POLARON-TYPE STATES IN ONE-DIMENSIONAL SEMICONDUCTORS

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The states of electrons and holes which interact with lattice vibrations in a one-dimensional semiconductor are considered. Moderately strong electron-phonon coupling leads to the self-trapping of carriers and polaron and bipolaron states for electrons or holes, as well as bound localized states of electron-hole pairs are formed. The self-trapping of carriers is accompanied by self-consistent lattice distortion which causes the appearance of bound electronic levels in the forbidden energy band, and, threfore, leads to the appearance of specific spectral lines within the gap region in the optical absorption spectra.

Introduction

The discovery that conjugated polymers, being insulators in their neutral forms, become highly conducting by oxidation or reduction [1—4], opened the field of conducting polymers. The emergence of these polymers as a new class of electronic materials has attracted considerable attention. In particular, a variety of applications using conducting polymers has been proposed such as rechargeable [5] and solar [6] batteries, information storage devices [7], sensors [8], electro-optical and nonlinear optical [9—12] devices.

Numerous, both experimental and theoretical, studies have shown that conjugated polymers exhibit semiconducting properties. Through doping (by oxidation, *p*-type, or reduction, *n*-type) the electronic and optical properties of conducting polymers are experimentally controlled over the full range from insulator to metal states. The study of physical properties of various polymers rules out the applicability of the conventional metallic band transport theory for these systems. Many investigations suggest the formation of nonlinear excitations, such as polarons, bipolarons, and solitons, in conducting polymers [13] under doping or photoexcitation.

Theoretical calculations of the electronic structure were performed either for oligomers with up to 40 units using some molecular orbital methods, or for infinite chains using band theory based on semiempirical, first principles and *ab initio* calculations. Calculations of the

energetics of the polaron and bipolaron formation are based on the tight-binding Hückel theory with using model Hamiltonians for polymer chains [14, 15]. For polymers with different conjugations and backbones, different versions of a model Hamiltonian should be used. In the present paper, a general approach to the theoretical description of polaron-like states in such systems is proposed. Of course, the electronic structure of polymers is determined by a chain structure (e.g., the number and kind of atoms in the repeated units) and its symmetry. But in general, conjugated polymers are semiconductors with the filled higher occupied band separated by an energy gap from the empty one (the lowest unoccupied band). The electronic band structure of a polymer appears as the result of the translational symmetry. Therefore, we can consider conducting polymers as one-dimensional semiconductors with corresponding conducting and valence bands. In one-dimensional systems, the electron-phonon interaction plays an important role, and it is nesessary to take it into consideration. Often, in some approximation, we can use such physical characteristics of semiconductors as effective masses of electrons and holes, phonons' frequencies, and electron- and hole-phonon coupling constants, which can be determined from quantum-chemical calculations or from experimental data. Although the linear and nonlinear optical properties of conducting polymers have been investigated for over a decade, there is a contraversy in describing elementary excitations. In this connection, a general consideration which combines the physical insight with explicit analytical expressions seems to be useful.

1. Adiabatic Approximation

Let us consider the simplest case of a one-dimensional semiconductor with nondegenerate valence and conducting bands separated by the energy gap Δ. The ground state $|\Phi_0\rangle$ describes a semiconductor with completely filled valence band and empty conducting

one. If these two bands are well isolated from others, the Hamiltonian which describes excitations in such a semiconductor can be written in the form:

$$H = \mathcal{E}_0 + E_I(N_e - N_h) + H_e + H_h + H_{ph} + H_{e-ph} + H_{h-ph}. \quad (1)$$

Here

$$H_{ph} = \sum_{k,j} \hbar\omega_j(k)\left(b_{k,j}^+ b_{k,j} + \tfrac{1}{2}\right) \quad (2)$$

is the phonon Hamiltonian with $b_{k,j}^+$ ($b_{k,j}$) being Bose operators of creation (annihilation) of phonons with wavenumber k and frequency $\omega_j(k)$ of the j-th branch of normal vibrations of a backbone,

$$H_e = \sum_{k,s} E_e(k)c_{k,s}^+ c_{k,s}, \quad H_h = \sum_{k,s} E_h(k)d_{k,s}^+ d_{k,s}, \quad (3)$$

are the energy operators for electrons in the conducting band ($c_{k,s}^+$ is the Fermi operator of creation of an electron with wavenumber k and spin s in the conducting band) and for holes in the valence band ($d_{k,s}^+$ is the Fermi operator of creation of a hole (electron annihilation) with wave number k and spin s in the valence band), respectively, and the operators

