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Competition between polarons and bipolarons in nondegenerate conjugated polymers

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The formation of polarons and bipolarons in conjugated polymers with nondegenerate ground states is studied theoretically. We use the Pariser-Parr-Pople model combined with the Su-Schrieffer-Heeger model of electron-lattice coupling and a Brazovskii-Kirova-type symmetry-breaking interaction. The relative stability of polarons and bipolarons is systematically studied within the unrestricted Hartree-Fock approximation as a function of the model parameters and the doping concentration. Coulomb interactions significantly suppress the stability of bipolarons, and for realistic parameters the doped carriers are most likely in the form of polarons at low doping levels. On the other hand, the high concentration of carriers tends to favor a bipolaron lattice, and our model predicts a possible doping-induced phase transition from a polaron lattice to a bipolaron lattice. The significance of these results is discussed in connection with experiments in polypyrrole and other polymers.

In conjugated polymers with nondegenerate ground state, two kinds of charge carriers can be generated upon doping or photoexcitation: polarons and bipolarons. A polaron has a spin 1/2 and an electric charge $\pm e$, whereas a bipolaron, which can be regarded as a confined pair comprising a charged soliton and a charged antisoliton, is spinless with charge $\pm 2e$. A basic description of these excitations was given by the Brazovskii-Kirova (BK) model,[1] in which a symmetry-breaking term is added to lift the ground state degeneracy in the Takayama-LinLiu-Maki model.[2] The BK model predicts that a bipolaron is always energetically more stable than two separate polarons. It also predicts a difference between the optical properties of a bipolaron and a polaron.[3] A polaron is accompanied by three subgap optical transitions associated with its localized levels in the band gap, while only two transitions are allowed in the case of a bipolaron. The difference comes from the occupancies of the localized levels. Similar results are obtained also in more realistic models taking into account molecular structures.[4,5]

Based on these expectations, many magnetic and optical experiments have been conducted in a variety of nondegenerate conjugated polymers such as polypyrrole,[6,7] polyaniline,[8] polythiophene,[9,10] and poly(p-phenylene vinylene).[11–13] It turned out that the experimental data did not necessarily follow the theoretical predications. In many cases a substantial spin density is observed at low doping concentrations, suggesting the existence of polarons.[6,8,10] In spite of this discrepancy, the bipolaron picture of the BK model still seems to be widely used in interpreting experimental data. An often used compromise is to assume that the polarons at low doping levels are not mobile enough among polymer chains to form bipolarons which are energetically more stable.

However, it is important to note that the BK model essentially neglects electron-electron interactions, which have been shown to play important roles in many aspects of conjugated polymers. Obviously, Coulomb repulsion between the two electrons (holes) confined in the lattice deformation of a bipolaron costs an extra energy compared to a separated pair of polarons.[14] Therefore, the relative stability of bipolarons and polarons should depend on the strength of electron-electron interactions. Although some phenomenological models have been used to claim that the effect of Coulomb repulsion is not strong enough to destabilize a bipolaron,[15] there has been no systematic study of this problem, to the best of our knowledge. In the present paper we report such a theoretical study using a model which includes electron-electron interactions. Our study shows that Coulomb interactions significantly suppress the stability of bipolarons, and that for realistic parameters the doped carriers are most likely in the form of polarons at low doping levels. This is consistent with the observations mentioned above. On the other hand, we demonstrate that the high concentration of carriers tends to favor a bipolaron lattice. Therefore, our model predicts a possible doping-induced phase transition from a polaron lattice to a bipolaron lattice. This provides a natural explanation of the doping-dependent spin density observed, e.g., in polypyrrole.[6]

First, we describe our model and calculation method. We adopt the Pariser-Parr-Pople (PPP) model for π electrons on a linear chain with N sites. The creation operator of a π electron with spin σ at site n is denoted as

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$C^\dagger_{n,\sigma}$, and the lattice displacement at site n is denoted by u_n. The PPP Hamiltonian consists of the hopping term between nearest neighbor sites, the on- and off-site Coulomb interactions, and the elastic energy of lattice:

$$\begin{aligned} H = &-\sum_{n,\sigma} t_{n,n+1}(C^\dagger_{n+1,\sigma}C_{n,\sigma} + C^\dagger_{n,\sigma}C_{n+1,\sigma}) \\ &+\sum_{n} U\rho_{n\uparrow}\rho_{n\downarrow} + \sum_{n\neq m}\sum_{\sigma,\sigma'} \frac{V}{2|n-m|}\rho_{n,\sigma}\rho_{m,\sigma'} \\ &+\sum_{n} \frac{K}{2}(u_{n+1}-u_n)^2. \end{aligned} \quad (1)$$

