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Correlation effects and configuration of a one-dimensional bipolaron

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ABSTRACT

The aim of the work is to study the structure of a one-dimensional (1D) bipolaron, taking into account three types of correlation effects: such as interelectronic correlations caused by the direct dependence of the wave function on the distance between electrons as well as the one-center and two-center correlations. Gaussian orbitals with exponentially-correlated multipliers were used for variational calculations. It is shown that in the domain of existence of an 1D optical bipolaron – unlike in a 3D system – a two-center bipolaron is formed. The one-center bipolaron configuration becomes energetically favorable as compared to the two-center one for $V_C \leq 1.2$ (where V_C is interelectronic repulsion parameter). This domain corresponds to an acoustical or acousto-optical bipolaron in the strong-coupling limit.

1. Introduction

Self-localized states (polarons and bipolarons) are investigated in a lot of papers which are overviewed in numerous reviews and monographs [1–4]. Passing on from three-dimensional (3D) systems to one-dimensional (1D) ones involves qualitative changes in the energy spectrum of polaron and bipolaron states. Examples of one-dimensional and quasi-one-dimensional systems that allow an electron-phonon interaction to be continually considered can be organic molecules containing consecutively arranged identical chromoform groups, different polymers consisting of identical molecules or atoms, the number of which can reach several million. Of particular interest is the process of charge transfer in systems of wildlife. One of the objects with conductivity properties close to one-dimensional systems can be biological macromolecules, such as DNA. The most likely carrier of charge in DNA are polarons, which can be considered within the framework of various models [5–9].

The development of nanotechnology has led to the creation of new objects of reduced dimensionality, such as quantum wires, quantum wells [10], quantum dots [11–13], and even linearly ordered quantum dots [14,15], which are an example of low-dimensional systems with polaron conductivity [16].

Experimental and theoretical methods for studying polaron effects used in 3D systems [17] are successfully applied in systems of lower dimensionality [18]. Leskinen et al. [18] find polaronic behavior in one-dimensional (1D) optical lattice qualitatively similar to that in the experiment by Schirotzek et al. [17], where radiofrequency spectroscopy was used to observe polarons in three-dimensional (3D) systems. Considerable attention is currently being paid to studying the mechanisms of polaron effects in 1D organic polymers [19,20] and wildlife objects [21–23].

The study of such molecular systems is relevant in connection with their use in solar energy converters [24], flexible TV displays, logical circuits [25], organic bioelectronics [26–28], using DNA in molecular lithography for the manufacture of monolithic microcircuits [29], as well as the prospects for their use in molecular electronics devices [16,30–32]

A polaron is a complex of electrons and the lattice distortions that accompany them. The lattice distortions can be created by optical and acoustic phonons. In 1D systems the strong coupling functionals of the optical and acoustic polaron are identical, and the Euler equation corresponding to the polaron functional has an exact solution [33,34]. In this paper we consider polarons in 1D-systems without specifying the physical nature of the electron-phonon interaction. The basic system is a continuum Holstein 1D polaron [34] and the corresponding strong-coupling functional. The influence of correlation effects on the coupling energy of a 1D bipolaron was considered earlier by Emin et al. in Ref. [35]. In the absence of correlation effects the bipolaron wave function is a product of polaron wave functions. The two types of correlation

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effects have already been considered in Ref. [35]: in-out and left-right correlations. The in-out correlations correspond to the one-center bipolaron configuration while the left-right correlations – to the two-center one. These correlation effects were considered independently, both of them together were not taken into account. In our paper these correlations are called one-center correlations and two-center ones, respectively. In three-dimensional systems stabilization of the bipolaron states mainly depends on the correlation effects associated with the direct dependence of the system's wave function on the interelectronic distance [4,36]. Correlation effects of this type were not considered in Ref. [35]. In Ref. [9] consideration was given to a one-center model of 1D bipolaron with regard for correlation effects of this type. In what follows such correlations will be called interelectronic correlations. In Ref. [22] consideration was given to the possibility of formation of bipolaron states in DNA in adiabatic approximation on the basis of Holstein-Habbard discrete mode. DNA can provide an example of a one-dimensional system possessing the properties of dielectrics [37,38], semiconductors [39–41], metals [42,43], and even superconductors [44,45]. The papers devoted to the study of various aspects of charge transfer in DNA are reviewed in Refs. [46–48]. Presently the bipolaron mechanism of superconductivity leads among the mechanisms for explaining the high-temperature superconductivity [4,49,50]. The superconducting state of DNA was observed at low temperatures $T \approx 1$ K for chaotic nucleotide sequences (λ - DNA) [44]. The low temperature of the superconducting transition can be caused by inhomogeneity of nucleotide composition. Therefore it is important to study the possibility of the formation of bipolarons in homogeneous nucleotide sequences where bipolaron states are more stable.