$$H_{e-ph} =$$
$$= \tfrac{1}{\sqrt{N}} \sum_{k,k's,j} \chi_{e,j}(k,k')c_{k,s}^+ c_{k',s}(b_{k-k',j} + b_{k'-k,j}^+), \quad (4)$$
$$H_{h-eh} =$$
$$= \tfrac{1}{\sqrt{N}} \sum_{k,k',s,j} \chi_{h,j}(k,k')d_{k,s}^+ d_{k',s}(b_{k-k',j} + b_{k'-k,j}^+) \quad (5)$$

describe, accordingly, the interaction of electrons and holes with phonons. In (1), E_I is the middle gap energy and N_e and N_h are the operators of the numbers of electrons and holes:

$$N_e = \sum_{k,s} c_{k,s}^+ c_{k,s}, \qquad N_h = \sum_{k,s} d_{k,s}^+ d_{k,s}.$$

Explicit expressions of energy dispersion in the conducting (c) and the valence (v) bands

$$E_{e(h)} = \tfrac{1}{2}\Delta + L_{c(v)}(k) \quad (6)$$

as well as the explicit dependence of the coupling functions $\chi_{e(h),j}(k,k') = \chi_{e(h),j}^*(k',k)$ on wave numbers are determined by polymer structure.

The ground state $|\Phi_0\rangle$ is the eigenvector of Hamiltonian (1) with energy $\mathcal{E}_0$:

$$H|\Phi_0\rangle = \mathcal{E}_0|\Phi_0\rangle$$

($c_{k,s}|\Phi_0\rangle = d_{k,s}|\Phi_0\rangle = 0$). The excited state of a semiconductor corresponds to the appearance of some number of electrons, ν_e, in the conducting band and/or holes, ν_h, in the valence one. This state $|\Psi\rangle = |\Psi(\nu_e,\nu_h)\rangle$ and the corresponding energy are found from the Schrödinger equation

$$H|\Psi(\nu_e,\nu_h)\rangle = E(\nu_e,\nu_h)|\Psi(\nu_e,\nu_h)\rangle. \quad (7)$$

The presence of quasiparticles (a charge, electrons or holes, under doping, or electron-hole pairs by photoexcitation) induces displacements of the nuclei of the polymer backbone from their equilibrium positions. In the adiabatic approximation, such a lattice distorsion or the renormalization of the phonon ground state is described by a unitary operator $\exp(S)$ which appears in the eigenstate vector $|\Psi\rangle$ as a multiplier [16]:

$$|\Psi(\nu_e,\nu_h)\rangle = e^S|\widetilde{\Psi}(\nu_e,\nu_h)\rangle,$$
$$S = \tfrac{1}{\sqrt{N}} \sum_{k,j}[\beta_j(k)b_{k,j}^+ - \beta_j^*(k)b_{k,j}]. \quad (8)$$

In this case, Eq.(7) can be rewritten as

$$\widetilde{H}|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = E(\nu_e,\nu_h)|\widetilde{\Psi}(\nu_e,\nu_h)\rangle, \quad (9)$$

where

$$\widetilde{H} = e^{-S}He^S = \mathcal{E}_0 + W + E_I(N_e - N_h) + \widetilde{H}_e + \widetilde{H}_h +$$
$$+ H_{ph} + H_{e-ph} + H_{h-ph} + \tfrac{1}{\sqrt{N}}\sum_{k,j}[\hbar\omega_j(k)\beta_j(k)b_{k,j}^+ +$$
$$+ \hbar\omega_j(k)\beta_j^*(k)b_{k,j}]. \quad (10)$$

Here

$$W = \tfrac{1}{N}\sum_{k,j}\hbar\omega_j(k)|\beta_j(k)|^2 \quad (11)$$

is the energy of the lattice deformation and

$$\widetilde{H}_e = \sum_{k,s} c_{k,s}^+\{E_e(k)c_{k,s} +$$
$$+ \tfrac{1}{N}\sum_{k',j}\chi_{e,j}(k,k')[\beta_j(k-k') + \beta_j^*(k'-k)]c_{k',s}\}, \quad (12)$$
$$\widetilde{H}_h = \sum_{k,s} d_{k,s}^+\{E_h(k)d_{k,s} +$$
$$+ \tfrac{1}{N}\sum_{k',j}\chi_{h,j}(k,k')[\beta_j(k-k') + \beta_j^*(k'-k)]d_{k',s}\}. \quad (13)$$

