. On the other hand, Coulomb repulsion between the two holes of a bipolaron $(\mathrm{BP})^{2+}$ increases the creation energy of the defect by U_B. In the second case, for photogenerated defects, there is no impurity potential and only the Coulomb interaction due to the double charge of the defect exists. This repulsion favors a configuration with two separated polarons and modifies the thermal equilibrium because the ratio of the polaron and bipolaron populations depends on the difference between the creation energy of a polaron E_P and that of a bipolaron E_B through the factor $\exp[(E_B-2E_P)/kT]$. Form analysis of optical absorption spectra, E_B-2E_P has been evaluated about 0.17 eV (Refs. 13 and 15) while a theoretical energetic study which does not take into account any explicit Coulomb interaction gives 0.43 eV.[14] In view of the importance of this variation, it would be interesting to evaluate more precisely the influence of Coulomb interactions which have not been explicitly considered and which can affect markedly the characteristics of polaron and bipolaron excitations.

We present in this paper a theoretical study of Coulomb effects on the polaron and bipolaron in PT in the framework of the Hückel theory. Calculations are carried out for the PT case; however, results for the other nondegenerate-ground-state polymers would be rather similar. We describe in Sec. II our Hamiltonian model and the parametrization used for PT. Results of the energetic study and the properties of polaron and bipolaron excitations in presence of interaction with dopant molecules are presented in Sec. III. Section IV contains a discussion of the implications of these results and proposes a coherent picture of polaron and bipolaron energetics in the presence of an impurity. The influence of Coulomb repulsion associated with double occupancy of gap states is then considered. This paper is concluded in Sec. V.

II. THEORETICAL MODEL

Our study of electronic excitations in PT has been performed in the framework of a generalized version of the Su-Schrieffer-Heeger (SSH) Hamiltonian[16] for nondegenerate-ground-state polymers. We will summarize the assumptions made in this one-electron theory. First, we consider PT as a linear arrangement of thiophene monomers. Interchain interactions are then neglected; however, as in $(\mathrm{CH})_x$, their influence should not alter strongly our results. Within the Hückel approximation, the π and σ electrons are not treated in the same manner. We consider only the π electrons explicitly because they are responsible for the electronic properties of PT in the neighborhood of the fundamental gap, the effect of σ electrons being taken into account in terms of bonding forces. This approximation is analogous to those used for other conjugated polymers as $(\mathrm{CH})_x$, polyparaphenylene (PPP),[17] and polypyrrole (PPy).[18] Moreover, a recent *ab initio* crystal orbital calculation[19] as well as a valence effective Hamiltonian (VEH) calculation[20] have shown that σ bands lie lower in energy than the π bands, which confirms our assumption for PT. The π electron Hamiltonian is

$$H_\pi=\sum_n \varepsilon_n C_n^\dagger C_n+\sum_{n,m\,(<n)} t_{n,m}(C_n^\dagger C_m+C_m^\dagger C_n)\ , \tag{1}$$

where $C_n^\dagger$ and C_n are the creation and annihilation operators. ε_n is the one-site Coulomb integral which is chosen equal for all the carbon atoms. The variation of the Coulomb integral $2\Delta\alpha = \varepsilon_C - \varepsilon_S$ with the chemical nature of the atom is treated as an adjustable parameter. The hopping integrals $t_{n,m}$ between atoms located on n and m sites are given by a Coulson-type relation[21]

$$t_{n,m} = -A \exp\left[\frac{r_{n,m}}{B}\right] , \qquad (2)$$

where $r_{n,m}$ is the bond length between n and m atoms. Furthermore, the nearest-neighbor approximation has been used for the hopping integrals, and the C—S transfer integral which is rather weak is, as commonly adopted, modeled with a scaling multiplicative constant $k_{\text{C—S}} = 0.6$.[22] σ electrons are described in the adiabatic approximation and contribute to the total energy by an elastic energy term,

$$f(r_{n,m}) = Ct_{n,m}(r_{n,m} - r_0 + B) , \qquad (3)$$

where r_0 is the length of a pure sp^2 bond. The value of parameters A, B, C, and $\Delta\alpha$ are determined in order to reproduce some experimental or theoretical results on the PT ground state: (i) the experimental band gap of 2 eV (ii) a 5-eV bandwidth of the two highest occupied π bands, (iii) the experimental bond lengths of the PT ground state,[23] and (iv) the distribution of the π charges on the heteroatom as calculated by the Hartree-Fock method.[24] All these conditions give $A = 20.3$ eV, $B = 0.86$ Å, $C = 3.79$ Å^{-1}, and $\Delta\alpha = 0.55$ eV; and for the bond lengths, within the rings, $r(\text{C—C}) = 1.36$ Å, $r(\text{C—C}) = 1.43$ Å, and $r(\text{S—C}) = 1.72$ Å; and between the rings $r(\text{C—C}) = 1.48$ Å.

