PHYSICAL REVIEW B VOLUME 49, NUMBER 9 1 MARCH 1994-I

Stability of transverse bipolarons in conducting polymers

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(Received 23 August 1993)

We present a calculation of bipolaron stability in doped conjugated polymers which emphasizes the role of the dopants as tunneling bridges between neighboring chains.

Most of the calculations which have been published on charge and spin excitations in conducting polymers are strictly one dimensional. In general they are based on empirical Hamiltonians like that of Holstein or Su, Schrieffer, and Heeger (SSH) and they predict the existence of large stable polarons or bipolarons.

However, experimental results on actual films of polypyrrole, polythiophene, or unstretched polyaniline never reveal any significant anisotropy in the macroscopic electronic transport properties. *A posteriori* the authors usually invoke a nonnegligible transfer integral $t_\perp$ from chain to chain in order to account for this evidence. As first emphasized by Emin and Holstein[1] and more recently by Mizes and Conwell,[2] the existence of such a transverse transfer integral destabilizes the large polaron into a small one and severely limits the strictly one-dimensional calculations. The present paper introduces a new transverse tunneling process which does not destabilize polarons and bipolarons while it provides an efficient possibility of transfer from one chain to a neighboring one. This result is obtained by considering the active role of the dopant counterion in the transfer process.[3] We shall see in the course of the present calculation that this process does not endanger the life of polarons and bipolarons because it is localized at the vicinity of the dopant only. On the contrary it can stabilize new polaronic and bipolaronic species which sit on two or more chains simultaneously. These we call transverse polarons or bipolarons.

The purpose of the present paper is to study the relative stability of some of these objects. For this purpose, we use a simple approach that is based on Holstein's Hamiltonian. Its merit is to include explicitly all the electron interactions which are usually neglected, the electron on-site repulsion U,[4] and the interaction with the charged dopant.[5]

In order to describe the ground state of a pair of carriers, we consider the ensemble of polymer chains linked by the dopants (Fig. 1). Far from the dopants, the transfer integral $t_\perp$ from chain to chain is considered to be negligibly small with respect to t_d (coupling through the dopant). When the transverse tunneling to the dopants is ignored, the ground state of the pair of carriers is a bipolaron which is localized on one chain.[5] When the transverse tunneling to the dopants is taken into account, one expects the carriers to be localized on the chains neighboring the dopants, and to give rise to a "transverse" bipolaron.

The transverse tunneling from a polaron site on chain k to the dopant site $\mathbf{R}_i$ is modeled by a localized transfer integral

$$\sum_{k=i+h} t_d \delta(X_{i,k}-x_k)(|\mathbf{R}_i\rangle\langle x_k|+|x_h\rangle\langle\mathbf{R}_i|) ,$$

where the summation is done on the chain $k=i+h$, linked to the dopant i. The absciss x_k of the carrier along the chain k is expressed in units of lattice constant a and $X_{i,k}$ is the absciss of the dopant D_i, located in $\mathbf{R}_i$, along the chain k (see Fig. 1). Following Ref. 4 the self-trapping of a pair of carriers along the chains k as a large bipolaron is considered within Holstein's adiabatic continuum model. Only the short-range part of the Coulomb repulsion between the electrons will be considered through an on-site repulsion $U\delta(\mathbf{r}^{(1)}-\mathbf{r}^{(2)})$, where $\mathbf{r}^{(1)}$ and $\mathbf{r}^{(2)}$ are the position of the two carriers. Within the adiabatic approximation, the energy of a pair of carriers on an ensemble of chains k, connected by the two dopants located in $\mathbf{R}_1$, $\mathbf{R}_2$ becomes

$$\begin{aligned} E = & -4t_\parallel \sum_k \int dx_k dx^{(1)} d\mathbf{r}^{(2)} |\phi|^2 \delta(x^{(1)}-x_k) + 2t_\parallel \sum_k \int dx_k dx^{(1)} d\mathbf{r}^{(2)} \left| \frac{\partial\phi}{\partial x^{(1)}} \right|^2 \delta(x^{(1)}-x_k) \\ & -4E_b \sum_k \int dx_k \left[\int dx^{(1)} d\mathbf{r}^{(2)} |\phi|^2 \delta(x^{(1)}-x_k) \right]^2 \\ & -2t_d \sum_{i=1,2} \sum_{k=i+h} \left\{ \left[\int d\mathbf{r}^{(1)} d\mathbf{r}^{(2)} \phi^x \delta(\mathbf{r}^{(1)}-\mathbf{R}_i) \int dx^{(1)} \phi \delta(x^{(1)}-X_{i,h}) \right] + \text{c.c.} \right\} \\ & -E_d \sum_{i=1,2} \int d\mathbf{r}^{(1)} d\mathbf{r}^{(2)} |\phi^2| [\delta(\mathbf{r}^{(1)}-\mathbf{R}_i) + \delta(\mathbf{r}^{(2)}-\mathbf{R}_i)] + U \int d\mathbf{r}^{(1)} d\mathbf{r}^{(2)} |\phi|^2 \delta(\mathbf{r}^{(1)}-\mathbf{r}^{(2)}) , \end{aligned} \quad (1)$$