Here, $\rho_{n,\sigma} = C^\dagger_{n,\sigma}C_{n,\sigma}$. The transfer integral $t_{n,n+1}$ contains the Su-Schrieffer-Heeger (SSH) electron-lattice coupling[16] α and the BK symmetry-breaking parameter δ_0:

$$t_{n,n+1} = [1 + (-1)^n\delta_0]t - \alpha(u_{n+1} - u_n). \quad (2)$$

Although the present model does not take into account the realistic backbone structure of each polymer, it is suitable for studying basic properties of nondegenerate conjugated polymers. The same model has been used to describe exciton polarons (or neutral bipolarons) and their optical properties.[17] The Coulomb potentials due to dopant ions and the effects of adjacent chains are neglected in the present study.

We apply the unrestricted Hartree-Fock (UHF) approximation to treat the electronic structure of the model. The periodic boundary condition is imposed to the system. Lattice deformation is treated within the adiabatic approximation. The change of bond length, $y_n = u_{n+1} - u_n$, is optimized by using the Hellmann-Feynman force equilibrium condition,

$$y_n = -\frac{2\alpha}{K}\left(p_{n,n+1} - \frac{1}{N}\sum_m p_{m,m+1}\right). \quad (3)$$

Here, $p_{n,m} = \sum_\sigma \langle C^\dagger_{n,\sigma}C_{m,\sigma}\rangle$ denotes the bond order.

We are mainly interested in the influence of Coulomb interactions (on-site U and long-range V) and the transfer modulation δ_0 on the relative stability of polarons and bipolarons. Another parameter which affects the stability is the dimensionless electron-lattice coupling constant $\lambda = 2\alpha^2/\pi tK$. In this report, we take $\lambda = 0.136$, which is the same as in our previous study[17] and somewhat smaller than the value used in the SSH model[16] of polyacetylene.

The self-consistency equations of the UHF approximation coupled with Eq. (3) were solved numerically by means of a standard iterative procedure, starting from appropriate initial trials. In most cases, both polaronic and bipolaronic states were obtained as self-consistent solutions for a given set of parameters. Besides the degeneracy resulting from translational invariance, no other kinds of solutions have been obtained. By comparing the energies of the two kinds of solutions, we determined the relative stability of polaronic and bipolaronic states systematically for a wide range of parameters.

Hereafter we present the main results of our calculations for hole doping, i.e., the case where the total number of electrons $N_e < N$. The situation in the case of electron doping ($N_e > N$) is the same because of the electron-hole symmetry in the present model.

First we consider the case of two holes, which may form a bipolaron or a separated pair of polarons. This situation corresponds to the dilute limit of doping. The calculations were carried out for the system with $N = 400$ sites and $N_e = 398$ electrons. In Figs. 1(a) and 1(b) we display examples of obtained lattice distortions of a separated pair of polarons and a bipolaron, respectively. The ordinate $(-1)^n y_n$ is the change of bond length with alternating signs. It is constant in the case of perfect bond alternation, i.e., for the ground state of an undoped system. The depth of the bipolaron deformation in Fig. 1(b) is larger than that of the polaron deformation in Fig. 1(a). The two polarons in Fig. 1(a) are well separated, interfering little with each other. Excess charge densities (and also spin densities in the case of polarons) are localized around the regions of the lattice deformations.

Figure 2 shows the obtained phase diagram of the ground state configuration of the two-hole-doped system in the parameter space of δ_0 and U. The solid (dashed) line indicates the phase boundary between the regions of a bipolaron (BP) and separated polarons (P+P) for the case of $V/U = 0.5$ (0.25). Clearly, the stability of a bipolaron is strongly suppressed by Coulomb interactions: the region of a stable bipolaron is limited to small U or small δ_0. The effect of on-site U can be understood easily. A bipolaron with a spatial extension $\xi_{\rm BP}$ costs energy of $\sim U/\xi_{\rm BP}$, while polarons hardly cost energy because of almost perfect separation of up and down spin densities between the two polarons.[14] The effect of increasing off-site V is further to destabilize the bipolaron, unless δ_0 is very small. This is because the bipolaron costs more energy than the polarons due to stronger confinement of charge density ($\xi_{\rm BP}$ is smaller than the twice of the polaron width $\xi_{\rm P}$). Increase in δ_0 results in decrease in $\xi_{\rm BP}$ and $\xi_{\rm P}$, thereby enhancing the effect of U and V. In the region of $\delta_0 \lesssim 0.005$, the effect of V is opposite, i.e., favorable for a bipolaron. In this region, the large value of V makes the charge densities of the bipolaron and the polaron alternate their signs site by site, so that V acts as a source of an energy gain. Note that Fig. 2 is obtained for a particular value of electron-phonon coupling $\lambda = 0.136$. When we increase λ, the phase boundary moves upward, expanding the bipolaron region.