The electronic structure of neutral PT is obtained providing Eq. (2) with appropriate bond lengths of neutral PT and then by diagonalizing the Hamiltonian (1). One can easily use this Hamiltonian for the study of polaron or bipolaron excitations. In this case, the bond lengths $r_{n,m}$ used in Eqs. (2) and (3) must be those of a PT chain with a localized bond deformation like in Fig. 1(c). By analogy with the solutions of the continuum model, we have chosen to represent the lattice deformation associated with the presence of polaron and bipolaron by hyperbolic functions. The length variation $\Delta r(s)$ for the bond of the s-type between the atom located at x and one of its nearest neighbors is described by

$$\Delta r(s) = \frac{\Delta_0(s)}{2}\left[\tanh\left[\frac{x+D/2}{L}\right] - \tanh\left[\frac{x-D/2}{L}\right]\right] , \qquad (4)$$

where $\Delta_0(s)$ is the maximum amplitude deformation of the s-type bond with respect to the bond length in neutral PT. The values chosen for $\Delta_0(s)$, which correspond to the quinoidlike structure shown in Fig. 1(b) are the following: within the ring, $\Delta_0(\text{C}=\text{C}) = 0.13$ Å, $\Delta_0(\text{C—C}) = -0.13$ Å, and $\Delta_0(\text{S—C}) = 0.11$ Å; and between the rings, $\Delta_0(\text{C—C}) = -0.22$ Å. This trial function can be viewed as a soliton and an antisoliton with the same half-width L and separated by D. That leads to a defect length definition $l = D + 2L$. D and L are two adjustable parameters to be varied so as to minimize the total energy of the system. Other forms of distortion have been used in other works with similar results for the energy of the polaron state.[25]

To model the perturbation introduced by an ionized dopant molecule on the electronic spectrum, we assume that the interaction between the impurity and the π electrons is simply a long-range Coulomb potential given in the case of a monovalent acceptor by

$$V = \sum_n V_n C_n^+ C_n \quad \text{with } V_n = \frac{e^2}{\epsilon(x_n^2 + d^2)^{1/2}} ,$$

where x_n denotes the location of the nth π orbital on the PT chain. d is the distance between the impurity and the chain; in the following we choose $d = 2$ Å and ϵ the bulk static dielectric constant equal to 10. This approximation ignores the anisotropy of the screening and local corrections for the sites near the impurity where the screening is incomplete. Because of the complexity of more sophisticated treatments which take into account these effects, we have limited our attention to this phenomenogical model which must provide some insight into the role of dopants.

The total energy of the system is the sum of an elastic and an electronic contribution. The elastic energy is a summation on all the bonds of the energy given by Eq. (3). The electronic energy has the form

$$E_{\text{el}} = \int_{-\infty}^{E_F} zN(z)dz .$$

The summation extends over all occupied states. $N(z)$ is the total density of states which can be calculated from the relation

$$N(z) = -\frac{2}{\pi}\text{Im}[\text{Tr}G(z)] ,$$

where $G(z)$ is the Green's function of the π Hamiltonian,

$$G(z) = (z - H_\pi)^{-1} .$$

The matrix element of the Green's function is obtained by a recursive method[26] and the positions of the bound states are found as poles of the Green's function.

In order to avoid spurious divergences with the Coulomb potential at infinity, the total energy of the configurations will be calculated with regard to a reference state taken as that of a perfect chain in the presence of the impurity with the same charge transfer as that of the kink. Our calculations are performed on finite PT chain up to 200 atoms, which is sufficient to model properties of the infinite chain.

III. POLARONS AND BIPOLARONS PINNING BY ACCEPTOR IMPURITY

We have first considered the influence of the dopant potential on the electronic structure of PT in the absence of any polaron or bipolaron on the chain. In case of p-type doping, one electron is transferred from the chain to the acceptor and the electronic structure of PT is distorted by the Coulomb potential due to the dopant charge. A

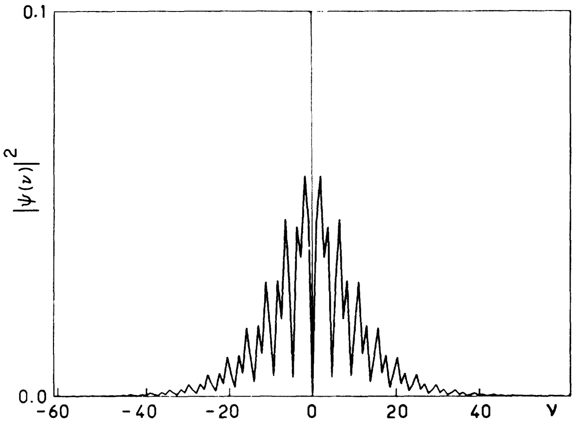

FIG. 3. Probability density of the impurity level vs atomic position for a PT chain with 27 rings.

