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Bipolaron singlet and triplet states in disordered conducting polymers

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We emphasize the role of the dopant potential on the stability and magnetic properties of bipolarons in a conducting polymer. For this purpose the singlet and the triplet states of a bipolaron have been calculated within an adiabatic deformable continuum model including short-range Coulomb repulsions between electrons and attractions by the ionized dopants. We derive a new interpretation of the spin-charge relation and of the so-called Curie and Pauli contributions to the susceptibility of disordered conducting polymers.

Conjugated polymers such as polypyrrole or polythiophene become conducting when doped with donor or acceptor counterions. The carriers generated in this process are known to be self-trapped by the conjugated polymeric chains in the form of polarons or bipolarons. In broad terms, the ground state of the bipolaron is determined by the competition between Coulomb repulsion and self-trapping net attraction between carriers.[1-4] In a recent work, Le Guenneck, Nechtschein, and Travers,[5] on the bases of an accurate revisitation of the magnetic properties of polynaniline, express the idea that the finite number of dopant ions near a single polymer chain is an important parameter. However, the effects of the charged counterions on the electronic and magnetic properties have not been studied extensively, and the few authors[6-8] who have explicitly included the dopant (or impurity) potentials in their calculations, do not consider electron-electron correlations between carriers explicitly.

In this paper, we present a calculation of the bipolaron stability in the presence of a pair of dopants, which includes electron correlations. We show that the positions of the self-trapped carriers are essentially determined by the position of the dopants. According to the interdopant separation the ground state of the system is either the singlet bipolaron or two separate polarons. Our results show that the distance l between the doping centers is the essential feature determining the energy and magnetic properties of the bipolaron. This calculation accounts for the usual spin-charge relation in conducting polymers[5] and the temperature dependence of the spin susceptibility.

Except the best polyacetylenes, many of the insoluble conducting polymers are composed of short chains of the order of a few ten monomers and only a small part of these materials is in a crystalline form. Thus the consideration of a pair of polarons can give a good insight in the physics of the system, provided that all the important interactions are included in the model. Our bipolaron together with its pair of dopant potentials can be considered as the motif of a "bipolaron glass" appropriate for the description of disordered conducting polymers such as polypyrroles, polythiophenes, and even part of the polyanilines. Of course more ordered systems, especially at high concentrations when bipolaron interactions are expected, require other treatments such as polaron lattice calculations.[2,4] The higher concentration considered in the present work corresponds to a pair of counterions on a chain segment of 12 pyrrole monomoners, for example.

The main assumption of this bipolaron model is the following: only the short-range part of the Coulomb interactions will be considered through an on-site repulsion U of the order of 1 eV and a dopant attraction U_d of the order -0.1 eV. As we deal with a relatively large Coulomb repulsion U, electron correlations will be considered within the Heitler and London approach. As in Ref. 1 self-trapping of a pair of carriers as a large bipolaron is considered within Holstein's adiabatic continuum model. The binding energy of a single polaron in Holstein's model is $E_p = E_b^2/12t$, where t is the transfer integral (2.5 eV) and $E_b = F^2/2k$ where F is the linear electron-phonon coupling constant and k is the stiffness constant associated with molecular deformations.[1] In our conducting polymer problem E_p is of the order of 0.1 eV.[9,10]

Within the adiabatic approximation, the energy of a pair of electrons on a chain is[1]

$$E_e = t \int dx_1 dx_2 \left[\left| \frac{\partial \varphi}{\partial x_1} \right|^2 + \left| \frac{\partial \varphi}{\partial x_2} \right|^2 \right] - F \int dx_1 dx_2 |\varphi|^2 [\Delta(x_1) + \Delta(x_2)] + U \int dx_1 dx_2 |\varphi|^2 \delta(x_1 - x_2) \ . \tag{1}$$