By the unitary transformation

$$c_{k,s} = \sum_\lambda \psi_\lambda(k)C_{\lambda,s}, \quad d_{k,s} = \sum_\mu \varphi_\mu(k)D_{\mu,s} \quad (14)$$

with

$$\sum_\lambda \psi_\lambda^*(k)\psi_\lambda(k') = \delta_{k,k'}, \quad \sum_k \psi_\lambda^*(k)\psi_{\lambda'}(k) = \delta_{\lambda,\lambda'},$$

$$\sum_\mu \varphi_\mu^*(k)\varphi_\mu(k') = \delta_{k,k'}, \quad \sum_k \varphi_\mu^*(k)\varphi_{\mu'}(k) = \delta_{\mu,\mu'}, \quad (15)$$

we can diagonalize the operators for electrons, $\widetilde{H}_e$, and holes, $\widetilde{H}_h$, (12)—(13), and get the expression

$$\widetilde{H}_e = \sum_{\lambda,s} E_\lambda C_{\lambda,s}^+ C_{\lambda,s}, \quad \widetilde{H}_h = \sum_{\mu,s} E_\mu D_{\mu,s}^+ D_{\mu,s}. \quad (16)$$

The coefficients of the unitary transformation (14) and adiabatic energy levels for electrons, E_λ, and holes, E_μ, are found from the equations

$$E_e(k)\psi_\lambda(k) + \frac{1}{N}\sum_{k',j}\chi_{e,j}(k,k')[\beta_j(k-k')+$$

$$+\beta_j^*(k'-k)]\psi_\lambda(k') = E_\lambda\psi_\lambda(k), \quad (17)$$

$$E_h(k)\varphi_\mu(k) + \frac{1}{N}\sum_{k',j}\chi_{h,j}(k,k')[\beta_j(k-k')+$$

$$+\beta_j^*(k'-k)]\varphi_\mu(k') = E_\mu\varphi_\mu(k). \quad (18)$$

The operators of the electron- and hole-phonon interaction, (4), read in the new representation (14) as

$$H_{e-\mathrm{ph}} =$$

$$= \frac{1}{\sqrt{N}}\sum_{\lambda,\lambda',s,k,j} F_{\lambda,\lambda';j}(k)C_{\lambda,s}^+ C_{\lambda',s}(b_{k,j} + b_{-k,j}^+), \quad (19)$$

$$H_{h-\mathrm{eh}} =$$

$$= \frac{1}{\sqrt{N}}\sum_{\mu,\mu',s,k,j} \Phi_{\mu,\mu';j}(k)D_{\mu,s}^+ D_{\mu',s}(b_{k,j} + b_{-k,j}^+), \quad (20)$$

where

$$F_{\lambda,\lambda';j}(k) = \sum_{k'}\chi_{e,j}(k+k',k')\psi_\lambda^*(k+k')\psi_{\lambda'}(k') , \quad (21)$$

$$\Phi_{\mu,\mu';j}(k) = \sum_{k'}\chi_{h,j}(k+k',k')\varphi_\mu^*(k+k')\varphi_{\mu'}(k'). \quad (22)$$

In the adiabatic approximation, the solution of Eq. (9) which describes the state of a semiconductor with ν_e electrons and ν_h holes can be written as

$$|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = \prod_{\lambda,s}(C_{\lambda,s}^+)^{n_{\lambda,s}} \prod_{\mu,s}(D_{\mu,s}^+)^{n_{\mu,s}} |\Phi_0\rangle, \quad (23)$$

where $n_{\lambda,s} = 0,1$ and $n_{\mu,s} = 0,1$ are occupation numbers which indicate the filling of adiabatic levels λ and μ by electrons and holes, correspondingly, with spins s and

$$\sum_{\lambda,s} n_{\lambda,s} = \nu_e, \quad \sum_{\mu,s} n_{\mu,s} = \nu_h. \quad (24)$$

Taking into account the properties of Fermi-operators, we can see that

$$C_{\lambda,s}|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = D_{\mu,s}|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = 0 \quad (25)$$

for those (λ, s) and (μ, s) for which $n_{\lambda,s} = n_{\mu,s} = 0$, and

$$C_{\lambda,s}^+|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = D_{\mu,s}^+|\widetilde{\Psi}(\nu_e,\nu_h)\rangle = 0 \quad (26)$$

for those (λ, s) and (μ, s) for which $n_{\lambda,s} = n_{\mu,s} = 1$. Therefore, with respect to the action of Fermi-operators on state (23), we can introduce the operators

$$C_{\lambda,s} = (1 - n_{\lambda,s})C_{\lambda,s} + n_{\lambda,s}\widetilde{D}_{\lambda,-s}^+,$$

$$D_{\mu,s} = (1 - n_{\mu,s})D_{\mu,s} + n_{\mu,s}\widetilde{C}_{\mu,-s}^+. \quad (27)$$

