Correlation between Large Polarons in Molecular Chains

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Summary: We studied few extra electrons in a molecular chain with respect of electron-phonon coupling in the adiabatic approximation. It is shown that the lowest state of two extra electrons in a chain corresponds to the singlet bisoliton state with one deformational potential well. Two electrons with parallel spins form a localised triplet state, which corresponds to the two-hump charge distribution function. Three extra electrons form an almost independent nonlinear superposition of a soliton and bisoliton states. In the case of four electrons, the two almost independent bisolitons are formed. These two states tend to separate in the chain at the maximal distance due to the Fermi repulsion, accounted for in the zero-order adiabatic approximation. This repulsion is partly compensated by the attraction between the solitons due to their exchange with virtual phonons, described by the non-adiabatic part of the Hamiltonian. The formation of solitons is characterised by the appearance of the bound soliton and bisoliton levels in the forbidden energy band. This constitutes the qualitative difference of the large polaron (soliton) states from the almost free electron states and small polaron states.

Keywords: collective state; conducting polymers; electron-phonon interaction; polaron; soliton

Introduction

The concept of a 'soliton' [1,2] or large polaron [3] in low-dimensional molecular systems has been intensively used to explain various phenomena in biological physics and condensed matter physics [2-4]. A large polaron state is formed due to the electron-phonon interaction at moderate values of the interaction constant and is theoretically described in adiabatic approximation. There are clear experimental pieces of evidence of the existence of large polarons or solitons in conducting polymers [3,5]. In this respect, a question arises about the interaction between large polarons. It was shown in [6] that, due to the interaction with local deformation of the chain, two electrosolitons with opposite spins bind in a localized bound singlet spin state called 'bisoliton'.

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Here we consider the localized states of few extra electrons in the conducting band of a molecular chain in the adiabatic approximation.

Model Hamiltonian

The state of electrons in an isolated conduction band accounting for the electron-phonon interaction and neglecting direct electron-electron interaction, is described by Fröhlich Hamiltonian $\hat{H} = \hat{H}_{\mathrm{q}} + \hat{H}_{\mathrm{e-ph}} + \hat{H}_{\mathrm{ph}}$. This Hamiltonian is in the site or quasimomentum representation:

$$\hat{H} = \sum_{n,\sigma} E_0 a^{+}_{n,\sigma} a_{n,\sigma} + \sum_{n \neq m,\sigma} J_{n,m} a^{+}_{n,\sigma} a_{m,\sigma} + \frac{1}{\sqrt{N}} \sum_{n,\sigma,q} \chi(q) \mathrm{e}^{iqan} a^{+}_{n,\sigma} a_{n,\sigma} (b_q + b^{+}_{-q}) + \sum_{q} \hbar\omega_q b^{+}_q b_q \quad (1a)$$

$$\hat{H} = \sum_{k,\sigma} E(k)\ a^{+}_{k,\sigma} a_{k,\sigma} + \frac{1}{\sqrt{N}} \sum_{k,\sigma,q} \chi(q) a^{+}_{k,\sigma} a_{k-q,\sigma} (b_q + b^{+}_{-q}) + \sum_{q} \hbar\omega_q b^{+}_q b_q , \quad (1b)$$

where creation and annihilation operators of an electron of the site n with the spin σ are associated with the creation and annihilation operators of an electron with the wavevector k by the unitary transformation $a^{+}_{k,\sigma} = \frac{1}{\sqrt{N}} \sum_{n} \mathrm{e}^{ikan} a^{+}_{n,\sigma}$. The electron energy dispersion in the conduction band, *E(k),* is related to the matrix elements of the exchange interaction, $J_{n,m}$, by the Fourier transformation, and the function $\chi(q)$ determines the short-range interaction of electrons with phonons of the frequency ω_q.