Here $\Delta(x)$ is the deformation of the chain at x, x_1 and x_2 are the positions of the two electrons expressed in units of the lattice constants, a, and $\varphi(x_1,x_2)$ is the electronic eigenfunction. As appropriate in a one-dimensional system we model the Coulomb repulsion between the electrons as $U\delta(x_1 - x_2)$. To this Hamiltonian we add the short-range attraction of the carriers to the dopants at $-l/2$, $+l/2$ with a strength U_d,

$$E_d = U_d \int dx_1 dx_2 |\varphi|^2 [\delta(l/2 + x_1) + \delta(l/2 - x_1) + \delta(l/2 + x_2) + \delta(l/2 - x_2)] \ . \tag{2}$$

To obtain the deformation pattern associated with the ground state, we minimize the sum of the electronic energy and the strain energy $E_{\mathrm{st}}=(k/2)\int[\Delta(x)]^2dx$, and we obtain

$$\Delta(x)=2F/k\int dx_1|\varphi(x_1,x)|^2\ . \tag{3}$$

Then the total ground-state energy of this bipolaron is $E_{\mathrm{bp}}=E_{\mathrm{st}}+E_e+E_d$ with the equilibrium displacement being given by Eq. (3). As in Ref. 1, our treatment of the two-electron variational wave function is written in terms of one-electron ground-state eigenfunctions centered about different sites:

$$\varphi_1(x)=(1/2L)^{1/2}\operatorname{sech}[(x+a_1)/L]\ ,$$
$$\varphi_2(x)=(1/2L)^{1/2}\operatorname{sech}[(x-a_2)/L]\ . \tag{4}$$

The bipolaron wave function is then written as

$$\varphi_{S,T}(x_1,x_2)=\frac{\varphi_1(x_1)\varphi_2(x_2)\pm\varphi_2(x_1)\varphi_1(x_2)}{\sqrt{2(1\pm s^2)}} \tag{5}$$

with $s=\int dx\ \varphi_1(x)\varphi_2(x)$. The + sign refers to the bipolaron singlet state and the − sign refers to the bipolaron triplet. Therefore the bipolaron energy depends on the width of the single-particle self-trapped state, L, and on the separation between the two self-trapped carriers a_1+a_2. The singlet (triplet) state is determined by minimizing the energy with respect to L, $b_1=a_1/L$, $b_2=a_2/L$: The minimization with respect to L yields $E_{\mathrm{bp}}=-2tC_ta^2/L^2$ with

$$a/L=\frac{E_bC_b-2UC_e+2U_dC_i}{8tC_t}\ , \tag{6}$$

where

$$C_t=\tfrac{1}{3}(1\pm s^2)^{-1}(1\mp3s^2\pm3sI_3)\ ,$$
$$C_b=[\tfrac{4}{3}+(1+2s^2)I_2\pm4sI_3][1\pm s^2]^{-2}\ ,\quad C_e=\tfrac{1}{4}(1\pm1)I_2(1+s^2)^{-1}\ ,$$
$$C_i=\tfrac{1}{2}(1\pm s^2)^{-1}[\operatorname{sech}^2(b_1-D/2)+\operatorname{sech}^2(b_2+D/2)\pm2s\operatorname{sech}(b_1-D/2)\operatorname{sech}(b_2+D/2)$$
$$+\operatorname{sech}^2(b_1+D/2)+\operatorname{sech}^2(b_2-D/2)\pm2s\operatorname{sech}(b_1+D/2)\operatorname{sech}(b_2-D/2)]\ ,$$

where $D=l/L$ is the normalized distance between the two dopants and $s=D\operatorname{sech}^{-1}D$,

$$I_2=4[(D/\tanh D)-1]\operatorname{sech}^{-2}D\ ,$$
$$I_3=(2/\operatorname{sech}D)[(1/\tanh D)-D\operatorname{sech}^{-2}D]\ .$$