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where $\phi(\mathbf{r}^{(1)},\mathbf{r}^{(2)})$ is the normalized electronic eigenfunction,

$$\sum_k \int dx^{(1)} d\mathbf{r}^{(2)} \delta(x^{(1)}-x_k)|\phi|^2 + \sum_{i=1,2} \int d\mathbf{r}^{(1)} d\mathbf{r}^{(2)} \delta(\mathbf{r}^{(1)}-\mathbf{R}_i)|\phi|^2 = 1 \,, \tag{2}$$

and $x^{(1)}$ $(x^{(2)})$ is the absciss of particle (1) [(2)] along chain $k^{(1)}$ $(k^{(2)})$.

The binding energy, $E_b = F^2/2K$, where F is the linear electron-phonon coupling constant and K is the stiffness constant associated with molecular deformations, is assumed to be smaller than the transfer integral along the chain $t_\parallel$.

Impurity only serves as an efficient dopant if the energy difference, Δ, between the dopant electronic state $-E_d$, and that associated with a chain's electronic state $\sim -2t_\parallel[1+O(Eb/t_\parallel)^2]$, is much greater than the transfer energy between the dopant and the chain t_d and, we can assume that $t_d \ll \Delta \sim 2t_\parallel - E_d$. Hence, to the lowest order in (t_d/Δ), the amplitude of the ground-state eigenfunction, for one carrier on the dopant site $\mathbf{R}_i$, is given by

$$\phi(\mathbf{r}^{(1)}=\mathbf{R}_i,\mathbf{r}^{(2)}) = \frac{t_d}{\Delta} \sum_{k=i+h} \int d\mathbf{r}^{(1)} \phi(\mathbf{r}^{(1)},\mathbf{r}^{(2)}) \delta(x^{(1)}-X_{i,k}) \tag{3}$$

and

$$\begin{aligned} E = {} & -4t_\parallel + 2t_\parallel \sum_k \int dx_k d\mathbf{r}^{(2)} \left| \frac{\partial\phi}{\partial x^{(1)}} \right|^2 \delta(x^{(1)}-x_k) - 4E_b \sum_k \int dx_k dx^{(1)} d\mathbf{r}^{(2)} |\phi|^4 \delta(x^{(1)}-x_k) \\ & + U \sum_k \int dx_k dx^{(1)} dx^{(2)} |\phi|^2 \delta(x^{(1)}-x^{(2)}) \delta(x^{(1)}-x_k) \\ & - \frac{2t_d^2}{\Delta} \sum_{i=1,2} \int d\mathbf{r}^{(2)} \left| \sum_{k=i+h} \int dx^{(1)} \phi \delta(x^{(1)}-X_{i,k}) \right|^2 . \end{aligned} \tag{4}$$

It is worth mentioning that the last term in Eq. (4) can be viewed as the short-range part of the Coulomb interactions between dopants and neighboring chains.[5] Thus, the quantity $(-2t_d^2/\Delta)$ can be identified with the Coulomb attraction to the dopant U_d. It is not surprising that a transfer integral through the dopant originates from a Coulomb attraction to it. As in Ref. 5, the ground-state energy is variationally determined.