This means that, for unoccupied states, $n_{\lambda,s} = n_{\mu,s} = 0$, $C_{\lambda,s} = C_{\lambda,s}$ and $D_{\mu,s} = D_{\mu,s}$ are the annihilation operators for electrons and holes, respectively. For occupied states $n_{\lambda,s} = n_{\mu,s} = 1$, these operators are renamed as the creation operators for new holes and electrons, respectively: $C_{\lambda,s} = \widetilde{D}_{\lambda,-s}^+$ and $D_{\mu,s} = \widetilde{C}_{\mu,-s}^+$. Substituting (27) into (10) with account of (16) and (19) and after putting the creation and annihilation operators in the normal order, we get

$$\widetilde{H} = \mathcal{E}_0 + W + \sum_{\lambda,s} n_{\lambda,s}E_\lambda + \sum_{\mu,s} n_{\mu,s}E_\mu +$$

$$+E_I(N_e - N_h) + H_{\mathrm{exc}} + H_{na} +$$

$$+\frac{1}{\sqrt{N}}\sum_{k,j}\{[\hbar\omega_j(k)\beta_j(k) + \sum_{\lambda,s} n_{\lambda,s}F_{\lambda,\lambda;j}^*(k) +$$

$$+\sum_{\mu,s} n_{\mu,s}\Phi_{\mu,\mu;j}^*(k)]b_{k,j}^+ + \mathrm{h.c.}\} . \quad (28)$$

Here the Hamiltonian H_{exc} describes "excited" states relatively to the state $|\widetilde{\Psi}(\nu_e,\nu_h)\rangle$, (23), (this Hamiltonian holds terms with $C_{\lambda,s}^+ C_{\lambda',s}$, $\widetilde{D}_{\lambda,s}^+ \widetilde{D}_{\lambda',s}$, $D_{\mu,s}^+ D_{\mu',s}$, and $\widetilde{C}_{\mu,s}^+ \widetilde{C}_{\mu,s}$) and H_{na} is the nonadiabaticity operator and contains terms which correspond to phonon-induced transitions between occupied and unoccupied adiabatic terms. The lattice configuration in state (23) will be stable provided that terms which are linear with respect to the phonon operators $b_{k,j}^+$ disappear in Hamiltonian (28). This condition leads to the following relation for the parameters $\beta_j(k)$:

$$\beta_j(k) = -\left[\sum_{\lambda,s} n_{\lambda,s}\frac{F_{\lambda,\lambda;j}^*(k)}{\hbar\omega_j(k)} + \sum_{\mu,s} n_{\mu,s}\frac{\Phi_{\mu,\mu;j}^*(k)}{\hbar\omega_j(k)}\right] . \quad (29)$$

In the adiabatic approximation, H_{na} is considered as a perturbation and can be omitted in the zero-order approximation. In this case, the wave vector (23) is an eigenstate of Hamiltonian (28) with the energy eigenvalue

$$E(\nu_e, \nu_h) = \mathcal{E}_0 + E_I(\nu_e - \nu_h) + W +$$

$$+ \sum_{\lambda, s} n_{\lambda, s} E_\lambda + \sum_{\mu, s} n_{\mu, s} E_\mu. \qquad (30)$$

The condition of applicability of the adiabatic approximation in a one-dimensional electron-phonon system has been obtained in [17].

We see that adiabatic electronic terms are determined by the lattice configuration (Eqs.(17)—(18)) which, in turn, depends on the states of electrons or/and holes (Eq.(29)). Thus, after substituting (29) into (17) and (18), it becomes clear that, to solve the problem, we have to solve, in the general case, the system of nonlinear equations for occupied states. The solution gives us the self-consistent states for electrons (or/and holes) and lattice distortions. All other virtual adiabatic electronic states are determined from the linear equations (17) and (18) with the given lattice deformation.

2.   Polaronic States

Near the bottom of quasiparticle bands (the top of the valence band and the bottom of the conducting one), the approximation of effective masses can be used:

$$E_{e(h)}(k) = \tfrac{1}{2}\Delta + \frac{\hbar^2(k-k_0)^2}{2m_{e(h)}}, \qquad (31)$$

where k_0 corresponds to the bottom of bands. The value of k_0 is determined by a chain symmetry but usually (for simple chains) k_0 is the same for the conducting and valence bands and $k_0 = 0$ or π/a with a being the lattice constant.