The aim of this paper is to calculate the coupling energy of a one-dimensional bipolaron with regard for the three above-mentioned correlation effects for various distances between the centers of polarization wells. The dependencies obtained will enable us to make a conclusion about the configuration of a 1D bipolaron depending on the parameters characterizing the value of the electron-phonon interaction and the value of Coulomb repulsion between the electrons in the system under consideration.

2. Effective functional of the ground state of a one-dimensional polaron

In continuum approximation the functional of a one-dimensional polaron can be written as in Refs. [35,9]:

$$E_1 = t\int \left|\frac{\partial \phi(x)}{\partial x}\right|^2 dx - E_b \int dx|\phi(x)|^4, \tag{1}$$

where t and E_b are parameters of the theory.

Functionals (1) can be obtained both by the adiabatic approximation method [35,9], and within the framework of the quantum approach describing the electron-phonon interaction by the Frohlich Hamiltonian [51].

By analogy with a three-dimensional polaron, the parameter $t = \hbar^2/2m^*$, where m^* is the effective mass of the band electron, E_b is the coefficient responsible for the electron-phonon coupling in a one-dimensional molecular chain. In the case of optical phonons, by analogy with a three-dimensional polaron, we can assume: $E_b = (1/\varepsilon_\infty - 1/\varepsilon_0)/2$. In a one-dimensional system in the strong-coupling limit the functional of an acoustical polaron has the same form as the functional of an optical polaron, therefore the integrated contribution of phonons into the energy of electron states can greatly exceed the contribution of optical phonons.

The energy of the ground state of a self-localized system can be found by minimization of functional (1). As shown by Rashba [33] and Holstein [34], Euler equation corresponding to this functional has an exact solution given by the expressions:

$$E_1 = -\frac{1}{12}\frac{E_b^2}{t}, \phi_1(x) = \sqrt{E_b/4t} \cdot \operatorname{sech}\left(\frac{E_b}{2t}x\right) \tag{2}$$

where E_1 and $\phi(x)$ are the energy and the wave function (WF) of the ground self-consistent state of a one-dimensional polaron, x is the electron coordinate.

3. Effective functional of the ground state of a one-dimensional bipolaron

The influence of correlation effects on the energy of a one-dimensional bipolaron was studied in Ref. [35] where consideration was given to one-center and two-center correlation effects. The one-center configuration of a one-dimensional bipolaron was investigated in Ref. [9] with regard for correlation effects related to the direct dependence of the bipolaron WF on the interelectronic distance. Here we will model bipolaron states with regard for correlation effects, such as the one-center and two-center correlations as well as the interelectronic correlations caused by the direct dependence of the WF on the distance between electrons. In the adiabatic approximation the effective functional of a one-dimensional bipolaron has the form [35]:

$$\begin{aligned} J_2 = &-t\int\int \Phi_{12}^*\triangle_{12}\Phi_{12}\,dx_1dx_2 \\ &-4E_b\int\int\int |\Phi_{12}^*|^2|\Phi_{23}^*|^2\,dx_1dx_2dx_3 \\ &+V_C\int|\Phi_{11}|^2\,dx_1 \end{aligned} \tag{3}$$

where $\Phi_{12} \equiv \Phi_{12}(x_1, x_2) = \Phi_{21}(x_2, x_1)$ is the symmetrized and normalized WF of the two-electron system; $\Phi_{11} \equiv \Phi_{12}(x_1, x_1)$; $\Delta_{12} = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}$; V_C determines the value of the Coulomb repulsion between the electrons.

The first term in functional (3) corresponds to the kinetic energy, the second one – to the total contribution of the phonon field and the electron-phonon interaction, the third term – to the contribution of the Coulomb repulsion.

Let the WF of a system consisting of two polarons whose polarization well centers reside at points a and b has the form:

$$\Phi_{12} = \frac{1}{\sqrt{N_{12}}}(\Psi_{a1}\Psi_{b2} + \Psi_{a2}\Psi_{b1})f(x_{12}), \tag{4}$$

where N_{12} is the normalization integral:

$$N_{12} = \int\int dx_1dx_2|(\Psi_{a1}\Psi_{b2} + \Psi_{a2}\Psi_{b1})f(x_{12})|^2, \tag{5}$$

$\Psi_{a1}(x_{a1})$, $\Psi_{b2}(x_{b2})$ are the wave function of the first and the second polaron, centered at points a and b, respectively; x_{a1}, x_{b2} are coordinates of the first and the second electron reckoned from the centers a and b, respectively; $f(x_{12})$ is the variational function depending on the distance between the electrons $x_{12} = x_1 - x_2$, located at the points with coordinates x_1 and x_1.

Let the origin be in the middle between the centers of polarization wells located at points a and b. Let us introduce the following notation:

$$\Psi_{1,2}^{\pm} = \Psi_{1,2}^{\pm}(x_{1,2} \pm R/2), \tag{6}$$

where R is the distance between the polarons.