The ground electron state in the conduction band is determined from the Schrödinger equation:

$$\hat{H}|\Psi\rangle = E|\Psi\rangle , \quad (2)$$

Depending on the value of the electron-phonon coupling, the three different types of the ground electron states can be realised in the system: (1) almost free electrons, (2) large polaron states, (3) small polaron states. Physical properties and mathematical tools of description of these three principal states of charge carriers are different. The realisation of one of the three regimes is determined by the relations between the three main parameters of the system [7]: (1) the electron band width, which is determined by matrix elements, (2) characteristic (or maximal) phonon frequency, ω_0, (3) electron-phonon interaction energy, which can be represented in the form:

$$E_b = \frac{1}{N}\sum_q \frac{|\chi(q)|^2}{\hbar\omega_q}. \qquad (3)$$

Here we discuss the state of few extra electrons in a molecular chain under adiabatic condition, which is necessary for the existence of large polarons. In this case the electron correlation is qualitatively different from the one in the two other cases. This is clear from the following analysis of the three limiting approximations.

Since the Hamiltonian (1) conserves the number of electrons, the state-vector of N_e electrons depends on the N_e creation operators. The solution of the Schrödinger equation can be written as $|\Psi\rangle = \hat{U}|\Psi_0\rangle$, where $\hat{U}(\{a^+\},\{b^+\}) = \exp(\hat{S})$ is a unitary operator. Then Eq. (2) can be transformed into the following one:

$$e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Psi_0\rangle \equiv \tilde{\hat{H}}|\Psi_0\rangle = E|\Psi_0\rangle. \qquad (4)$$

1. In the **weak interaction limit,** the electron-phonon interaction is assumed to be small, i.e., it is proportional to a small parameter ε. In this case the operator $\hat{S}$ in (4) is also proportional to the small parameter. The operator expansion can be used: $\tilde{\hat{H}} = \hat{H} + [\hat{H},\hat{S}] + \frac{1}{2}[[\hat{H},\hat{S}],\hat{S}] + \ldots$ In the first order of the perturbation theory the operator $\hat{S}$ can be found from the condition $\hat{H}_{e-ph} + [\hat{H}_e + \hat{H}_{ph},\hat{S}] = 0$, which gives

$$\hat{S} = \sum_{k,q,\sigma} f(k,q)a^+_{k,\sigma}a_{k-q,\sigma}b^+_q - \text{h..c.}, \qquad f(k,q) = \frac{1}{\sqrt{N}}\frac{\chi^*(q)}{\hbar\omega_q + E(k+q) - E(k)}. \qquad (5)$$

This transforms Hamiltonian (4) into the next one

$$\tilde{\hat{H}} = \sum_{k,\sigma}[E(k) + \Delta E(k)]a^+_{k,\sigma}a_{k,\sigma} + \sum_{k,k',q,\sigma,\sigma'} V(k,k',q)a^+_{k+q,\sigma}a^+_{k'-q,\sigma'}a_{k',\sigma'}a_{k,\sigma} + O(\varepsilon^3). \qquad (6)$$

Here *ΔE(k)* determines the standard renormalisation of the electron energy and effective mass in the second order of the perturbation theory [8]. The new term in (6) accounts for the direct electron-electron interaction, induced by phonons, $V(k,k',q) \sim |\chi(q)|^2$. This interaction is of the attraction type, it does not influence the state of an extra isolated electron, but it leads to the binding of the two isolated electrons into a Cooper pair [9]. In the case of a large number of electrons at the finite density, the ground electron state at zero temperature is the superconducting state.