When we dope more carriers into the system, we obtain a regular lattice of polarons or bipolarons. Figures 1(c) and 1(d) show the displacement patterns $(-1)^n y_n$ of the polaron lattice and the bipolaron lattices, respectively, for $U = 0.5t$, $V = 0.5U$, and $\delta_0 = 0.05$ with $N_e = 390$ electrons on $N = 400$ sites. This corresponds to a doping concentration $x = (N - N_e)/N$ of 2.5% per site. There are overlaps of lattice deformations between adjacent polarons or bipolarons, particularly in the case of the polaron lattice. This affects the relative stability of the polarons and bipolarons. Figure 3 shows how the critical U of the bipolaron lattice depends on the doping concentration x in the particular case of $\delta_0 = 0.05$ and $V = 0.5U$. The calculations were carried out for various combinations of N and N_e so as to arrange polarons and

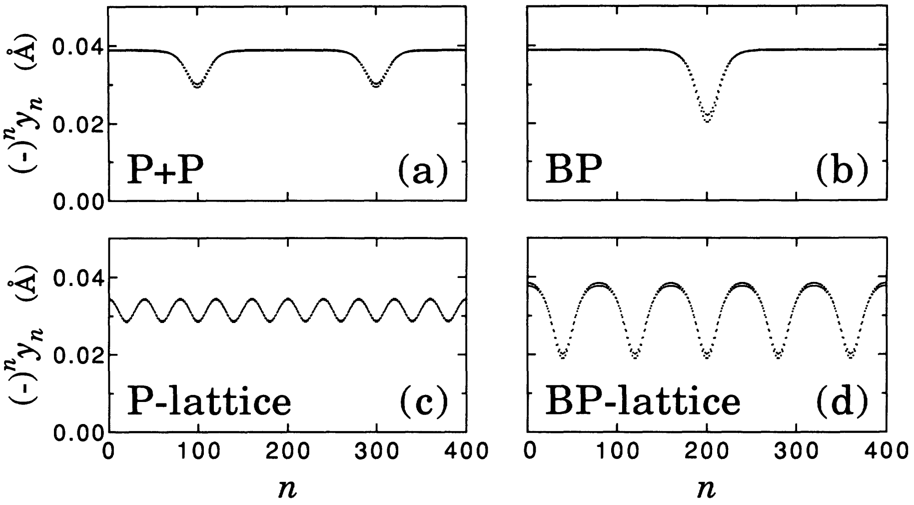

FIG. 1. Spatial patterns of relaxed bond length variations with alternating signs, $(-1)^n y_n$, of (a) two separated polarons (P+P), (b) a bipolaron (BP), (c) polaron lattice (P-lattice), and (d) bipolaron lattice (BP-lattice) for $U = 0.5t$, $V/U = 0.5$, $\delta_0 = 0.05$, and $\lambda = 0.136$. In (a) and (b), two electrons are removed from the half-filled case with $N = 400$ sites. In (c) and (d), ten electrons are removed, which corresponds to a doping concentration of 2.5% per site. In (c), polarons are located at every 40 sites whereas in (d) the interval between neighboring bipolarons is 80 sites. In calculating the lattice displacements, we took $\alpha/K = 0.084$ Å, which gives a bond alternation ~ 0.08 Å in the half-filled case. This value is typical in conjugated polymers.

bipolarons at regular intervals. Clearly, higher doping x favors the bipolaron lattice. This is because the substantial overlaps among polarons in the polaron lattice results in the reduction of the energy gain due to electron-lattice coupling. An important implication of Fig. 3 is the possibility of a doping-induced phase transition from a polaron lattice to a bipolaron lattice if electron-electron interactions are not extremely strong.

The on-site Coulomb energy U in conjugated polymers is considered to be larger than $\sim t$, being located above the phase boundary in Fig. 2 unless δ_0 is extremely small. For example, $U = 3t$, $V = 0.433U$, and $\delta_0 = 0.05$ were

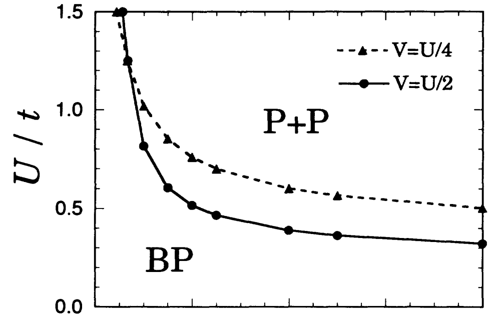

FIG. 2. Phase diagram of the ground state of a two-hole (or two-electron) doped chain with $N = 400$ sites in the parameter space of the symmetry-breaking transfer modulation δ_0 and the on-site Coulomb energy U. P+P (BP) indicates the region where a separated pair of polarons (a bipolaron) is energetically most stable when two electrons are removed from (or added to) the half-filled system. Solid and dashed lines indicate phase boundaries for $V = 0.5U$ and $0.25U$, respectively. The dimensionless coupling constant λ is taken as 0.136.