With regard for (6) WF (4) takes the form:

$$\Phi_{12} = \frac{1}{\sqrt{N_{12}}}(\Psi_1^+\Psi_2^- + \Psi_2^+\Psi_1^-)f(x_{12}). \tag{7}$$

WF (7) corresponds to the singlet state of a bipolaron.

4. Derivation of analytical expressions of the bipolaron functional

In order to investigate the spatial configuration of a bipolaron let us choose the approximation of WF (7) in the form:

$$\Phi_{12} = \frac{1}{\sqrt{N_{12}}} \cdot (1 + P_{12})\Psi_{12}, \tag{8}$$

$$\Psi_{12} = \exp\left[-a^2(x_1 + R/2)^2 - c^2(x_2 - R/2)^2\right] \cdot \exp(-b\, x_1 x_2), \tag{9}$$

where P_{12} is the operator of permutations of electron coordinates; a, b, c are variational parameters. The normalization integral N_{12} is determined by expressions (10)-(12):

$$N_{12} = 2 \cdot (N + S), \tag{10}$$

$$N = \int\int |\Psi_{12}|^2\, dx_1 dx_2 = \int\int |\Psi_{21}|^2\, dx_1 dx_2, \tag{11}$$

$$S = \int\int \Psi_{12}^* \Psi_{21}\, dx_1 dx_2, \tag{12}$$

where $\Psi_{21} = P_{12}\Psi_{12}$.

Having calculated integrals determined by expressions (11) and (12) we get:

$$N = \frac{\pi}{\sqrt{4a^2c^2 - b^2}} \cdot C^2(R) \cdot \exp\left(2a^2c^2 \cdot \frac{a^2 + c^2 + b}{4a^2c^2 - b^2} \cdot R^2\right), \tag{13}$$

$$S = \frac{\pi}{\sqrt{(c^2 + a^2)^2 - b^2}} \cdot C^2(R) \cdot \exp\left(\frac{1}{2} \cdot \frac{(c^2 - a^2)^2}{c^2 + a^2 + b} \cdot R^2\right), \tag{14}$$

where $C(R) = \exp\left(-\frac{a^2+c^2}{4} R^2\right)$.

All the integrals involved in bipolaron functional (3) can be calculated exactly with the use of WF (8). Analytical expressions that we have obtained are rather cumbersome and omitted here. In the limit cases corresponding to the one-center ($R = 0$, $a \neq c$) and two-center ($R = R_m \neq 0$, $a = c$) configurations, for $b = 0$, the expressions obtained coincide with relevant expressions derived in Ref. [35]. Having calculated all the integrals in functional (3) with the use of probe function (8), we can find the energy of a one-dimensional bipolaron E_2 for each value of R by varying the three-parameter function corresponding to functional (3) over parameters a, b and c:

$$E_2 = \min_{\{a,b,c\}} J_2 = T + E_{ph} + E_C, \tag{15}$$

where T is the average value of the kinetic energy; E_{ph} is the energy equal to the integrated contribution of the phonon field and the energy of electron interaction via the phonon field, E_C is the energy of Coulomb repulsion between the electrons; the averaged potential energy of the two-electron system in the phonon field is determined by the expression: $E_{pot} = E_{ph} + E_C$.

5. Results of numerical calculations

For computational convenience we will choose dimensionless units assuming that $t = 1$, $Eb = 1$. Then the unit of energy, according to (2), is E_b^2/t, the unit of length is t/E_b. The exact polaron energy according to (2) in the dimensionless units is $E_1 = -1/12$.

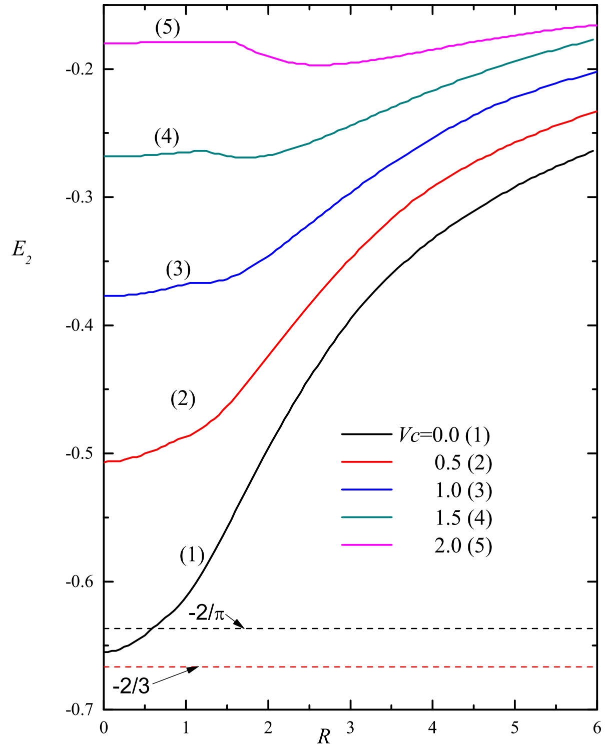

Fig. 1. Dependence of the bipolaron energy on the distance between the centers of polarization wells for different V_C. Variational function is chosen in the form (8) for $b = 0$ in expression (9). The parameters are $E_b = 1$, $t = 1$.