discrete energy level is extracted from the valence band and appears in the gap at 0.21 eV above it. This "impurity" state is twice degenerate and is occupied by an electron. The probability density $|\psi|^2$ for this state is plotted on Fig. 3 versus the atomic site number for a PT chain with 27 rings. This state is localized and 75% of the hole charge is contained in an extent of about 20 Å. This configuration will be taken as the energy reference configuration for the study of the pinned hole poloran because the charge transfer is the same in the two cases; this is shown on Fig. 6(d), which corresponds to a configuration with two pinned holes without interaction. Let us now consider a PT chain with a polaron in presence of an impurity [Fig. 6(e)]. After minimization of the energy with repsect to L and D, the energy of this configuration is found to be lower than this of the reference state by an amount $\Delta E(P_I^+)=0.17$ eV. Therefore the doping process occurs through the formation of charged polarons pinned by the impurities. Ignoring the

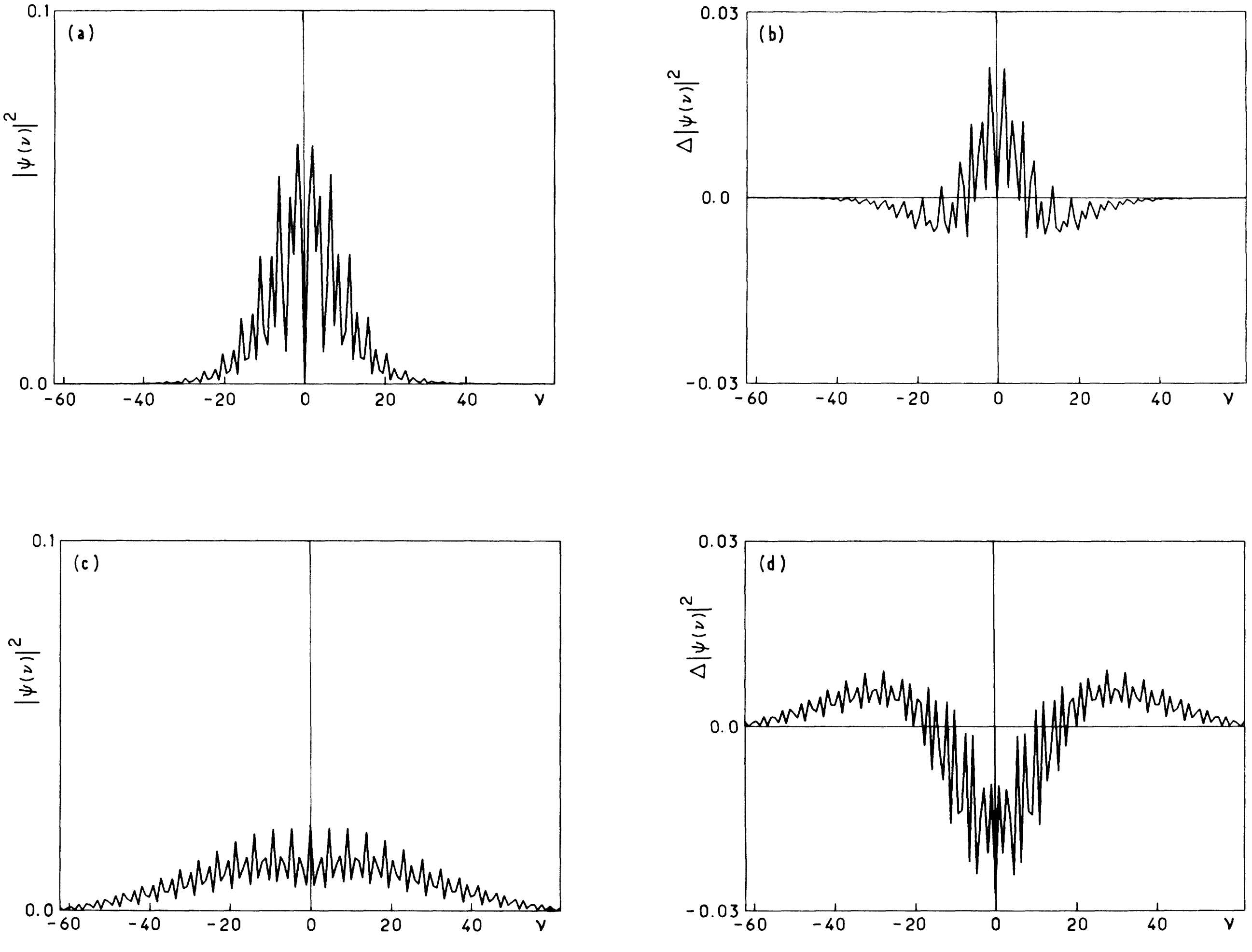

FIG. 4. Probability density of pinned hole polaron for (a) the lower level and (c) upper level and variation of these densities with respect to the free polaron case for (b) lower level and (d) upper level.