We first discuss the ground state of a single carrier transverse polaron $\varphi_i(x,k)$ centered on the dopant i and smeared over n chains (Fig. 2). We construct a trial wave function for the self-trapped carrier, which is written in terms of the usual polaron eigenfunctions:

$$\varphi_i(x,k) = \frac{1}{\sqrt{2nL}} \sum_{k=1}^{n} \operatorname{sech}[(x_k - X_{i,k})/L] \,,$$

where the summation is done over the n chains that are connected by the dopant. The transverse polaron energy is then expressed in terms of this eigenfunction. It is a function of the free parameter L, which measures the extension of the transverse polaron along the chains. To determine the ground state, the energy is minimized with respect to the parameter L, and one gets

$$E = -2t_\parallel - \frac{[E_b + (3/2)n^2 U_d]^2}{12n^2 t_\parallel} \,, \tag{5}$$

where $n^2 U_d = n^2 t_d^2/\Delta$ is the lowering of an electron's energy due to its transfer between sites and different chains as the result of an intermediate dopant. Le Guennec has obtained a similar result within the SSH model.[6] This transverse polaron is more stable than the usual one-dimensional polaron localized on a single chain provided that $E_b < (3/2)nU_d$.

In the following, we deal with bipolaron configurations

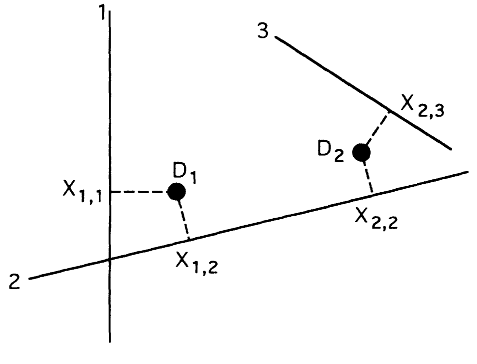

FIG. 1. Schematic representation of chains (1, 2, and 3) and dopants (D_1, D_2) in a disordered conducting polymer.

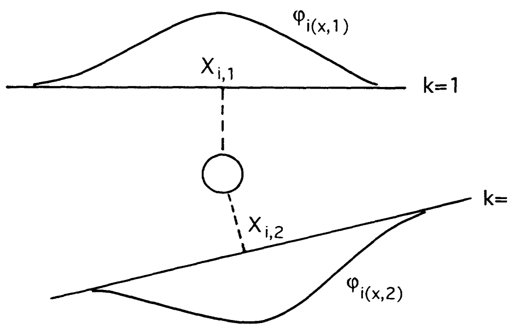

FIG. 2. The transverse polaron smeared over $n=2$ chains connected by the dopant i.

equivalent to those pictured in Figs. 1 and 4(a) and 5(a) where each dopant has only two neighboring chains. The electron correlations will be considered within the Heitler and London approach.[5] A two-electron variational wave function $\phi(x^{(1)},k^{(1)},x^{(2)},k^{(2)})$, where $x^{(1)}$ ($x^{(2)}$) is the absciss of particle (1) [(2)] along chain $k^{(1)}$ ($k^{(2)}$), is written in terms of a one-electron eigenfunction $\varphi_i(x,k_i)$ centered on different sites a_i, and localized on n chains $n=\{k_i\}$ [notice that, in general, a_i is not necessarily equal to $X_{i,k}$ (Ref. 5)]. The bipolaron variational wave function is written as

$$\phi_{S,T}(x^{(1)},x^{(2)})=\frac{\varphi_1(x^{(1)},k^{(1)})\varphi_2(x^{(2)},k^{(2)})\pm\varphi_2(x^{(1)},k^{(1)})\varphi_1(x^{(2)},k^{(2)})}{\sqrt{2(1\pm s^2)}} \tag{6}$$

with

$$s=\sum_{k_1,k_2}\int dx\,\varphi_1(x,k_1)\varphi_2(x,k_2)\delta_{k_1,k_2}\ ,$$

while the amplitude at the dopant site $\mathbf{R}_i$ can be written [according to the general equation (3)]

$$\phi(\mathbf{r}^{(1)}=\mathbf{R}_i,\mathbf{r}^{(2)})=\frac{t_d}{\Delta}\sum_{k=1,2}\int dx^{(1)}\phi_{S,T}(x^{(1)},k^{(1)},\mathbf{r}^{(1)})\delta(x^{(1)}-X_{i,k})\ .$$

The + sign refers to the singlet state ϕ_s.