To illustrate how we calculated the energy of a system consisting of two polarons placed at a distance of R from each other we present in Fig. 1 the dependencies of the bipolaron energy on the distance R for different parameters V_C in the domain $V_C \le 2$. The probe function was chosen in the form (8). We believed $b = 0$ in expression (9), i.e. both one-center and two-center correlations were taken into account together, but the interelectronic correlations due to the correlation coefficient (16)

$$f_{12} = \exp(-b\, x_1 x_2) \tag{16}$$

were not considered. In the limit $R \to \infty$ all the dependencies given in Fig. 1 tend to doubled polaron energy calculated in the same approximation, i.e. with the use of the polaron probe function chosen in the form:

$$\Psi_{1G}(x) = C \exp(-\alpha^2 x^2),\ C = \left(\frac{2\alpha^2}{\pi}\right)^{1/4}, \tag{17}$$

where C is the normalization constant, α is a variational parameter.

For $R = 0$, $V_C = 0$ the bipolaron energy calculated with the use of the exact function should tend to $8E_1$, where $E_1 = -1/12$. In Fig. 1, the energy dependence corresponding to $V_C = 0$ for $R = 0$ takes an intermediate value lying in the range of $8E_1 < E_2(R = 0) < 8E_{1G}$. As the versatility of the probe function grows, $E_2(R = 0) \to 8E_1$. The choice of the bipolaron probe function in the form of a product of exact polaron functions (2) leads to fulfillment of the exact equality $E_2(R = 0) = 8E_1$ for $V_C = 0$.

The curves presented in Fig. 2 illustrate how the calculated value of the bipolaron energy changes as the versatility of the probe WF (8) varies for $V_C = 2$. For $V_C > 2$ a non-correlated bipolaron decays into 2 polarons. For $V_C < 2$ the potential well formed by the phonon system interacting with an electron is so deep that a non-correlated bipolaron may form. Correlation effects stabilize the bipolaron state and expand the domain of existence of a bipolaron with respect to parameter V_C.

Curve (1) in Fig. 2 is obtained with regard for only two-center correlations for $a = c$, $b = 0$ in (9). The only energy minimum corresponds to the two-center bipolaron configuration. In two limit

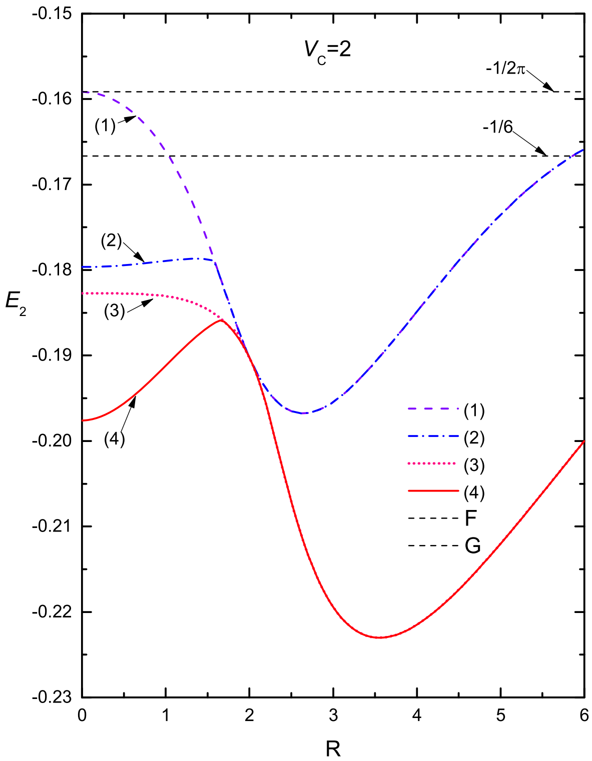

Fig. 2. Dependence of the bipolaron energy in E_b^2/t units for $V_C = 2$ on the distance between the polarons for different WF (8) of the polarons: (1) $a = c$, $b = 0$; (2) $a \neq c$, $b = 0$; (3) $a = c$, $b \neq 0$; (4) $a \neq c$, $b \neq 0$. The distance R is presented in units t/E_b. Horizontal lines correspond to exact value of the doubled polaron energy $2E_1 = -1/6$ and polaron energy $2E_{1G}$ calculated with the use of the one-parameter Gaussian function (17).

cases corresponding to $R = 0$ and $R \to \infty$ the bipolaron energy exactly coincides with the doubled polaron energy obtained by variational method with the use of the one-parameter Gaussian function (17). In Fig. 2, the exact doubled polaron energy is indicated by horizontal line $-1/2\pi$. In 3D systems the case of $V_C/E_b = 2$ corresponds to extremely strong electron-phonon coupling with longitudinal optical phonons when $\varepsilon_\infty/\varepsilon_0 \to 0$ (where ε_∞ and ε_0 are the high-frequency and static dielectric permittivities, respectively). In this case the non-correlated optical bipolaron decays into two polarons.