For solving Eqs. (17)—(18), let us introduce the functions

$$\psi_\lambda(x) = \frac{1}{\sqrt{Na}} \sum_k e^{i(k-k_0)x} \psi_\lambda(k),$$

$$\varphi_\mu(x) = \frac{1}{\sqrt{Na}} \sum_k e^{i(k-k_0)x} \varphi_\mu(k) \qquad (32)$$

of the continuum variable x. Note, that, at $x = an$, the functions

$$\sqrt{a}\,\psi_\lambda(na)e^{ik_0 an} = \frac{1}{\sqrt{N}} \sum_k e^{ikan} \psi_\lambda(k)$$

(and similarly for φ_μ) are the coefficients of transformation (14) in the site representation.

For levels which are close to the bottom of bands, $\psi_\lambda(k)$ and $\varphi_\mu(k)$ are essentially nonzero for values of k which are close to k_0. Taking this into account and using (31), Eqs.(17)—(18) can be represented as the Schrödinger equations for functions (32),

$$-\frac{\hbar^2}{2m_e}\frac{d^2\psi_\lambda(x)}{dx^2} + V_e(x)\psi_\lambda(x) = (E_\lambda - \tfrac{1}{2}\Delta)\psi_\lambda(x), \qquad (33)$$

$$-\frac{\hbar^2}{2m_e}\frac{d^2\varphi_\mu(x)}{dx^2} + V_e(x)\varphi_\mu(x) = (E_\mu - \tfrac{1}{2}\Delta)\varphi_\mu(x), \qquad (34)$$

with

$$V_e(x) = -2a\big(G_e \sum_{\lambda, s} n_{\lambda, s} |\psi_\lambda(x)|^2 +$$

$$+ G_{e,h} \sum_{\mu, s} n_{\mu, s} |\varphi_\mu(x)|^2\big), \qquad (35)$$

$$V_h(x) = -2a\big(G_{h,e} \sum_{\lambda, s} n_{\lambda, s} |\psi_\lambda(x)|^2 +$$

$$+ G_h \sum_{\mu, s} n_{\mu, s} |\varphi_\mu(x)|^2\big). \qquad (36)$$

Here the following notations are introduced:

$$G_e = \sum_j |g_{e,j}|^2, \quad G_h = \sum_j |g_{h,j}|^2,$$

$$G_{e,h} = G_{h,e}^* = \sum_j g_{e,j} g_{h,j}^*, \qquad (37)$$

where

$$g_{e(h),j} = \lim_{k,k' \to k_0} \frac{\chi_{e(h),j}(k,k')}{\sqrt{\hbar\omega(k-k')}}.$$

A) P o l a r o n s   a n d   b i p o l a r o n s. Let us consider the case where, under doping, one or two identical quasiparticles appear in a semiconducting chain. In this case, only one adiabatic level E_0 is occupied either by one quasiparticle ($n_{0,s} = 1, n_{0,s'} = 0$) or by two quasiparticles with opposite spins ($n_{0,\uparrow} = n_{0,\downarrow} = 1$). Other occupation numbers are zero. The corresponding state (23) is characterized by filling numbers (24) $\nu_i = 1$ or $\nu_i = 2$ and $\nu_j = 0$ ($i = e$ when quasiparticles are electrons and $i = h$ in the case of holes; and $j \neq i$ indicates alternative quasiparticles).The self-consistent potentials in (35)—(36) become

$$V_i(x) = -2a\nu_i G_i |\psi_{i,0}(x)|^2,$$

$$V_j(x) = -2a\nu_i G_{j,i} |\psi_{i,0}(x)|^2. \qquad (38)$$

Thus, acording to (33)—(34) and (38), the occupied state $\psi_{i,0}(x)$ is determined from a nonlinear Schrödinger equation (NLSE) [18],[19] with the well-known solution

$$\varphi_{i,0}(x) = \sqrt{\frac{\alpha}{2}} \frac{1}{\cosh[\alpha(x-x_i)]}, \quad E_{i,0} = \frac{1}{2}\Delta - \frac{\hbar^2\alpha^2}{2m_i}. \quad (39)$$

This solution describes the self-trapped state of quasiparticles with localization parameter α which depends on the number of quasiparticles ν_i, quasiparticle effective mass m_i, and strength of electron-phonon coupling G_i,(37),

$$\alpha = \nu_i\alpha_i, \qquad \alpha_i = \frac{m_i a G_i}{\hbar^2}. \quad (40)$$