The energy of a pair of carriers writes

$$E_{S,T}=-4t_{\parallel}+\frac{2t_{\parallel}C_t}{L^2}-\frac{E_bC_b-2UC_e+2U_dC_d}{2Ln} \tag{7}$$

with

$$C_t=1/3(1\pm s^2)^{-1}(1\mp 3s^2\pm 3sI_3)\ ,$$

$$C_b=(1\pm s^2)^{-2}[4/3+(1+2s^2)I_2\pm 4sI_3]\ ,$$

$$C_e=(1+s^2)^{-1}(1\pm 1)I_2/4\ ,$$

$$C_d=\tfrac{1}{2}(1\pm s^2)^{-1}\sum_{i=1,2}\left\{\frac{(\lambda i_1)^2}{ch^2(\bar{a}_1-\bar{X}_i)}+\frac{(\lambda i_2)^2}{ch^2(\bar{a}_2-\bar{X}_i)}\pm 2s\frac{\lambda i_1\lambda i_2}{ch(\bar{a}_1-\bar{X}_i)ch(\bar{a}_2-\bar{X}_i)}\right\}\ ,$$

where

$$I_2=4\lambda[(\bar{a}/th\bar{a})-1]sh^{-2}\bar{a}\ ,$$

$$I_3=2\lambda[th^{-1}\bar{a}-\bar{a}/sh^2\bar{a}]/sh\bar{a}\ ,$$

$$s=\lambda\bar{a}/sh\bar{a}\ ,$$

$$\bar{a}=(a_1-a_2)/L\ ,$$

$$\bar{X}_i=X_i/L\ ,$$

$$\lambda=\frac{1}{n}\sum_{k_1,k_2}\delta_{k_1,k_2}\ .$$

λ_{i1} is the number of chains connected to the dopant i over which the wave function 1 extends [in the situation depicted in Figs. 4(a) and 5(a) all the λ's are equal to 2]. Minimizing the energy with respect to the polaronic extension L yields

$$E_{S,T}=-4t_{\parallel}-2t_{\parallel}C_t(a^2/L^2)$$

with (8)

$$\frac{a}{L}=\frac{E_bC_b-2UC_e+2U_dC_d}{8nC_tt_{\parallel}}\ .$$

For a given polymer, i.e., for given values of the Coulomb repulsion U, the Coulomb attraction U_d to the dopant, and the polaron binding energy E_b, the ground state is determined by the distance between dopants. If the two dopants are far from each other $\|\mathbf{R}_1-\mathbf{R}_2\|\gg L$, the configuration which minimizes $E_{S,T}$ is either a singlet bipolaron corresponding to two charges sitting close to

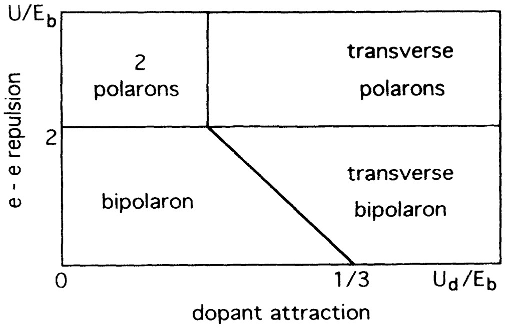

FIG. 3. Phase diagram giving the ground state of a pair of carriers when the dopants are far from each other with respect to the typical polaron extension.

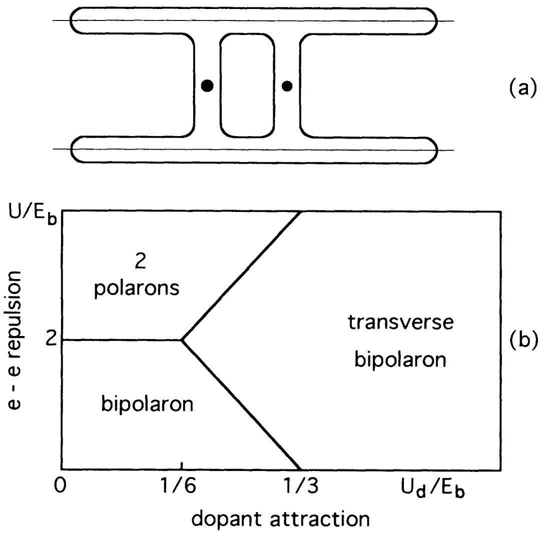

FIG. 4. Transverse bipolaron of the first type (a) and phase diagram giving its stability domain (b).