Curve (2) corresponds to consideration of both one-center and two-center correlations: $a \neq c$, $b = 0$. As we can see, in the vicinity of $R = 0$, there is a wide though a shallow energy minimum. As R grows, one-center correlations recede into the background as compared to two-center ones, curves (2) and (1) merge into one line which coincides with the dependence presented by curve (1), when $a = c$. The bipolaron stabilizes oneself in the two-center configuration. Curve (3) corresponds to $a = c$, $b \neq 0$, when account is taken of both two-center correlations and correlations associated with the direct dependence of the system's WF on the interelectronic distance. The energy minimum corresponding to the two-center configuration becomes much deeper, while the one-center configuration is unstable. Curve (4) corresponds to consideration of three types of correlation effects. In the vicinity of $R = 0$ there is a minimum separated by the energy barrier from another minimum which corresponds to the two-center bipolaron. As R grows, curves (3) and (4) merge into one line which indicates the decrease of the role of one-center correlations with a rise of R.

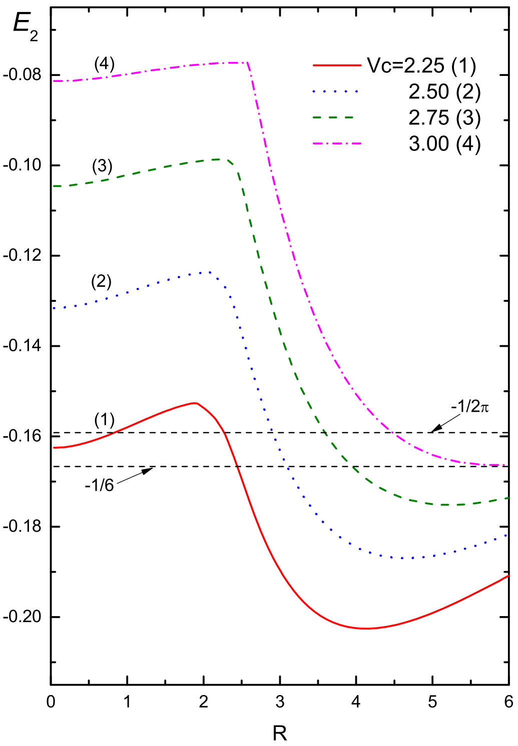

Fig. 3. Energy dependencies of a two-polaron system on the distance between the polarons for different values of the interelectronic repulsion parameter V_C.

Fig. 3 illustrates the energy dependencies of a two-polaron system on the distance between the polarons for different values of the Coulomb repulsion parameter V_C in the domain of existence of an optical bipolaron. For Ψ_{12} in (8) we have chosen the three-parameter function (9). The dependencies presented in Fig. 3 correspond to a bound state of a two-center bipolaron with the energy minimum at $R_m \neq 0$. Horizontal lines in Fig. 3 correspond to the polaron doubled energy $2E_{1G} = -1/2\pi$ calculated with the use of Gaussian approximation and the exact value of a one-dimensional polaron $2E_1 = -1/6$. Thus, in the case of $V_C \geq 2$, interelectronic correlations due to the direct dependence of the bipolaron WF (8) on the distance between the electrons stabilize the two-center configuration.

The dependence E_2 on the parameter V_c is shown in Fig. 4. The same figure shows the dependence of the equilibrium distance between polarons R_m in the energy minimum on the parameter V_c.

Fig. 5 shows different contributions into the bipolaron energy as a function of a distance between the centers of polarization wells of two polarons. The virial theorem:

$$E_2 = -\overline{T}, \quad E_2 = \overline{E}_{pot}/2, \quad E_{pot} = E_{ph} + V_C, \tag{18}$$

where $\overline{E}_{pot}$ is the average potential energy, holds for three values of interpolaronic distances: $R = 0$, $R = R_m$ and $R \to \infty$, which correspond to energy minima of a two-polaron system. When $V_C = 2$ for $R = 0$ and $R \to \infty$ the bipolaron energy tends to doubled polaron energy calculated in the same approximation.

Virial theorem (18) is also valid for the maximum on the dependence $E_2(R)$ shown in Fig. 5. The occurrence of two energy minima on the $E_2(R)$ curve raises the question of the possibility of coexistence of two types of bipolarons (one-center and two-center ones) in one-dimensional systems. However, it seems likely that investigation of the energy barrier value requires more precise calculations which is beyond the scope of this paper.