In the absence of impurity potentials ($U_d=0$), the energy of the singlet state coincides with the result of Emin, Ye, and Beckel.[1] When the electron repulsion U becomes larger than $2.5E_b$, the bipolaron becomes unstable with respect to dissociation into infinitely separated polarons. Here the triplet state is also considered. In the absence of long-range Coulomb interactions, the energy of the triplet state does not depend explicitly on U. It is just the energy of two separated polarons:

$$-2E_p=-E_b^2/6t=-\tfrac{2}{3}t(a^2/L_0^2)\ .$$

When dopant pairs are introduced ($U_d\neq0$), the results are quite different. Even low pinning potentials ($|U_d/U|\leq0.1$) confine the two carriers sufficiently that their centroids are determined by the positions of the dopants. The ground-state energy is obtained by minimizing the energy values of Eq. (4) with respect to the centroids of the self-trapped carriers for each interdopant separation. The results of this optimization are summarized in Fig. 1 where the bipolaron energy expressed in units of E_p is plotted as a function of the interdopant separation expressed in units of the single-polaron width L_0, for two different values of the Coulomb repulsion expressed in units of E_b. The pinning potential is $U_d=0.2$ in both cases. As a function of U, we find a transition between two clearly different regimes separated by a thresold $U_t=2.5(1-0.75U_d)$. When $U>U_t$, the exchange energy $2J=E_{\mathrm{singlet}}-E_{\mathrm{triplet}}$ exponentially vanishes with the distance l, while, below the threshold, J remains finite.

We shall see that the experiments fix U unambiguously above the threshold U_t and below the $l=0$ singlet bipolaron stability limit, $U_{\mathrm{bp}}=2.5(1+0.7U_d)$. The attraction

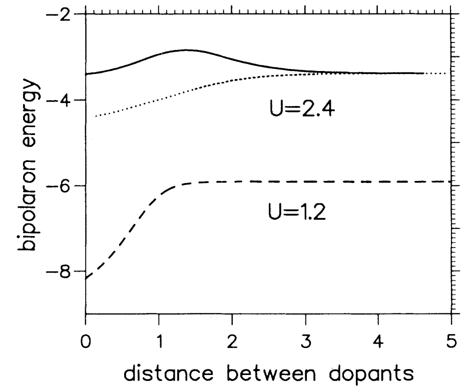

FIG. 1. The bipolaron energy is plotted in units of E_p as a function of the distance between dopants (in units of L_0). The dashed and dotted curves represent singlet-state energies plotted for two different values of the electron repulsion (in units of E_b), while the solid line represents the triplet-state energy. In all cases, the impurity attraction U_d was +0.2.

to the dopants produces a nonmonotonic dependence of the triplet energy on the interdopant separation. By using different asymptotic expansions of Eq. (6), we can deduce the following expressions of the exchange energy J (here, the bipolaron binding energy $E_{\rm bp}-2E_p$ is also $2J$) when $U_t < U < U_{\rm bp}$.

(i) When the normalized distance between dopants $D < 2$, the exchange energy is roughly constant, $J=-J_0$,

$$2J_0=8(1+1.1U_d-0.2U)^2-2(1+1.5U_d)^2 . \tag{7}$$

(ii) When $2 < D < D_{\rm crit}$, the exchange energy exponentially decreases,

$$2J_0=-2J_0\exp[-2(D-2)] . \tag{8}$$

The polaron position cannot be determined with an accuracy larger than the lattice constant a and the exchange energy J is determined with an accuracy $\Delta J=3a^2U_d/2L^2$. Thus exchange energies J lower than ΔJ are irrelevant. This limit ΔJ fixes a critical distance $D_{\rm crit}$ between the dopants, beyond which the two polarons are independent. We find

$$a^2/L^2=16D_{\rm crit}\exp(-2D_{\rm crit})\left[D_{\rm crit}+\frac{2-U}{U_d}\right] . \tag{9}$$

(For usual parameters values $D_{\rm crit}$ remains in the range 3.5–4.5.)

(iii) When $D > D_{\rm crit}$, $J=0$, the two polarons are independent.

