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Correlation effects and Pekar bipolaron (arbitrary electron-phonon interaction)

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Buimistrov-Pekar method of canonical transformation was used to calculate the energies of the lowest singlet and triplet terms of bipolarons in crystals with ion binding. An arbitrary electron-phonon interaction described by Fröhlich Hamiltonian was considered. It was shown that in the whole parametric range of electron-phonon interaction, the value of the free bipolaron ground state energy obtained by Buimistrov-Pekar method is the lowest than those found in the framework of direct variational approaches [1] and only slightly exceed (relative error $< 0.3\%$) the ones obtained by integration over trajectories for $\alpha \leq 7$ [2].

The calculations have shown that any metastable triplet states corresponding to the lowest triplet term of a bipolaron are absent for all the parameters of the electron-phonon interaction, the results being in complete analogy with Hill's theorem about the absence of any bound excited states for an H^- ion [3].

The study of the wave function of a more general form has demonstrated that a two-center bipolaron is energetically less advantageous than a one-center one for all the parameters of the electron-phonon interaction. Control calculations performed with the system of functions used in the paper have yielded 1.173 a.u. for the hydrogen molecule energy which is in good agreement with the experimental value.

1 Introduction

A bipolaron is a simplest two-electron system in polar crystals. For this reason it is very suitable to test the methods of calculation of electron systems for which the interaction with a field of elementary excitations of the crystal is of importance. An example is given by a field of optical phonons, the interaction with which is described by Fröhlich Hamiltonian. Some other examples of the fields in question are acoustical phonons, plasmons, spin waves, discharge density waves, etc.

Bipolaron subject-matter has been a focus of preoccupation for more than 50 years both in the context of purely academic interest and for its importance in semiconductor technology just as in relation to the problem of high-temperature superconductivity (HTSC) [4, 5, 6, 7].

The idea that HTSC may be explained by Bose-condensation of electron pairs arising in real space dates back to Ogg's investigations [8]. Later on [9] a bipolaron model was suggested where a bipolaron was treated as a hypothetical particle in which two electrons bind together in one potential well as a result of an interaction of the two-electron system with long-wave optical phonons (one-center, or Pekar bipolaron). Observation of HTSC in CuO_2-based layered ceramic materials [10] has given an impetus to investigations on bipolarons. A model of small-radius bipolarons in narrow-band metals was considered in [11] in the strong coupling limit in connection with superconductivity caused by their Bose-condensation. In studies of such states the bipolaron coupling energy is usually assumed to be a phenomenological parameter. Various aspects of the theory of large-radius bipolarons in view of the problem of HTSC are dealt with in [12, 13, 14, 15]. In [16, 17] a system of large-radius bipolarons in layered HTSC is treated as a Wigner crystal which develops plasma oscillations favourable for pairing of charge carriers in conducting layers.

A comprehensive discussion of the theory of large-radius bipolarons is given in the reviews [12, 18].

Note that after the discovery of high-temperature superconductivity in CuO2-based layered ceramic materials, the subject-matter in question has assumed popularity in relation to low dimensional systems (see review [18] and references therein). The works [2, 19] are devoted to the study of bipolarons in three-dimensional (3D) and two-dimensional (2D) systems. The paper [20] deals with a bipolaron in a crystal with anisotropic effective masses and dielectric permittivities. In the limit case of the absence of anisotropy, the system corresponds to a one-center Pekar bipolaron. In [2] a simple dimensional relation is suggested which relates bipolaron energy in (3D) and (2D) systems. In [20] this relation is checked numerically and confirmed by direct variation of the wave function of a two-electron system. From this viewpoint studies of bipolarons in (3D) and (2D) systems are practically equivalent. In this work we consider continuum bipolarons in a three-dimensional isotropic crystal.

The lowest values of the bipolaron energy were obtained in [1] by the method of canonical transformations for Fröhlich coupling constant $\alpha \geq 8$ and in [2] by Feynman method of integration over trajectories for $\alpha < 8$. When we pass on form a polaron to two-electron systems and bound polarons, indisputable advantages of integration over trajectories are offset since the method fails to describe Coulomb interactions of electrons with a nucleus, not does it suit to treat interelectron interactions. At the same time the advantages concerned with the simplicity of consideration of the polaron problem are also lost. Thus, Feynman method gives the lowest polaron energy for virtually all values of the coupling constant as a result of minimization of a simple two-parameter functional [21]. A relevant functional for a bipolaron has rather a cumbersome form which makes difficult numerical calculations and hinders the application of the method to more complicated systems (such as exchange-bound pairs in polar crystals, etc.).