Solution (39) determines potentials (38) in the Schrödinger equations (33)—(34) which describe renormalized unoccupied adiabatic states. For quasiparticles of the same sort i as dopped ones, state (39) is a single bound state. Others belong to the quasicontinuum band spectrum which is characterized by the wave number k:

$$\psi_{i,k}(x) = \frac{1}{\sqrt{Na}} \frac{k - i\alpha \tanh[\alpha(x-x_i)]}{\sqrt{k^2+\alpha^2}} e^{ikx},$$

$$E_i(k) = \frac{1}{2}\Delta + \frac{\hbar^2(k-k_0)^2}{2m_i} \quad (41)$$

For quasiparticles of another sort, j, a solution of the corresponding Schrödinger equation depends on the parameter

$$C = \frac{m_j G_{j,i}}{m_i G_i}. \quad (42)$$

The energy spectrum consists of the quasicontinuum band states with the corresponding eigenfunctions and eigenenergies

$$\psi_{j,k}(x) = A_k e^{ikx} F(-s, 1+s, 1-i\frac{k}{\alpha}, \xi),$$

$$E_j(k) = \frac{1}{2}\Delta + \frac{\hbar^2(k-k_0)^2}{2m_j} \quad (43)$$

where $\xi = (1/2)(1 - \tanh[\alpha(x-x_i)])$, A_k is a normalization constant,

$$s = \frac{1}{2}(\sqrt{1+8C} - 1), \quad (44)$$

and $F(\alpha, \beta, \gamma, \xi)$ is the hypergeometric function. The presence of bound localized states and their number depend on the value of parameter C, (42). If $C \leq 0$ $(G_{j,i} \leq 0)$, there are no bound states. $G_{j,i} = 0$ corresponds to the case where electrons and holes interact with different phonon branches. At $C > 0$, the bound states appear in the spectrum with the energy levels

$$E_{j,n} = \frac{1}{2}\Delta - \frac{\hbar^2\alpha^2}{2m_j}(s-n)^2, \quad (45)$$

where $n = 0, 1, \ldots, [s]$ ($[s]$ is the integral part of a number s (44)). The corresponding wavefunctions $\psi_{jn}(x)$ are

$$\psi_{j0}(x) = \frac{A_0}{\cosh^s[\alpha(x-x_i)]},$$

$$\psi_{j1}(x) = \frac{A_1}{\cosh^{s-1}[\alpha(x-x_i)]} \tanh[\alpha(x-x_i)], \ldots \quad (46)$$

where A_n are normalization constants.

Quasiparticle self-trapping is accompanied by chain distortion (29) which requires energy consumption (11). Neverseless, energy (30) in the state $|\widetilde{\Psi}(0,\nu_i)\rangle$ with $\nu_i = 1, 2$,

$$E(0,\nu_i) = \mathcal{E}_0 \pm \nu_i E_I + W + \nu_i E_{i,0} =$$

$$= \mathcal{E}_0 \pm \nu_i E_0 + \frac{1}{2}\nu_i\Delta - \nu_i \frac{\hbar^2\alpha^2}{6m_i}, \quad (47)$$

is less than the energy $\mathcal{E}_0 \pm \nu_i E_0 + \frac{1}{2}\nu_i\Delta$ of ν_i delocalized quasiparticles (with the wave number $k = k_0$). Here the signs "+" and "−" correspond to electrons and holes, respectively. The gain of the total energy due to self-trapping is $\nu_i \frac{\hbar^2\alpha^2}{6m_i}$. Such a self-trapped state can propagate along the chain with constant velocity without changing its form and without losing the energy. At $\nu_i = 1$, state (39) describes a polaron and at $\nu_i = 2$ it corresponds to a bipolaron. After A.S. Davydov [20], such states are often called "electrosolitons" (at $\nu_i = 1$) and "bisolitons" (at $\nu_i = 2$) [21, 22].

A polaron or an electrosoliton state, $\nu_i = 1$, extends over several chain units and its width is inversely proportional to the parameter α_i, (40). The presence of a polaron on the chain introduces localized electronic levels in the gap. In the case of an electron polaron, $i = e$ and $j = h$, there are a singly occupied bound polaron level

$$E_{ip} = \frac{\hbar^2\alpha_i^2}{2m_i} \quad (48)$$

below the conducting band edge and doubly occupied localized levels

$$E_{jn} = (m_i/m_j)E_{ip}(s-n)^2 \quad (49)$$

above the valence band edge in the gap. In the case of a hole polaron, $i = h$ and $j = e$, the singly occupied bound polaron level (48) above the valence band edge and the empty localized levels (49) below the conducting band edge appear in the gap. If $0 < C \leq 1$ $(0 < s \leq 1)$, there is only one bound level, E_{j0}. At $1 < C \leq 3$ $(1 < s \leq 2)$, the second bound level with $n = 1$ is splitted from the quasiparticle band and so on. Usually $C \sim 1$ and if the

second bound level is present, it is very close to the band edge because of the inequality $(s - 1) \ll 1$.