From the dependence of J on the normalized distance $D=l/L$ between dopants the magnetic susceptibility χ of the bipolaron glass can be calculated at temperature T, within the simple approximation of an assembly of $N/2$ independent pairs:

$$\chi(T)=\frac{N\mu_B^2}{k_BT}\int\frac{4p(l)dl}{3+\exp(-2J/k_BT)} , \tag{10}$$

where μ_B and k_B are the usual universal constants, and $p(l)$ the probability distribution for finding two dopants and the distance l. In general, the random distribution of counterions $p(l)$ is unknown. An explicit expression of the susceptibility $\chi(T)$ is obtained for a random distribution of the dopants along the chain with a low distance cutoff l_0.

$$p(l)=(1/l_i)\exp[-(l-l_0)/l_i] , \tag{11}$$

where l_i is the width of the distribution and the average distance between dopants is $\langle l\rangle=l_0+l_i$. By using the expressions of J deduced here above,

$$\chi(l_0,l_i,T)\cong\frac{N\mu_B^2}{k_BT}\exp(l_0/l_i)\left[\exp[-(D_{\rm crit}L/l_i)]+\frac{1}{2}\left[\frac{k_BT}{2|J_0|e^4}\right]^{L/2l_i}\Gamma(L/(2l_i))\right] , \tag{12}$$

where $\Gamma(x)$ is the usual gamma function.

It is important to notice that the details of the random distribution of counterions $p(l)$ do not affect the general shape of the susceptibility versus temperature curve: in any case, the product $T\chi(T)$ is an increasing function of the temperature T and for the temperature less than some typical value $J(l)$, it is almost temperature independent.

Relation (12) is in good agreement with the numerical calculation of the susceptibility presented in Fig. 2. Indeed it contains two contributions: the first term in the bracket is the Curie component and the second term provides a high-temperature upturn in the susceptibility, which is sometimes referred to as a Pauli component. In Fig. 2 the spin susceptibility has been plotted as a function of T for various values of $\langle l\rangle$. The decrease of the susceptibility with the concentration of dopants reflects the usual spin-charge relation. (Notice that in the present formulation the total number of spins is constant.)

It is worth noting the values of the parameters that we have used to plot Figs. 1 and 2 where only reduced units appear. Thinking about polymers such as polypyrrole or polythiophene[9,10] and choosing the polaron formation energy in the absence of dopant interaction $E_p=0.1$ lead to

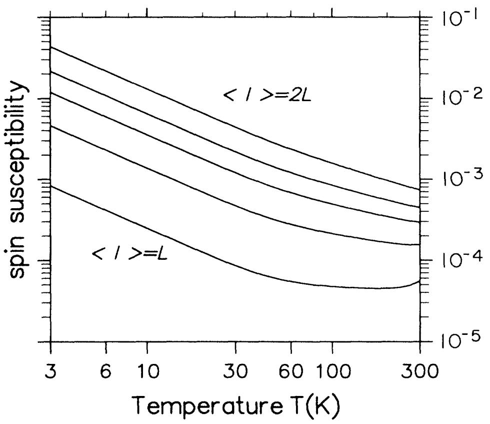

FIG. 2. The spin susceptibility in units of $N\mu_B^2/k_B$ is plotted vs the temperature between 3 and 300 K for different dopant concentrations. $\langle l\rangle$ is the average distance between dopant pairs. The minimal distance l_0 between dopants was considered to be two lattice constant $2a$ in all cases. The other parameters are the same as in Fig. 1 and in the text. There is no adjustable parameter. The higher concentration considered here ($\langle l\rangle=L$) corresponds, for instance, to a pair of counterions on a chain segment of 12 pyrrole monomers ($L=4$).

$E_b=1.7$ eV, $U=4$ eV, $U_d=0.3$ eV, $L_0=2.9a$ (single polaron width); then the model yields a formation energy of the polaron in the presence of a dopant of 0.17 eV and a bipolaron binding energy at low distances $2J_0=-0.17$ eV. These values are surprisingly reasonable and consistent with each other. With this reasonable set of values and no adjustable parameters, the spin susceptibility resembles the experimental data from different groups in the world[5,11] including recent results measured in our group in disordered polypyrrole.[12]

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