2. In the **small polaron approximation** the matrix elements of the exchange interaction, $J_{n,m}$, are assumed to be small in the Hamiltonian. The unitary transformation is chosen in the form [10]:

$$\hat{S} = \sum_{n,q,\sigma} f(n,q) a^{+}_{n,\sigma} a_{n,\sigma} b^{+}_{q} - h.c., \qquad f(k,q) = \frac{1}{\sqrt{N}} \frac{\chi^{*}(q)}{\hbar\omega_q}. \tag{7}$$

In this case the transformed Hamiltonian in the nearest-neighbour approximation reads

$$\tilde{\tilde{H}} = \sum_{n,\sigma} [(E_n - E_b) a^{+}_{n,\sigma} a_{n,\sigma} - J e^{-G} (a^{+}_{n,\sigma} a_{n+1,\sigma} e^{-B^{+}_{n}} e^{B_n} + \text{h.c.})] -$$

$$- \sum_{n,m,\sigma,\sigma'} V(n-m) a^{+}_{n,\sigma} a^{+}_{m,\sigma'} a_{m,\sigma'} a_{n,\sigma} + \sum_{q} \hbar\omega_q b^{+}_{q} b_q . \tag{8}$$

Here the term proportional to the exponential operators describes jumps of a polaron from a site to a site with the creation of a certain number of phonons: $B_n^{+} \sim b_q^{+}$. In view of the small value of this term at strong coupling, $G \sim |\chi(q)|^2 >> 1$, it can be considered as a perturbation, so that the zero-order term of the Hamiltonian accounts for the processes with the conservation of the total number of phonons only. Then, in the wavevector presentation, one extra electron in a chain is described by a small polaron state in a narrow conduction band, $\tilde{J} = J\exp(-G)$. Moreover, the direct attraction type polaron-polaron interaction via phonons appears in Hamiltonian (8), which is given by the term $V(n-m)$. Therefore, the two extra electrons in a chain form a bipolaron [11]. The adiabatic limit will be considered in more details in the next section.

Adiabatic limit

In this case the kinetic energy of atom vibrations, which is a part of phonon Hamiltonian, $\hat{H}_{\text{ph}}$, is considered as a small term of the total Hamiltonian. Due to this, the vector state can be represented as the product of electron and phonon wavefunctions, which corresponds to the Born-Oppenheimer approximation. Accordingly, let us represent the unitary transformation, $\hat{U}$, as a product of $\hat{U}_{\text{e}}$ and $\hat{U}_{\text{ph}} = \exp(\hat{S})$.

$$\hat{S} = \frac{1}{\sqrt{N}} \sum_{q} \beta_q b^{+}_{q} - h.c., \qquad a_{k,\sigma} = \sum_{\lambda} \psi_{\lambda}(k) A_{\lambda,\sigma} \tag{9}$$

where the coefficients of the unitary operators are chosen in such a form that the electron part of the Hamiltonian $\tilde{\tilde{H}}$ is diagonal and, thus, they satisfy the equations:

$$E(k)\psi_\lambda(k)+\frac{1}{N}\sum_q \chi(q)(\beta_q+\beta_{-q}^*)\psi_\lambda(k-q)=E_\lambda\psi_\lambda(k). \tag{10}$$

These two transformations are not independent, electron state is determined by the lattice configuration, which, in turn, depends on the electron state. The transformed Hamiltonian now takes the form:

$$\tilde{\tilde{H}}=W+\sum_{\lambda,\sigma}E_\lambda A_{\lambda,\sigma}^+A_{\lambda,\sigma}+\sum_q\hbar\omega_q b_q^+b_q+\sum_q\{[\beta_q+\frac{1}{\sqrt{N}}\sum_{\lambda,\sigma}\varphi_{\lambda,\lambda}(q)A_{\lambda,\sigma}^+A_{\lambda,\sigma}]b_q^+ + \text{h.c.}\}+$$
$$+\sum_{\lambda\neq\lambda',\sigma}\varphi_{\lambda,\lambda'}(q)A_{\lambda,\sigma}^+A_{\lambda',\sigma}(b_q+b_{-q}^+). \tag{11}$$