Coulomb potential, the binding energy of a hole polaron have been found to be equal to $\Delta E(P_0^+)=0.12$ eV.[14] There is a slight increase in the binding energy and consequently the impurity potential increases the stability of a charged polaron by 0.05 eV. The value calculated for PT agrees well with these found in polyacetylene, which is $\Delta E(P_I^+)=0.16$ eV.[25,27] The equilibrium lengths are $D=2$ and $L=2.6$, which leads to a polaron width $l \simeq 7$ rings (29 Å). Without impurity potential, the corresponding values are $D=3$, $L=3$, and $l \simeq 9$ rings (36 Å). The presence of the impurity reduces then the polaron length of 20%, while the amplitude of deformation decreases from 46% to 37% of the maximal deformation.

One expects three localized levels in the gap: two corresponding to the presence of a polaron on the chain, the third being an impurity level. The first two levels move towards the conduction band by an amount of 0.3 eV, which is close to the mean value of the Coulomb potential. As this shift is next to the distance between the highest polaron level and the conduction band, this level merges with the conduction band edge and only two levels lie in the gap. The lower polaron state is located at 0.54 eV above the valence band edge. The impurity level lies at 0.1 eV above the valence band, closer than without a polaron, indicating that the polaron and the impurity levels repel each other. The probability density $|\psi|^2$ of each polaron level and its variation with respect to the case without impurity are plotted on Fig. 4. One can clearly see an increase in the probability density near the impurity which corresponds to a localization of the lower level under Coulomb pinning [Figs. 4(a) and 4(b)]. This is consistent with the larger localization of wave function for deeper level in the gap. Contrary to this level, the probability density of the upper state decreases around the impurity and a large delocalization of the wave function is observed [see Figs. 4(c) and 4(d)] in agreement with the merging of the level in the conduction band.

Let us now consider the case of bipolarons which are doubly charged defects and take the same reference state as previously [Fig. 6(d)]. By minimization versus L and D, the energy of the configuration formed by a bipolaron pinned to an impurity is 0.73 eV lower than that of the