In early papers devoted to calculation of the two-electron system energy in continuum approximation, electron correlations were not taken into account which considerably underestimated the coupling energy of the D^--center (or bound bipolaron as in [22]) and even led researchers to conclude that a bipolaron is energetically disadvantageous [9, 23]. Nevertheless, Buimistrov-Pekar method suggested in [23] to calculate the energy of one-electron and two-electron states in crystals with arbitrary strength of coupling between the electron system and phonons is, in our opinion, one of the simplest and most efficient methods for calculation of the energy spectrum of electron systems in a solid body. Buimistrov-Pekar method correctly reproduces the limits of weak and strong coupling and gives satisfactory results in the range of intermediate coupling especially as applied to bound electron states when the translation symmetry of the system is broken. In this connection many researchers consider Buimistrov-Pekar method to be a most promising and reliable tool for calculation of particular systems [24]. In [25] the method was used to calculate a bipolaron. As a result of inappropriate choice of a wave function (WF) (which was not sufficiently versatile) the values of the bipolaron energy for all α were much higher than the results obtained in [1].

In this paper we use Buimistrov-Pekar method to calculate a bipolaron energy with a more versatile WF consisting of a sum of Gaussians. We will show that in the whole domain of a bipolaron existence, the value of a bipolaron energy obtained by Buimistrov-Pekar method is lower than that found in the framework of direct variational approaches [1] and only slightly exceeds (relative error $< 0.3\%$) the one obtained by integration over trajectories for $\alpha \leq 7$.

2 Main relations

Hamiltonian of a bound bipolaron has the form

$$H = \hbar\omega \sum_{\mathbf{k}} a^{+}_{\mathbf{k}} a_{\mathbf{k}} + \frac{e^2}{\varepsilon_\infty r_{12}} +$$

$$+\sum_{j=1}^{2}\left[-\frac{1}{2m^*}\Delta_j-\frac{e^2}{\varepsilon_0 r_j}+\sum_{\mathbf{k}}V_{\mathbf{k}}(a_{\mathbf{k}}+a^+_{-\mathbf{k}})\exp(i\mathbf{k}\mathbf{r}_j)\right], \tag{1}$$

$$V_{\mathbf{k}}=\hbar\omega\sqrt{\frac{4\pi\alpha L_0}{V}}\frac{1}{k} \tag{2}$$

$$\alpha=\frac{e^2}{2\hbar\omega}\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\frac{1}{L_0} \tag{3}$$

$$L_0=\sqrt{\hbar/2m^*\omega} \tag{4}$$

where $\mathbf{r}_j$ is the radius-vector of the j-th electron with the effective mass m^* in the conductivity band, r_{12} is the distance between electrons. We assume that the Coulomb charge is concentrated at the origin of the coordinates. The influence of the crystal polarization on the Coulomb field of a static charge is taken into account by introducing a static ε_0 dielectric permittivity. The operator of electron-phonon interaction involves a high-frequency dielectric permittivity ε_∞, $a^+_{\mathbf{k}}(a_{\mathbf{k}})$ is the operator of birth (annihilation) of a longitudinal optical phonon with the wave vector $\mathbf{k}$. We assume that the phonon frequency is independent of $\mathbf{k}$ and equal to ω, α is a dimensionless constant of Fröhlich coupling, V is the crystal volume.

Hereafter we will use the system of units in which $\hbar=1$, $\omega=1$ and $2m^*=1$. It follows that the unit of energy is $\hbar\omega$ and the unit of length is L_0. In these units Hamiltonian (1) takes the form

$$H=\sum_{\mathbf{k}}a^+_{\mathbf{k}}a_{\mathbf{k}}+\frac{\beta}{r_{12}}+$$
$$+\sum_{j=1}^{2}\left[-\Delta_j-\frac{\gamma}{r_j}+\sum_{\mathbf{k}}\sqrt{\frac{4\pi\alpha}{V}}\frac{1}{k}(a_{\mathbf{k}}+a^+_{-\mathbf{k}})\exp(i\mathbf{k}\mathbf{r}_j)\right], \tag{5}$$

$$\beta=\frac{e^2}{\hbar\omega\varepsilon_\infty L_0}=\frac{2\alpha}{1-\eta}, \tag{6}$$

$$\gamma=\frac{e^2}{\hbar\omega\varepsilon_0 L_0}=\frac{2\alpha\eta}{1-\eta},\qquad \eta=\frac{\varepsilon_\infty}{\varepsilon_0}. \tag{7}$$

3 Buimistrov-Pekar method as applied to two-electron systems in polar crystals with intermediate electron-phonon coupling

In modern presentation, Buimistrov-Pekar method implies that Hamiltonian (5) is subjected to a canonical transformation $\exp(\alpha S)\, H \exp(-\alpha S)$ with unitary operator $S = \sum_{\mathbf{k}} (F^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) a_{\mathbf{k}} - F_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) a^+_{\mathbf{k}})$, where $F_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2)$ is a coordinate function of the electron system. Then the following expressions: $\exp(S)\, a_{\mathbf{k}} \exp(S) \Rightarrow a_{\mathbf{k}} + F_{\mathbf{k}}$, $\exp(S)\, a^+_{\mathbf{k}} \exp(S) \Rightarrow a^+_{\mathbf{k}} + F^*_{\mathbf{k}}$ are valid.