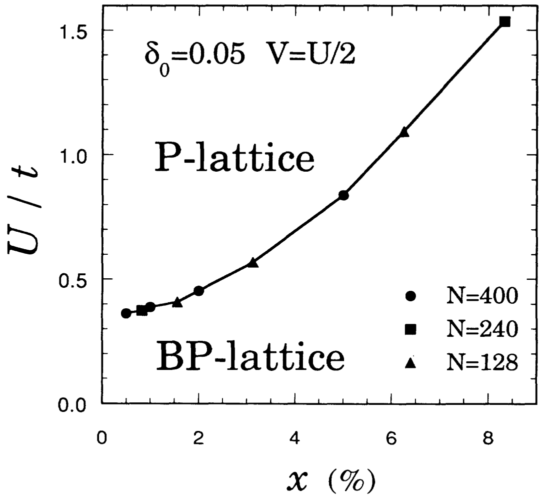

FIG. 3. Phase diagram of the ground state of a doped chain as functions of doping concentration x and on-site Coulomb energy U in the case of $V/U = 0.5$, $\delta_0 = 0.05$, and $\lambda = 0.136$. The region where a polaron (bipolaron) lattice is most stable is indicated as P- (BP-) lattice.

used in our previous paper to reproduce the photoinduced absorption of polydiacetylene.[17] Although these parameters may vary for different polymers, it is unlikely that U/t becomes much smaller than unity. Therefore, we conclude that the carriers at low doping concentrations are most likely polarons. This is in accordance with many magnetic and optical experiments.[6–8,10] Only at higher doping concentrations the carriers may form bipolarons.

Our model predicts the transition from a polaron lattice to a bipolaron lattice with increasing x. This is consistent with the electron spin resonance experiments in polypyrrole.[6] With increasing doping concentration, the spin density first increases linearly, saturates, and then decreases. The maximum of the spin density was observed at a doping concentration of about one electron per six pyrrole units, corresponding to $x \sim 3.3\%$ per atom (C and N). This decrement of the spin density is interpreted in our model as due to the transition into the bipolaron lattice. The results of optical absorption measurements are also consistent with this interpretation.[7] The critical concentration of about $x \sim 3.3\%$ implies, according to Fig. 3, that U must be relatively small ($< t$), if $\delta_0 \sim 0.05$. The fact that the observed transition from polarons to bipolarons occurs over a relatively wide range of x may be ascribed partly to the thermal population in metastable states and partly to disorder in the system and inhomogeneity in doping.

In the case of polyaniline, there is an indication of the polaron lattice even at high doping concentrations of $x \sim 7\%$.[8] This is interpreted as the case of a stronger U or larger δ_0, for which the formation of bipolarons, even if possible, would require a much higher doping concentration. The formation of polarons has been suggested also in lightly doped and photoexcited poly(p-phenylene vinylene).[11–13]

In polythiophene, contradictory results have been reported. Schärli *et al.* detected almost the same amount of spin carriers as that of injected charges up to a doping concentration of $\sim$ 10% per thiophene ring ($x \sim$ 2.5%), and observed the Pauli-type magnetic susceptibility at higher doping levels, suggesting charge storage as polarons.[10] On the other hand, Chen, Heeger, and Wudl did not observe an appreciable increase of spin density from undoped system up to a doping concentration of $x \sim 3.5\%$, suggesting the formation of bipolarons.[9]

Finally, it should be mentioned that our model is a simplified one and contains a phenomenological BK parameter δ_0, which is rather difficult to relate to the σ-backbone structure of each polymer. For further quantitative comparison between experiment and theory, it will be necessary to take into account the structures of individual materials, as well as interchain coupling and dopant potentials.

Related problems have been discussed in other fields. For instance, the problem of two electrons in three-dimensional phonon fields has been studied,[18,19] elucidating a phase diagram consisting of three regions of the ground state: a bipolaron, a pair of polarons, and free electrons. The idea of an effective attractive Hubbard model has been used to interpret the electronic structures of amorphous semiconductors.[20]

In summary, we have studied the effects of Coulomb interactions and doping concentration on the relative stability of bipolarons and polarons in nondegenerate conjugated polymers. We have demonstrated that charge carriers at low doping levels are most likely polarons in the case of the intermediate strength of Coulomb interaction and that a transition from a polaron lattice to a bipolaron lattice can occur with increasing carrier concentration.

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