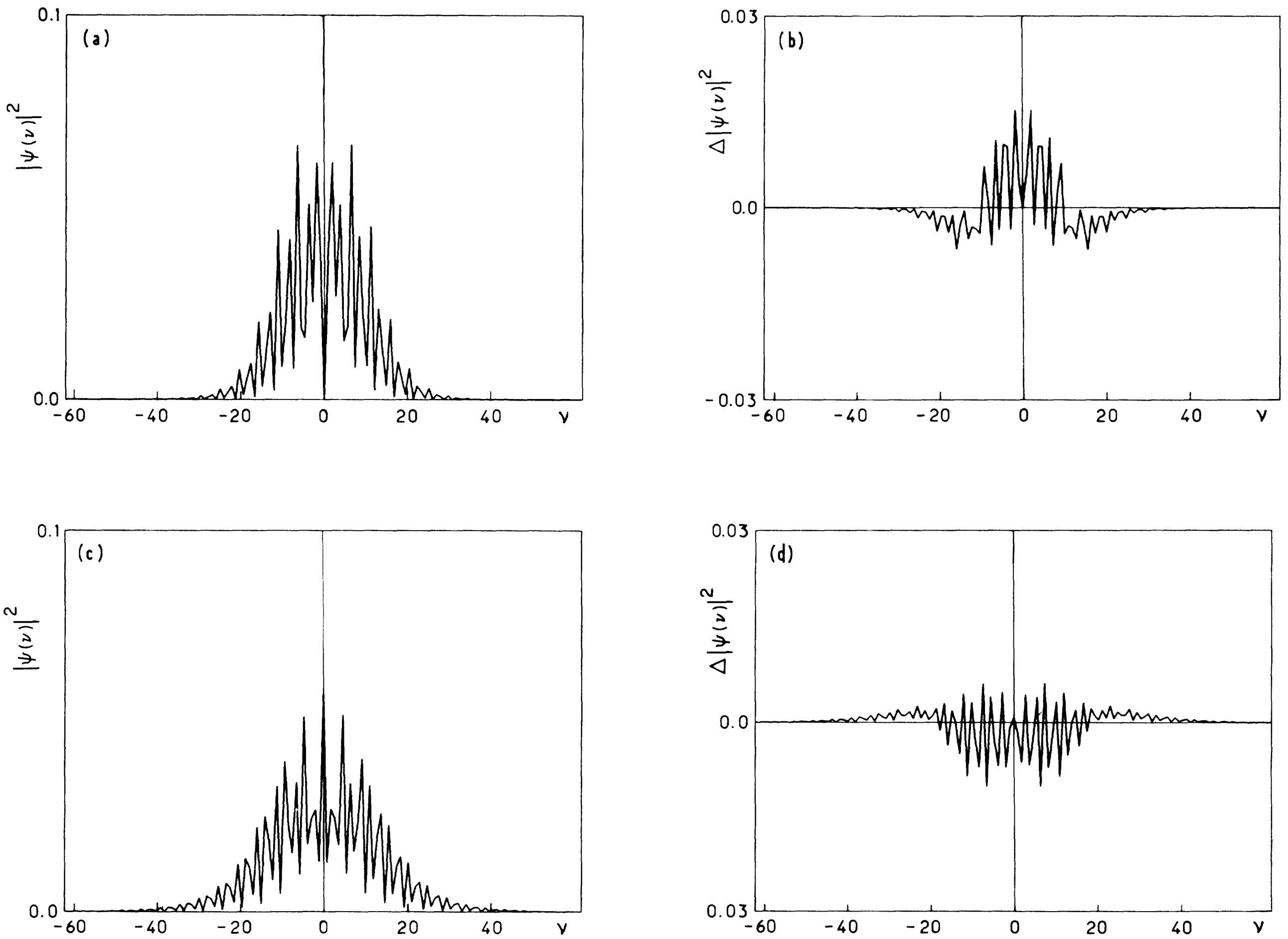

FIG. 5. Probability density of pinned hole bipolaron for (a) the lower level and (c) upper level and variation of these densities with respect to the free bipolaron case for (b) lower level and (d) upper level.

reference state. Like in the polaron case, only a small difference of 0.06 eV is found with the binding energy of a bipolaron without impurity. Doping through bipolarons is always a more probable event than the traditional doping process for semiconductors. The same trends as in the polaron case are observed for defect width and deformation. The equilibrium lengths are $D=4$, $L=1.4$, and $l\simeq 9$ rings. The bipolaron width decreases by about 13% from 31 to 27 Å and the amplitude is 89% of the maximal deformation instead of 95% without impurity. However, contrary to the polarons, the three levels expected lie in the gap. As the deformation of bond lengths is larger for bipolaron than for polaron, the bipolaron gap states are deeper than the polaron states and the strength of the Coulomb potential is not sufficient to merge the upper level in the conduction band. The upper level is at 0.33 eV from the condution band while the lower is about the midgap at 0.91 eV from the valence band edge. The impurity level at 0.2 eV from the valence band is deeper than in the pinned polaron case. The probability density of the two upper levels is shown on Fig. 5. The upper level, pulled up near the conduction band, is slightly delocalized [Figs. 5(c) and 5(d)]. The density is nearly the same as for the free bipolaron with only a weak decrease in the impurity neighboring. The lower level density is much altered and its important increase near the impurity displays the localization [Figs. 5(a) and 5(b)].

To summarize, the effects of an impurity potential on hole polarons and bipolarons are the appearance of an impurity level near the valence band, the shift of the polaron and bipolaron levels towards the conduction band, no significant change of the creation energies of the hole defects, and decrease of length and amplitude of the lattice deformation.

IV. ENERGETIC STUDY

We now analyze these different results in order to obtain the creation energies of the defects with or without impurity. We first review the characteristics of the different states involving kinks with or without impurities. For simplicity, we have considered configurations corresponding to the same charge state with two holes transferred from two dopant molecules to a PT chain. In the first three configurations, we considered two holes or kinks kept away from each other and both alike located very far from two infinitely separated acceptors. These states correspond to neglecting the influence of the Coulomb potential of the dopant molecule. The first configuration that we will take as the reference energy state is a PT chain with two holes without interaction between them and with the acceptors [Fig. 6(a)]. These two free holes are in the state of lower energy at the top of the valence band. The energy of that configuration is taken as origin $E_a=0$ eV. As previously quoted,[14] this system is not in its lowest energy state and a lattice distortion arises around the holes and gives rise to two free polarons P_0^+. Figure 6(b) displays this configuration of two free polarons and corresponds to the neglecting of Coulomb potential on polarons. The energy of this configuration is equal to twice the free polaron energy