Here $\varphi_{\lambda,\lambda'}(q)=\chi(q)\sum_k\Psi_\lambda^*(k)\Psi_{\lambda'}(k-q)$. The last term in (11) describes the transitions between the adiabatic terms with the absorption and radiation of phonons and is the nonadiabaticity operator. Provided the condition of the adiabatic approximation is fulfilled, it can be neglected and the problem can be studied in the zero-order adiabatic approximation. Unlike in the considered cases of almost free electrons and small polarons, the direct electron-electron interaction is absent in the zero-order Hamiltonian. Nevertheless, as mentioned above, electrons are not independent and move in the common self-consistent potential. In this case the ground electron state can be represented as the product of N_e electron creation operators and of the vacuum state

$$|\Psi_0\rangle=\prod_{\lambda,\sigma}A_{\lambda,\sigma}^+|0\rangle \tag{12}$$

which is the eigenstate with the energy $E=W+\sum_\lambda n_\lambda E_\lambda$. Here n_λ = 0,1,2 are the occupation numbers of the adiabatic level and $\sum_\lambda n_\lambda = N_e$. The coefficients β_q ought to satisfy the relation

$$\beta_q+\frac{1}{\sqrt{N}}\sum_\lambda n_\lambda\varphi_{\lambda\lambda}^*(q)=0. \tag{13}$$

Using the longwave (continuum) approximation and switching to spatial representation, we can give Eq. (10) in the form:

$$-\frac{d^2\Psi_\lambda}{dx^2}+U(x)\Psi_\lambda=\frac{2ma^2}{\hbar^2}E_\lambda\Psi_\lambda, \tag{14}$$

where the deformational potential, accounting for the expression (13), has the form

$$U(x) = -2g\sum_{\lambda} n_{\lambda}\left|\Psi_{\lambda}\right|^{2} \tag{15}$$

where m is the effective electron mass and g is the electron-phonon interaction constant. Because the deformational potential (15) is determined by the occupied adiabatic levels, the problem reduces to solving the system of many-component nonlinear Schrödinger equations for the occupied states [12]. Unoccupied excited states are determined by Eq. (15) with the given potential.

One extra electron is described by the conventional nonlinear Schrödinger equation for a single adiabatic level, $n = 1$, whose solution corresponds to the soliton state with the energy $E_1 = -\hbar^2\mu^2/(2ma^2)$, where $\mu = g/2$. The ground state of the two extra electrons in a chain also corresponds to one adiabatic level occupied by the two electrons with opposite spins, $n = 2$. The corresponding energy is $E_1 = -\hbar^2\mu^2/(2ma^2)$, where $\mu = g$.

In the case of three extra electrons, the ground state corresponds to the two occupied adiabatic levels with the occupation numbers $n_1 = 2$, $n_2 = 1$, which are determined by the two-component nonlinear Schrödinger equation which admits the solution[12]

$$\Psi_1 = \sqrt{\frac{\mu_1^2 - \mu_2^2}{g}}\,\frac{\mu_1\cosh(\phi_2)}{D}, \quad \Psi_2 = \sqrt{\frac{\mu_1^2 - \mu_2^2}{g}}\,\frac{\mu_2\sinh(\phi_1)}{D}, \tag{16}$$

where

$$D = \mu_1\cosh(\phi_1)\cosh(\phi_2) - \mu_2\sinh(\phi_1)\sinh(\phi_2), \quad \phi_1 = \mu_1(x+l), \quad \phi_2 = \mu_2(x-l). \tag{17}$$

The constant l in (17) can take arbitrary values. These two states correspond to energies $E_j = -\hbar^2\mu_j^2/(2ma^2)$, with $\mu_1 = g.$, $\mu_2 = g/2$. Therefore, the three electrons form a bisoliton and a soliton, which are described by essentially changed wavefunctions as compared with an isolated soliton function, and which have the total energy in the form of the sum of soliton and bisoliton energies. The constant l in this case determines the distance between soliton and bisoliton center of mass coordinates. This gives us an example of a nonlinear superposition of quasiparticles, when the energy is independent of the distance between them, although the total wavefunction is not a superposition of the functions. The corresponding wavefunctions (16) are shown in Fig. 1.