Fig. 6 demonstrates the dependencies of variational parameters a, b and c on the distance R between the polarons for $V_C = 2$. As can be seen, as R grows the role of one-center correlations caused by different values of the parameters a and c decreases. On the graph we can see that as the distance between the polarons in-

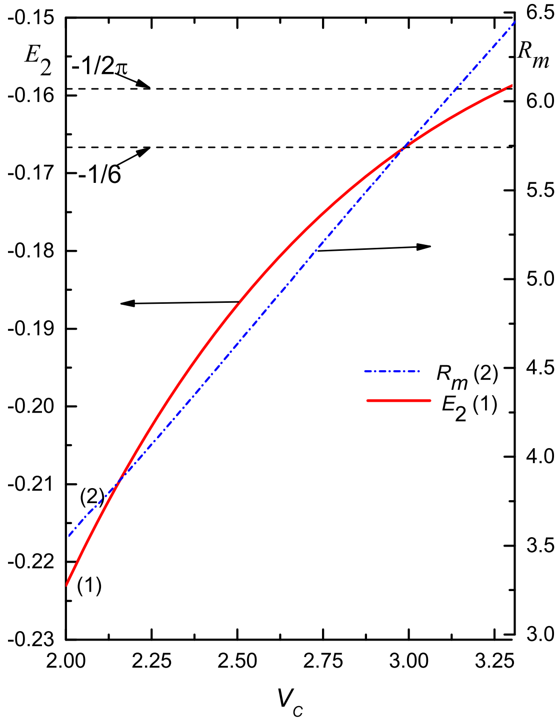

Fig. 4. Dependence of the bipolaron energy E_2 and the interpolaron distance corresponding to the energy minimum R_m on the Coulomb repulsion parameter V_C.

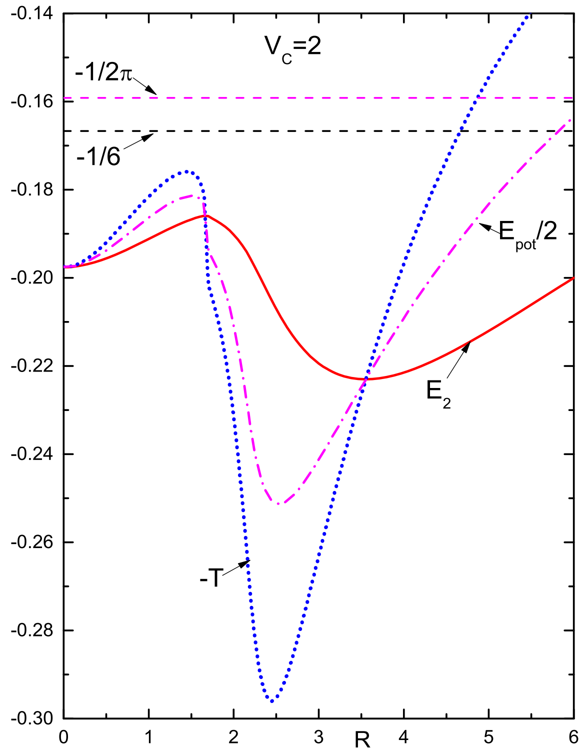

Fig. 5. Dependence of different contributions into the bipolaron energy in E_b^2/t units for $V_C = 2$ on the interpolaronic distance R for the most flexible polaron WF with $a \neq c$, $b \neq 0$ in eq. (8). E_2 is the energy of the ground state of a singlet bipolaron, T is the kinetic energy, $E_{pot} = E_{ph} + E_C$ is the potential energy of a bipolaron.

creases, the dependencies of a and c on merge into one line. For a configuration corresponding to a two-center bipolaron, we can assume with good accuracy that $a = c$.

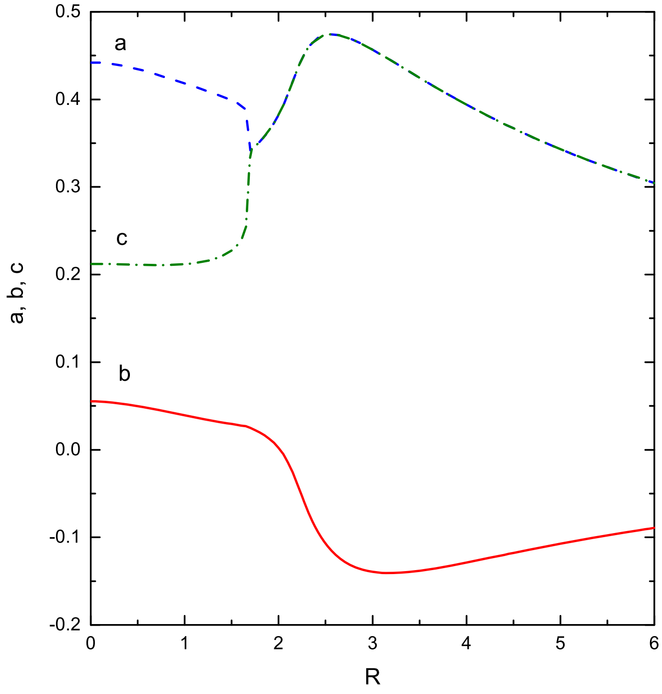

Fig. 6. Dependence of variational parameters a, b, c on the distance between the polarons for $V_C = 2$.