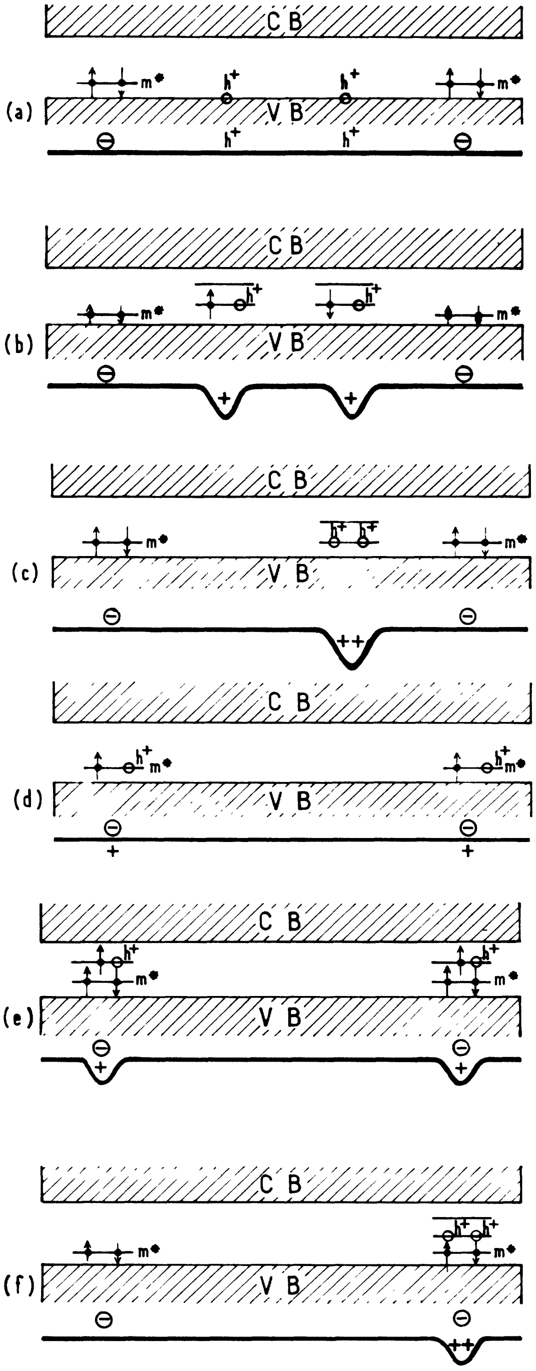

FIG. 6. Configurations of two impurities and two holes on a PT chain. The first three configurations describe the case of two holes kept away from each other and lying very far from two infinitely separated acceptors. They correspond to the neglecting of the impurity potential on (a) two holes, (b) two hole polarons, and (c) one hole bipolaron. In the following three configurations, the attractive interaction of the dopant molecule is considered and the holes are located near the acceptors, giving (d) two pinned holes, (e) two pinned polarons, and (f) one pinned bipolaron. θ denotes the position of the acceptor dopant molecules, CB and VB the conduction and the valence bands. The bold straight line symbolizes the deformation of the PT chain. The gap states diagram near the acceptors and near the defects with the occupation of levels is shown, the impurity level being indicated by m^*.

$E_b=-2\,\Delta E(P_0^+)=-0.24$ eV. As the two polarons can recombine into a bipolaron through the reaction $P_0^+ + P_0^+ \longrightarrow (\mathrm{BP})_0^{2+}$, a third configuration shown in Fig. 6(c) will be obtained and the energy gain is that of a free bipolaron formation $E_c=-0.67$ eV.

In reality, as discussed in this paper, holes, polarons P_0^+ and bipolarons $(\mathrm{BP})_0^{2+}$ are under the influence of the impurities and we now review the changes which result from it. In the traditional semiconductor picture, each impurity donates a hole to the valence band and the holes are pinned by the Coulomb potential. This configuration with two pinned holes [Fig. 6(d)] has been chosen as reference state in our calculation on charged states in the previous section. Its energy is equal to twice the energy of the impurity level, which gives $E_d=-0.42$ eV. As shown in Sec. III, the configuration does not correspond to the lowest energy state and the creation of two pinned polarons decreases the energy by $2\,\Delta E(P_I^+)$. Thus the energy of this configuration shown in Fig. 6(e) is $E_e=E_d-2\,\Delta E(P_I^+)=-0.76$ eV. We can now evaluate the change in the formation energy V_P of a polaron whether the attraction of the dopant ion is considered or not. The difference between the configurations 6(b) and 6(e) enables us to obtain $2V_P=E_b-E_e$ and $V_P=0.26$ eV. The change from 6(e) to 6(b) can be viewed like the trapping removal of two hole pinned polarons P_I^+ to two free polarons P_0^+. It requires 0.26 eV for each polaron. In reality, this result holds for infinitely separated polarons, for a given doping level, the Coulomb potentials centered on impurities overlap which can significantly reduce V_P. The value of the barrier energy V_P is therefore very sensitive to the relative position of the two impurities and 0.26 eV is an upper limit in the case of dilute concentrations and weak dopant diffusion. This theoretical value of V_P almost agrees with the one obtained for the soliton in $(\mathrm{CH})_x \simeq 0.3$ eV.[25,27] In the case of a pinned hole bipolaron $(\mathrm{BP})_I^{2+}$ [Fig. 6(f)], we have obtained in Sec. III that the energy with respect to the configuration shown in Fig. 6(d) is $\Delta E((\mathrm{BP})_I^{2+})=0.73$ eV, which leads to $E_f=-1.15$ eV. On the other hand, $E_e-E_f=0.39$ eV is the energy difference involved in the reaction $P_I^+ + P_I^+ \longrightarrow (\mathrm{BP})_I^{2+}$. This energy is slightly reduced by the impurity presence, the corresponding value for free kinks being $E_b-E_c=0.43$ eV. The pinning energy of bipolaron V_B can be obtained by comparison between the two configurations c and f so that $V_B=E_c-E_f=0.48$ eV is the change on the formation energy produced by the pinning of a free bipolaron. This value confirms the result $V_B \simeq 2V_P$ that we have previously inferred from the characteristics of kinks.[14] Since the spatial extent of polarons and bipolarons is nearly the same while the ratio of their charges is 2, it follows that the bipolaron pinning energy is approximatively twice as large as the polaron one V_P. It is sometimes expected that the energy shifts of the levels in the gap produced by an impurity are of the same order as the binding energy of the defects trapped on this impurity. Our results show that it is an oversimplified point of view. For instance, for pinned bipolaron $(\mathrm{BP})_I^{2+}$, $V_B=0.48$ eV, the shifts of the two gap levels from their positions in free bipolaron are 0.18 and 0.34 eV for the lower and upper levels, respectively. The corresponding shifts are 0.18 eV and more than 0.28 eV for the P_I^+ polaron levels. These differences are originated in the symmetry of the wave function of the levels. Since the defects are mirror symmetric about their center, the wave functions must be symmetric or antisymmetric under this transformation. By treating the Coulomb potential V_C as a perturbation, one can estimate its effect on the energy of a gap state ψ from the value of the matrix element $\langle \psi | V_C | \psi \rangle$. For a symmetric state, the probability density $|\psi|^2$ is maximum at the center of the kink, near the impurity, in a region where the Coulomb potential is large. Contrary to this, an antisymmetric state has a density which is zero in this region and the Coulomb contribution to the energy is weaker than for a symmetric state. It follows that care must be taken in obtaining the V_B and V_P values from the optical shifts of transitions to the gap levels. Only a rough estimate of V_B and V_P can be obtained by this approach.