In the case of four extra electrons, the two adiabatic levels are occupied, with the occupation numbers $n_1 = n_2 = 2$. Similar situation takes place for the two electrons with polarised spins, so that $n_1 = n_2 = 1$. In these latter cases $\mu_1, \mu_2 \rightarrow \mu_0$, where $\mu_0 = g$ for two bisolitons, and $\mu_0 = g/2$ for

the triplet state. The wavefunctions $\Psi_{1,2}$ describe the two bisolitons (two solitons) separated by the large distance

$$L = \frac{1}{2\mu_0} \ln \frac{2\mu_0 \cosh(2\mu_0 l)}{\Delta} \to \infty \quad \text{at} \quad \Delta = \mu_1 - \mu_2 \to 0. \tag{18}$$

The total energy

$$E = -\frac{n^2}{6} Jg^2 + 2Jg^2 \cosh^2(gl) \exp(-2ngL), \tag{19}$$

where n = 1 for the triplet state, and n = 2 for the two bisolitons. The corresponding wavefunctions of four electrons are shown in Fig. 2. In this case the constant l characterises the level of collectivisation of the two separated potential wells.

The energy expression includes the term which depends on the distance between the centers of mass coordinates, L, and describes the repulsion due to the Pauli principle.

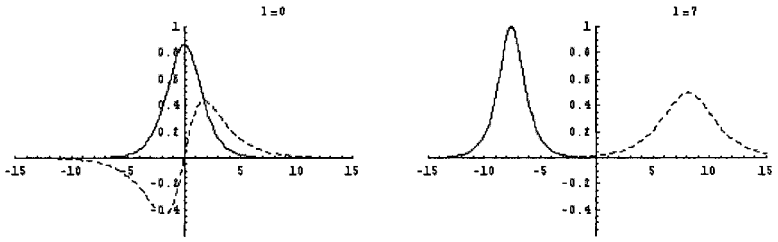

Fig.1. The wavefunctions of three extra electrons in a chain: (a) l = 0, (b) l = 7.

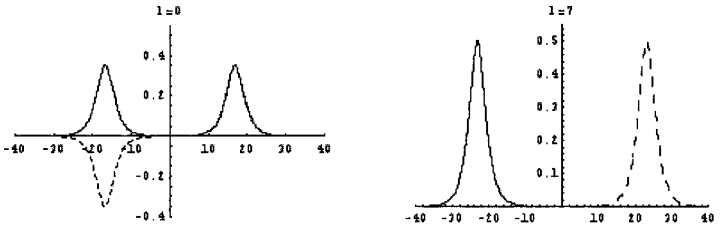

Fig.2. The wavefunctions of four extra electrons in a chain: (a) l = 0, (b) l = 7.

Non-adiabatic corrections

The nonadiabatic term in the Hamiltonian (11) results in the additional direct interaction between the two solitons or bisolitons via the phonon field. This additional interaction partly compensates the Fermi repulsion and stabilizes the two-bisoliton and triplet state solutions. Considering the nonadiabatic term of the Hamiltonian as a perturbation, one can write the first-order energy correction in the form

$$\Delta E = \langle \Psi_0 | \hat{H}_{\text{na}} \frac{1}{E - H_0} \hat{H}_{\text{na}} | \Psi_0 \rangle . \tag{20}$$

Here the wavefunctions correspond to the zero-order adiabatic approximation $\hat{H}_0$, and $\hat{H}_{\text{na}}$ is the non-adiabatic part of the Hamiltonian, i.e., the last term in (11). To calculate the energy of (20), it is necessary to find the total energy spectrum of the system. This includes the localised (bound) levels and delocalised (continuum) spectrum. The localised levels are always occupied, and unoccupied levels belong to the continuum spectrum. The corresponding calculations show that the energy correction term (20) contains two terms. One of these terms is independent of the distance between centres of mass coordinates and determines the renormalisation of their energy, while the second term depends on the distance. The latter term accounts for the additional attraction, and results in the stabilisation of the state. The total energy with the account of the correction term (20) has the form [13]:

$$E = -\frac{n^2}{6} Jg^2 \left(1 + \frac{3\gamma}{8\pi^6 g}\right) + 2Jg^2 \cosh^2(gl) \exp(-2ngL) - \frac{3Jg\gamma}{8\pi^3 L^2 \cosh(\lg)} . \tag{21}$$

Here γ is the so-called non-adiabaticity parameter determined as $\gamma = \hbar\omega_{\max}/J$.