A bipolaron or bisoliton state, $\nu_i = 2$, is more narrow because its localization parameter is $2\alpha_i$. In this case, the created localized electronic levels in the gap are: (i) a doubly occupied bound bipolaron level $4E_{ip}$ below the conducting band and doubly occupied localized levels $4E_{jn}$ above the valence band in the case of an electron bipolaron, $i = e$ and $j = h$ and (ii) an empty (doubly occupied by holes) bound bipolaron level $4E_{ip}$ above the valence band and empty localized levels $4E_{jn}$ below the conducting band in the case of a hole polaron, $i = h$ and $j = e$.

The bipolaron energy (47) is less than that of two isolated polarons with the gain of the total energy equal to $2E_{ip}$. This indicates that the formation of bipolaron is favored as compared with that of two isolated polarons [21—23]. Because a bipolaron is formed by two identical quasiparticles with opposite spins, it is a spinless doubly charged carrier (negative in the case of electrons and positive in the case of holes). Due to the Fermi statistics, a pair of quasiparticles in the triplet state form two isolated polarons [24].

B) E l e c t r o n - h o l e p a i r s. Let an electron-hole pair appear in a one-dimensional semiconductor under excitation. In this case, the excited state (23) is $|\widetilde{\Psi}(1,1)\rangle$ ($\nu_e = \nu_h = 1$) in which an electron and a hole occupy their own levels $\lambda = \lambda_0$ and $\mu = \mu_0$. Below we denote $\lambda_0 = \mu_0 = 0$. In this case, the self-consistent potentials in Eqs.(17)—(18) are

$$V_e(x) = -2a\left(G_e|\psi_0(x)|^2 + G_{e,h}|\varphi_0(x)|^2\right), \qquad (50)$$

$$V_h(x) = -2a\left(G_{h,e}|\psi_0(x)|^2 + G_h|\varphi_0(x)|^2\right) \qquad (51)$$

and, for determining the occupied adiabatic terms, it is nesessary to solve the system of two nonlinear equations (17)—(18) for $\psi_0(x)$ and $\varphi_0(x)$. This system admits a solution in the form of two independent electron and hole polarons (39) separated by the enough large distance $|x_e - x_h| \to \infty$ such that $\psi_0(x) = 0$ in the region where $\varphi_0(x) \neq 0$ and vice versa. In this case, the total energy (30) is

$$E_f(1,1) = \mathcal{E}_\prime + W + E_{\lambda_0} + E_{\mu_0} = \mathcal{E}_\prime + \Delta - \frac{\hbar^2\alpha_e^2}{6m_e} - \frac{\hbar^2\alpha_h^2}{6m_h}, (52)$$

where α_i $(i = e, h)$ is given by (40).

The general solution can be obtained easily in the case where $C = 1$ (the parameter C is determined in (42)). In this case, the solution $\psi_0(x) = \varphi_0(x)$ is described by the same function as that in (39) and the electron and hole eigenenergies are

$$E_{ep} = \frac{\hbar^2\alpha_0^2}{2m_e}, \qquad E_{hp} = \frac{\hbar^2\alpha_0^2}{2m_h}. \qquad (53)$$

Here the localization parameter α_0 is

$$\alpha_0 = \frac{m_e a(G_e + G_{e,h})}{\hbar^2} = \frac{m_h a(G_h + G_{h,e})}{\hbar^2}. \qquad (54)$$

This solution corresponds to an electron-hole pair bound in the common self-consistent lattice potential. The total energy (30) in this state is

$$E_b(1,1) = \mathcal{E}_0 + \Delta - \frac{\hbar^2\alpha_0^2}{6\mu}, \qquad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}. \qquad (55)$$

The diference between energy (52) of isolated electron and hole polarons and the energy (55) of an electron-hole bipolaron (or bisoliton) is

$$\Delta E = \frac{1}{6}G_{e,h}(2\alpha_0 + \alpha_e + \alpha_h)a. \qquad (56)$$

Therefore, at $G_{e,h} > 0$, the formation of a bound electron-hole pair is favored over that of two isolated polarons with the gain in total energy by (56). An electron-hole bipolaron is a neutral nonlinear formation which can be in a singlet state (electron and hole have opposite spins) and in a triplet one (electron and hole have equal spins). Due to the processes of radiative recombination, a lifetime of singlet pairs is small, whereas a triplet electron-hole bipolaron is long-lived.