Another Coulomb effect that has been neglected in our calculation is the U repulsion associated with the double occupation of a gap state for the bipolaron. To investigate the influence of this interaction, we have introduced a simple phenomenological model and we have assumed that the effective Coulomb repulsion is of the form used by Rice and Mele[28] in their study on $(\mathrm{CH})_x$:

$$U(l)=\frac{U_0}{\epsilon(lb)} .$$

Here, ϵ is the PT bulk dielectric constant, l the equilibrium bipolaron length (in number of cycles) which accommodates the two charges, and b is the PT lattice constant. We have taken for U_0 the same value as for $(\mathrm{CH})_x$, $U_0/a\epsilon=5.3$ eV, where a is the $(\mathrm{CH})_x$ lattice constant. The same $1/l$ dependence is found with the SSH Hamiltonian improved with a first-order perturbation Hubbard term.[29]

This correction must be added to the total energy of the configurations involving bipolarons, and the total energy has to be minimized again with respect to the length l, which depends on L and D parameters. In the case of a free bipolaron with hole-hole repulsion, the minimization of the total energy is obtained for $D=5$ and $L=2.2$ (Fig. 7). This leads to an increase of the bipolaron length to $l=9.4$ rings (37.6 Å). The creation energy of a free bipolaron is $E_g=-0.48$ eV; it is reduced by an amount $U_B=0.19$ eV with respect to the case where this repulsion is not considered (configuration c). This value of U_B is coherent with the value (0.25 eV) deduced by Vardeny *et al.* from their experiments,[12] which is rather weak and causes a considerable consequence in the free polarons recombination process into bipolaron. Even with U_B contribution, the energy of a free bipolaron is still weaker than those of two free polarons,

$$E_g-E_b=-0.24 \text{ eV} .$$

The bipolaron is the most stable excitation, and the creation of free bipolaron as in photogeneration experiments, for instance, is greatly favored as compared to the creation of two polarons.

The same optimization process of L and D has been performed for pinned bipolaron with hole-hole repulsion. The minimum of the total energy is reached for $D=4$ and $L=1.8$ (see Fig. 7) and the estimated length is $l=7.6$ cycles (30.4 Å). The creation energy of a pinned bipolaron is $E_h=-0.93$ eV. This is weaker than in the case without U interaction (configuration f) by an amount of $U_B^d=0.22$ eV. Considering all the Coulomb contributions, the energy difference between a bipolaron and two polarons is equal to $E_h-E_e=-0.17$ eV and the bipolaron is always the lowest excitation induced by doping. The optimized characteristics of bipolarons as width and deformation amplitude are slightly different and depend on whether impurity is present or not, as shown in Fig. 7, where the variation of the total energy in function of these parameters has been represented. The equilibrium values result from opposite effects of potential impurity and of the repulsive Coulomb potential. The latter tends by itself to move the two holes away from each other and causes an increase of the bipolaron length. The former adds an attractive effect which give rise to a localization and reduces this length. The Coulomb repulsion U_B will be greater for two charges localized on an smaller extent and that causes U_B^d to be higher than U_B. The same trends have been observed for $(CH)_x$ in Ref. 28.