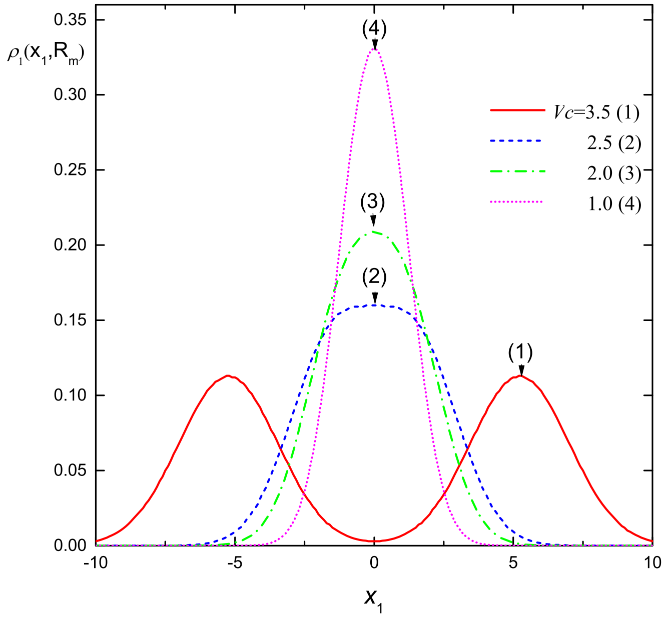

Fig. 7. Dependence of the one-electron probability density of the state (19), corresponding to the bipolaron WF (8) for the parameters which minimize the bipolaron functional (3).

Fig. 7 presents the dependencies of the one-electron probability density ρ_1 on the distance between the polarons:

$$\rho_1(x_1, R) = \int \rho_{12}(x_1, x_2, R)dx_2 \tag{19}$$

where $\rho_{12}(x_1, x_2, R) = \Phi_{12}(x_1, x_2)^2$, WF Φ_{12} is determined by equation (8).

The domain of existence of a bipolaron with respect to parameter V_C can be determined with reference to the doubled polaron energy calculated in the same approximation or with reference to the exact value of the doubled polaron energy given by expression (2):

$$2E_{1G} - E_2 \geq 0, \quad (V_C \leq V_C^{*}), \tag{20}$$

$$2E_1 - E_2 \geq 0, \quad (V_C \leq V_C^{**}), \tag{21}$$

where $E_{1G} = -1/4\pi$, $E_1 = -1/12$ in our units ($E_b = 1$, $t = 1$), the polaron energy E_{1G} is calculated with the use of a one-parameter Gaussian function (17). As follows from Fig. 4 $V_C^{**} \approx 2.98$, $V_C^{*} \approx 3.30$.

The one-center bipolaron configuration becomes energetically advantageous as compared to the two-center one for the values

$$V_C < V_{C0} \approx 1.2. \tag{22}$$

As it follows from Fig. 7, the one-electron probability density of the state assumes the shape of a curve with two maxima near the boundary of the domain of existence of a bipolaron with respect to the parameter V_C.

As it follows from expression (3) in the limit $V_C \to 0$ the bipolaron energy 8 times exceeds the polaron energy. The value of the bipolaron energy E_2 calculated with the use of the three-parameter WF (9) in the limit $V_C \to 0$ is equal to:

$$8E_1 = -\frac{2}{3} < E_2 \approx -0.655569 < 8E_{1G} = -\frac{2}{\pi}. \tag{23}$$

If in expression (9) we assume $a = c$, $b = 0$, we obtain $E_2 = -2/\pi = 8E_{1G}$ for $R = 0$, $V_C = 0$. Having chosen functions (2) for one-electron functions in expression (4) we get $E_2 = -2/3 = 8E_1$ for $R = 0$, $V_C = 0$. In this case correlation effects are lacking and the bipolaron WF can be presented as a product of polaron functions which are the exact solution of polaron equation (1).

6. Results and discussion

The calculated values of the energy and the domain of existence of a one-dimensional bipolaron should be compared with the results obtained by other authors. The influence of one-center and two-center correlations on the coupling energy of a one-dimensional bipolaron was investigated in Ref. [35] where the one-center correlations were considered for the one-center bipolaron and the two-center ones – for the two-center model. Electron correlations related to consideration of the direct dependence of the system's WF in the phonon field were not taken into account. We have obtained energy dependencies of a two-polaron system on the distance between the centers of polarization wells where the three types of correlation effects are taken into account together. The analytical expressions of the bipolaron functional for the Gaussian approximation and numerical values of the bipolaron ground state energy obtained in Ref. [35] for $V_C = 0, 1, 2$ are reproduced from our expressions and results of variational calculations with the use of WF (8) for the limit cases of one-center (for $a \neq c$, $b = 0$, $R = 0$) and two-center (for $a = c$, $b = 0$, $R = R_m \neq 0$) bipolaron configurations.