the same dopant [$\mathbf{a}_1=\mathbf{a}_2$ in Eq. (7)] or a pair of polarons sitting on each dopant ($\bar{a}_1=\bar{X}_1$, $\bar{a}_2=\bar{X}_2$). This ground state is the singlet bipolaron providing that $U<2E_b$.[4,5] The transverse extension of this object depends on the sign of $U-4E_b+6U_d$. When $U>4E_b-6U_d$, the solution which minimizes $E_{S,T}$ extends over two chains (neighboring the dopant) [Fig. 3(a)] with a typical extension L along each chain given by

$$\frac{a}{L}=\frac{(8/3)E_b-(2/3)U+8U_d}{(16/3)t_\parallel} .$$

When the electron repulsion U becomes larger than $2E_b$, the bipolaron becomes unstable with respect to dissociation into separate polarons that are centered on each dopant. Moreover, if $U_d>E_b/3$ both polarons are transverse and they extend on the two chains that neighbor each dopant, with $a/L=[(4/3)E_b+8U_d]/(16/3)t_\parallel$. The singlet ground-state configurations for different values of U_d/E_b and U/E_b are summarized in Fig. 3 in the case of separated dopants. Notice that when the dopants are far from each other the pair of polarons, either longitudinal or transverse, can also be viewed as a triplet bipolaron.

If the dopants are closer $\|\mathbf{R}_1-\mathbf{R}_2\|\ll L$, the ground-state configuration is either a singlet bipolaron or two separated polarons, according to the values of (U,U_d). We have considered the two configurations depicted in Figs. 4(a) and 5(a). In the first case (Fig. 4), the ground state is a singlet transverse bipolaron when $4-12U_d/E_b<U/E_b<12U_d/E_b$. Its energy is $E=-4t_\parallel-2/3t_\parallel(a/L)^2$, with

$$\frac{a}{L}=\frac{(8/3)E_b-(2/3)U+16U_d}{(16/3)t_\parallel} .$$

In the second case (Fig. 5), similar results are obtained. The singlet ground-state configuration is a transverse bipolaron [Fig. 5(b)] (which extends on three chains) provided that $4-3U_d/E_b<U/E_b<\frac{21}{2}U_d/E_b-2$. Its energy is $E=-4t_\parallel-(2/3)t_\parallel(a/L)^2$,

$$\frac{a}{L}=\frac{(8/3)E_b-(2/3)U+16U_d}{8t_\parallel} .$$

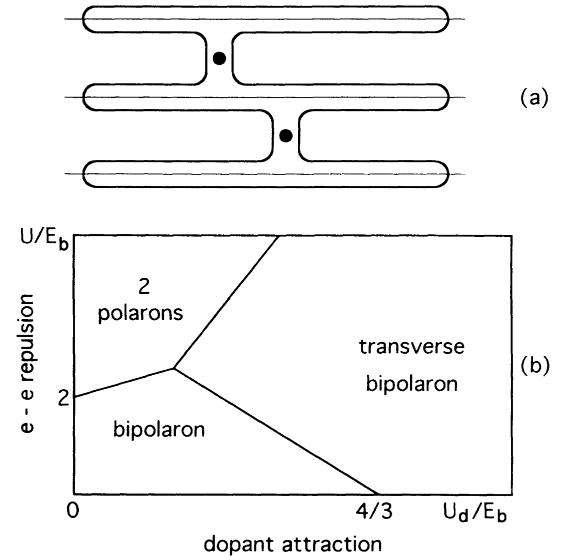

FIG. 5. Transverse bipolaron of the second type (a) and related stability diagram (b).

The interpolation between the two limiting cases that have been treated here (close or separated dopants) can be obtained by following the same procedure as in Ref. 5.

A disordered conducting polymer such as polypyrrole or polythiophene and even, very often polyaniline, can be viewed as a bipolaron glass composed of motifs similar to those that have been presented in the present paper. Most of the experimental results, especially those based on the study of the magnetic excitations[5] suggest a value of the Coulomb repulsion U close to $2E_b$. The diagrams of Figs. 3–5, show that, depending on the effective short-range attraction potential to the dopant ($U_d\sim t_d^2/\Delta$) and on the distance between adjacent dopant pairs, two situations are likely: (1) either the carriers spend most of their time in the proximity of the dopant and form transverse bipolarons ($U_d>E_b/6$ in Fig. 4), or (2) the on-chain nonlinear deformation is dominant and they form longitudinal bipolarons. Both of these species contribute to the hopping transport which will be studied in a subsequent paper.[7]

In our recent paper[5] the magnetism of the bipolaron was studied as a function of the distance between dopants, by assuming that the carriers were sitting on the same chain. This work could be easily extended to the transverse bipolarons defined here and similar results are obtained.

The present work was partially supported by the KWF Contract No. 2334.1.

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