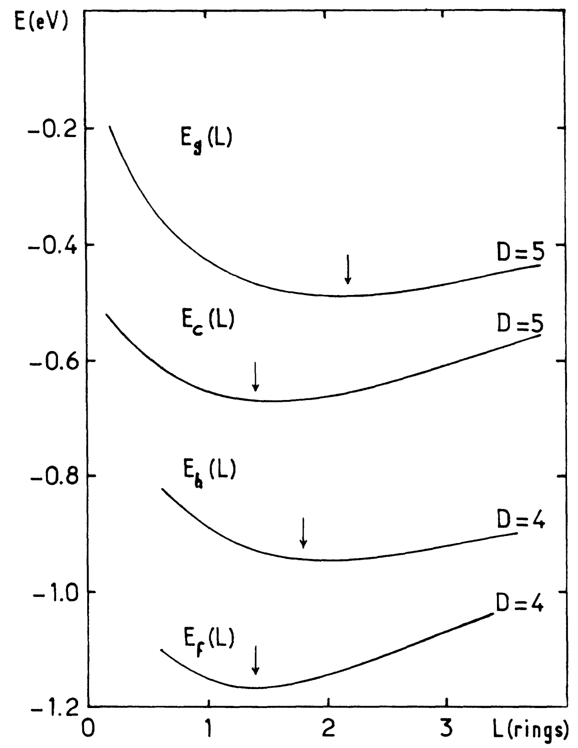

FIG. 7. Total energy of a bipolaron vs parameter L for the D equilibrium value for a free bipolaron (E_c), a free bipolaron with Coulomb repulsion (E_g), a pinned bipolaron (E_f), and a pinned bipolaron with Coulomb repulsion (E_h). The arrows indicate the equilibrium value for L.

The energies of formation of kinks are of crucial importance to know if bipolarons are the lowest energy charged configurations. Let us examine successively the two experimental ways of creating bipolarons and polarons. In the case of photogeneration of defects, we have shown that the interaction of two free polarons produces a bipolaron with an energy gain of 0.24 eV. It follows that photogenerated polarons must recombine in bipolarons. This result agrees well with the photoinduced absorption data,[12] which indicate that charges are stored in spinless bipolarons. However, at a low rate of photogenerated charges, few polarons could exist if they were trapped by impurities, structural defects, or disorder, which prevent their recombining into bipolarons. This is consistent with the decrease in the number of polarons by improvement of the structural order by the PT sample annealing.[30] Analysis of theoretical and experimental results leads to a relatively small value of Coulomb repulsion between charges stored in biploran: $U_B/E_g \simeq 0.1$.[12] For defects created by doping, our results indicate that the recombination of polarons into bipolarons must be expected because this corresponds to an energy gain of about 0.17 eV. However, the decay of a pair of polarons is only possible if they are free to diffuse and a charged polaron is bound rather strongly to the charged impurity by a pinning energy V_P. This gives a barrier to recombination of a pair of widely separated polarons because the charge on a polaron must be removed from this Coulomb interaction before being pulled up to the second pinned polaron. This barrier depends on many phenomena such as the diffusion of the dopant molecules and is difficult to evaluate. Moreover, with increasing doping level, the impurity potentials overlap and the energy barrier is lowered in a complex manner. However, we can point out some qualitative trends of the V_P effects. At low doping level, V_P has to be considered and leads to the enhancing of the number of polarons at the expense of the number of bipolarons. At higher doping level, the lowering of V_P makes the bipolaron creation from polarons easier. The experimental presence of polarons at low doping level can be then understood by the existence of the pinning potential in spite of the fact that a pinned bipolaron is energetically favored with respect to two pinned polarons.

At higher doping level, only bipolarons are experimentally found which is consistent with our results which show that they are the lowest energy configuration.

V. CONCLUSION

In conclusion, we have presented in this work the main effects that the Coulomb repulsion and the attraction of dopant can have on the electronic properties of polarons and bipolarons in polythiophene. This study has been carried out within the framework of the Hückel approximation for chains with polaron and bipolaron deformations and long range impurity potential. The binding energy of these defects pinned by an acceptor has been calculated taking into account the lattice relaxation. Hole polarons and bipolarons are found to be energetically stable with respect to the direct transfer of holes from the dopant molecules to the valence band. The length and amplitude of the two kinks are reduced, the discrete energy levels in the gap are pushed up and an impurity level appears near the valence band, according to the attractive effect of the impurity potential. All those features agree well with previous calculations in $(CH)_x$.[25,27] Then the Coulomb repulsion associated with the presence of two holes in a bipolaron has been included within a phenomenological model in order to obtain trends for its influence on the defects. This repulsion leads to an increase of the length and creation energy of the defect. These effects are only slightly lowered by the impurity presence. Finally, a coherent scheme for the energetics of polarons and bipolarons is obtained. The contribution of the Coulomb repulsion associated with the double charge of the bipolaron is found to be sufficiently weak to permit the polaron recombination into bipolarons, whether they are created by doping or by photogeneration as well. However, in the case of weak doping, the polaron presence could be explained by their pinning on the impurity which prevents them from interacting.

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