The two-center bipolaron was studied in Ref. [35] using two types of one-electron functions in WF (8): exact polaron functions (2) (secant approximation) and Gaussian functions (17) (Gaussian approximation), correlation factor f_{12} was not taken into account. For Vc = 2, the bipolaron energy $E_2^{(sec)} = -0.2021$ and $E_2^{(G)} = -0.1968$ for the secant and Gaussian approximations respectively. Curve (1) in Fig. 2 reproduces the energy of a two-center bipolaron obtained in Ref. [35] for Gaussian functions, curve (4) is the energy, calculated by us taking into account three types of correlation effects. In this case $E_2^{(4)} = -0.2230$. The bipolaron binding energy determined in relation to the exact value of the doubled polaron energy $2E_1 - E_2$ increased by 86.7% and 56% compared with the Gaussian and secant approximations used in Ref. [35] respectively.

In Ref. [9] the one-center bipolaron configuration was considered. Account was taken of correlation effects related to the direct dependence of the WF on the interelectronic distance. The probe function was chosen in the form:

$$\Psi_{12} = A\left(1 + \beta(x_1 - x_2)^2\right)\exp(-a^2x_1^2)\exp(-a^2x_2^2) \tag{24}$$

The bipolaron energy obtained in Ref. [9] using the WF (24) for $V_C = 2$ was $E_2 = -0.2093$. The critical value of the Coulomb repulsion parameter V_C, above which there is not a stable bipolaron state for WF (24) lies in the range:

$$3.18 \leq \widetilde{V}_C \leq 4.07 \tag{25}$$

Higher value of binding energy obtained with the use of function (8), as compared to those obtained with the use of WF (24), are related to the fact that two-center correlations are not taken into account in WF (24). As it is shown in Ref. [9], in the region near the boundary of the bound state with respect to V_C, in a 1D system, the curve for one-electron probability density of the state, determined by WF (24), has the same shape as that for the density of the two-center configuration. In three-dimensional systems the situation is the opposite: in an isotropic crystal, the one-center bipolaron configuration corresponds to a spherically symmetric probability density of the state, while the minimum corresponding to axially symmetric two-center bipolaron configuration disappears when all three types of correlation effects are taken into account together [52].

The dependencies of the one-electron probability density of a bipolaron, shown in Fig. 7, agree well with the conclusions obtained in Ref. [22] where a possibility for bipolaron states to be formed in nucleotide chains was considered on the basis of the discrete Holstein-Habbard model with a discrete Hamiltonian. As is shown in Ref. [22], in one-dimensional systems both two-center and one-center bipolarons can be formed. As the binding energy decreases, the energy of holes localized at two neighboring sites differs slightly from that of holes localized at two sites spaced far apart. We can say that in this case the bipolaron state has low stability with respect to decay into two individual polaron states. In Fig. 7 this state is represented by the curve of the state density for $V_C = 3.5$.

The use of WF (8) allows one to obtain not only the energy of a two-center bipolaron $E_2(R_m)$, but also to study the interaction energy of polarons as a function on the distance R between them $E_2(R)$, and to obtain the limit transition to a system, consisting of two noninteracting polarons at $R \to \infty$. Models of single-center configuration lack this advantage.

The choice of a multi-parameter two-electron wave function in the form of the sum of Gaussian orbitals with exponentially correlated multipliers made it possible to obtain the lowest values for the bipolaron energy in 3D systems [53]. However, the correct conclusions related to the study of the spatial configuration of the 3D-bipolaron have already been obtained using the simplest three-parameter function with correlation factors, selected in the form (8), where, x_1 and x_2 should be replaced by the radius vectors r_1 and r_2 of the first and second electrons correspondingly (see eq. (8) and Fig. in Ref. [54]). The study of multi-parameter functional, using a more flexible WF, consisting of the sum of Gaussian orbitals with correlation multipliers, will be performed in another work.

In 3D-systems, a bipolaron is a spherically symmetric formation (one-center configuration). The two-center configuration corresponds to a local minimum, which disappears, when the correlations, associated with the direct dependence of the WF on the distance between the electrons are taken into account. On the contrary, as follows from our results, in one-dimensional systems in the region where the optical bipolaron exists, the lowest minimum corresponds to a two-center configuration. Such behavior of the bipolaron energy in 1D systems is connected just with the low dimensionality of the system under consideration.

7. Conclusion

Calculations of the coupling energy of a one-dimensional bipolaron with regard for one-center and two-center correlations as well as correlations related to the direct dependence of the bipolaron WF on the interelectronic distance has shown that a two-center configuration is formed in one-dimensional systems in the region corresponding to an optical bipolaron ($V_C \geq 2$). On the curve for the dependence of the interaction energy of two polarons on the distance between them this two-center configuration corresponds to a deeper minimum. A possibility of coexistence of the two-center and one-center bipolarons (the latter corresponding to a shallower minimum) requires further investigation. In the region of $V_C \leq 1.2$ the one-center bipolaron configuration becomes energetically more advantageous. This region could correspond to an acoustic or acousto-optical bipolarons.

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