Conclusion

The presence of polaron states leads to the appearence of bound electron levels in the gap region. These localized electronic levels can become apparent in optical absorption data. Due to the different filling of localized levels in cases of polarons and bipolarons, optical measerments allow one to distinguish polarons and bipolarons. In the case of bipolarons within the gap region, there are two additional features in absorption spectra. In the case of hole polarons, these two lines correspond to transitions between the valence band and two unoccupied localized levels. In the case of electron bipolarons, the additional lines correspond to transitions between two filled bound levels and the conducting band. In the case of a polaron state, there appears the third absorption line which corresponds to the transition between localized levels. Such an evolution of the optical spectrum upon a doping of the conducting polymer poly(pyrrol) (PP) have been observed experimentally [25]. At low levels of oxidation of PP, there are three additional features of absorption within the gap region. As the level of oxidation increases, the middle

absorption line disappears. In the fully oxidized sample, two intensive broad absorption bands are present. This observation led the authors to suggest that such an evolution could be explained by the formation of polaron and bipolaron states.

The formation of a bipolaron is favored over that of two isolated polarons. Indeed, many experimental observations can be explained by relating charge carriers to doubly charged spinless bipolarons [26] and, in some polymers (e.g., in poly(thiophene) [27]), the kinetics of recombination of polaron pairs into lower-energy bipolarons is sufficiently rapid. In [26], it is also found that there is no correlation of the ESP spectrum with the transport properties, and, moreover, it is possible, by electrochemical cycling, to reduce the spin concentration without affecting the conductivity. Hence, the authors conclude that the paramagnetic species are predominantly neutral and, conversely, that the charge carriers are spinless. It is suggested that these latter species are bipolarons, singlet-bound states of two positively charged polarons (hole bipolarons), and it is possible to suggest that the former species are electron-hole bipolarons.

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СТАНИ ПОЛЯРОННОГО ТИПУ В ОДНОВИМІРНИХ НАПІВПРОВІДНИКАХ

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Р е з ю м е

В адіабатичному наближенні розглянуто стани електронів та дірок, що взаємодіють з коливаннями гратки в одновимірних напівпровідниках. Помірно сильна електрон-фононна взаємодія приводить до автолокалізації носіїв з утворенням поляронних і біполяронних станів. Одна квазічастинка автолокалізується в електронний або дірковий полярон. Дві квазічастинки внаслідок взаємодії з деформацією гратки зв'язуються в біполяронні стани, що відповідають (і) електронним або дірковим біполяронам з подвійним зарядом і нульовим спіном та (ii) нейтральним локалізованим електрон-дірковим парам в триплетному стані. Автолокалізація носіїв супроводжується самоузгодженою деформацією молекулярного ланцюжка, що спричинює появу локалізованих електронних рівнів у забороненій енергетичній зоні. Наявність цих рівнів проявляється в оптичних спектрах поглинання одновимірних напівпровідників у вигляді характерних спектральних ліній, що розташовані нижче порога міжзонних переходів.

СОСТОЯНИЯ ПОЛЯРОННОГО ТИПА В ОДНОМЕРНИХ ПОЛУПРОВОДНИКАХ

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Р е з ю м е

В адиабатическом приближении рассмотрены состояния электронов и дырок, взаимодействующих с колебаниями решетки,

в одномерных полупроводниках. Умеренно сильное электрон-фононное взаимодействие приводит к автолокализации носителей с образованием поляронных и биполяронных состояний. Одна квазичастица, самозахватываясь решеткой, образует электронный или дырочный полярон. Две квазичастицы вследствие взаимодействия с деформацией решетки связываются в биполяронные состояния, соответствущие (i) электронным или дырочным биполяронам с двойным зарядом и нулевым спином и (ii) нейтральным локализованным электрон-дырочным парам в триплетном состоянии. Автолокализация носителей сопровождается самосогласованной деформацией молекулярной цепочки, что приводит к появлению локализованных электронных уровней в запрещенной зоне. Наличие этих уровней проявляется в оптических спектрах поглощения одномерных полупроводников в виде характерных линий, расположенных ниже порога межзонных переходов.