Because of the competition between the repulsion force due to the Pauli principle and the attraction force due to the phonon field, the two bisolitons or two solitons with parallel spins are separated by the equilibrium distance, which is determined from the condition $dE/dL = 0$, where E is determined in (21).

Conclusion

We have shown that the lowest state of two extra electrons in a chain corresponds to the singlet bisoliton. Three extra electrons form almost independent nonlinear superposition of a soliton and bisoliton states. In the case of four electrons or two electrons with parallel spins, the two

independent bisolitons (solitons) are formed. These two states tend to separate in the chain at the maximal distance due to the Fermi repulsion. This repulsion is partly compensated by the attraction between the solitons due to their exchange by the virtual phonons. The formation of large polarons is characterised by the appearance of the bound soliton and bisoliton levels in the forbidden energy band. This constitutes a qualitative difference of the large polaron (soliton) states from the almost free electron states and small polaron states. In the case of a finite density of extra electrons in a chain at the zero temperature, the charge density wave is formed in a system [14]. The repulsion between bisolitons leads to the formation of a periodic lattice of bisolitons with the distribution period $l = N/N_{bs}$, $N_{bs} = N_e/2$, which corresponds to the many-electron solution of the Peierls-Froehlich problem at zero temperature [15].

It is worth noting that the self-consistent deformation potential of the lattice is a reflectionless one. In the case of one extra electron or a singlet state of two electrons that occupy the same level (bisoliton), this potential has a single bound state. In the case of a triplet state of two electrons (two bisolitons), when Fermi statistics forbids one-level occupation, lattice deformation forms a reflectionless potential with two bound levels. In the case of an arbitrary number of electrons, the corresponding self-consistent deformation potential is a reflectionless single-band potential with one gap, which separates the occupied sublevels from the vacant ones [15].

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[1] A.S. Davydov, N.I. Kislukha, *Phys. Status Solidi,* (b) **1973,** *59*, 465.
[2] A.S. Davydov, "*Solitons in Molecular Systems*", Reidel, Dordrecht, 1985.
[3] A.J. Heeger, et al., *Rev. Mod. Phys.,* **1988,** *60,* 781.
[4] A.C. Scott, *Phys. Rep.*, **1992**, *217,* 1.
[5] I. Gontia, et al., *Phys. Rev. Lett.,* **1999,** *82,* 4058.
[6] L.S. Brizhik, A.S. Davydov, *Fiz. Nizk. Temp.*, **1984**, *10,* 748.
[7] L.S. Brizhik, A.A. Eremko, *Synth. Met.,* **2000,** *109*, 117.
[8] H. Haken, *Quantenfeldtheorie des Festkörpers*, B.G. Teubner, Stuttgart, 1973.
[9] L.N. Cooper, *Phys. Rev.*, **1956,** *104,* 1189.
[10] Yu.A. Firsov (Ed.), *"Polarons"*, Nauka, Moscow, 1975.
[11] A.S. Alexandrov, J. Ranninger, *Phys. Rev. B,* **1981,** *23,* 1794; *24,* 1164.
[12] L.S. Brizhik, A.A. Eremko, *Physica D,* **1995,** *81,* 295.
[13] L.S. Brizhik, A.A. Eremko, *Ukr. J. Phys.*, **1999,** *44,* 1022.
[14] G. Gruner, *Rev. Mod. Phys.*, **1988**, *60*, 1129.
[15] A.A. Eremko, *Phys. Rev. B,* **1992**, *46*, 3721.