Having averaged over phonon variables we will obtain

$$H = \frac{\beta}{r_{12}} + \sum_{j=1}^{2} \sum_{\mathbf{k}} \nabla_j F^*_{\mathbf{k}} \nabla_j F_{\mathbf{k}} +$$

$$+ \sum_{j=1}^{2} \sum_{\mathbf{k}} \left[-\Delta_j - \frac{\gamma}{r_j} + V_{\mathbf{k}} (F_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}_j) + F^*_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}_j)) \right] + \sum_{\mathbf{k}} F_{\mathbf{k}} F^*_{\mathbf{k}} \tag{8}$$

which will serve as an initial expression for subsequent derivations.

Let us choose function $F_{\mathbf{k}}$ in the form

$$F_{\mathbf{k}} = C_{\mathbf{k}} + \gamma_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2), \tag{9}$$

where $C_{\mathbf{k}}$, $\gamma_{\mathbf{k}}$ are variational parameters.

Having substituted (9) into (8) and varied the relation obtained over $C_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$ we express the functional of the ground state of a two-electron system as:

$$E_{Bp} = J_s + J_i, \tag{10}$$

$$J_i = -\sum_{\mathbf{k}} V^2_{\mathbf{k}} \frac{\widetilde{U}^2_{\mathbf{k}}}{2k^2 + U_{\mathbf{k}} \omega_{\mathbf{k}}}, \tag{11}$$

$$\widetilde{U}_{\mathbf{k}} = \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle \langle \Psi_{12} | L^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle -$$

$$- \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) L^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle, \tag{12}$$

$$L^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) = \exp(-i\mathbf{k}\mathbf{r}_1) + \exp(-i\mathbf{k}\mathbf{r}_2), \tag{13}$$

$$U_{\mathbf{k}} = \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle \langle \Psi_{12} | f^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle -$$

$$- \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) f^*_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) | \Psi_{12} \rangle, \tag{14}$$

where J_i is an addition which has appeared for the case of intermediate coupling and J_s corresponds to the functional of a strong coupling bipolaron

$$J_s = \bar{T}_{12} + \beta \bar{V}_{ee} - \gamma \bar{V}_e + \sum_{\mathbf{k}} V_{\mathbf{k}}^2 \left| \langle \exp(-i\mathbf{k}\mathbf{r}_1) + \exp(-i\mathbf{k}\mathbf{r}_2) \rangle \right|^2 , \tag{15}$$

$$\bar{T}_{12} = \int \Psi_{12} (\Delta_1 + \Delta_2) \Psi_{12} d\tau, \tag{16}$$

$$\bar{V}_{ee} = \int \frac{|\Psi_{12}|^2}{r_{12}} d\tau, \tag{17}$$

$$\bar{V}_e = \int \frac{|\Psi_{12}|^2}{r_1} d\tau + \int \frac{|\Psi_{12}|^2}{r_2} d\tau. \tag{18}$$

4 Functional of the ground state of a two-electron system

Having chosen $f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) = L_{\mathbf{k}}^*(\mathbf{r}_1, \mathbf{r}_2)$ and, consequently, $\widetilde{U}_{\mathbf{k}} = U_{\mathbf{k}}$ we will have

$$J_i = -\sum_{\mathbf{k}} V_{\mathbf{k}}^2 \frac{U_{\mathbf{k}}^2}{2k^2 + U_{\mathbf{k}} \omega_{\mathbf{k}}}. \tag{19}$$

And in a particular case of the absence of any electron correlations, when the WFs of the electron system are written as a product of one-electron WFs $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$, expression (19) yields

$$J_i = -\sum_{j=1}^{2} \sum_{\mathbf{k}} V_{\mathbf{k}}^2 \frac{(1 - F_{\mathbf{k}}^2(\mathbf{r}_j))^2}{k^2 + (1 - F_{\mathbf{k}}^2(\mathbf{r}_j))\omega_{\mathbf{k}}}, \tag{20}$$

where $F_{\mathbf{k}}(\mathbf{r}_j)) = \int \psi(\mathbf{r}_j) \exp(i\mathbf{k}\mathbf{r}_j) \psi^*(\mathbf{r}_j) d\tau_j$.

The latter functional coincides with formula (20) from the paper [23] by Buimistrov and Pekar. When we choose a WF in a nonmultiplicative form which corresponds to consideration of electron correlations we should use a more general functional where the addition corresponding to intermediate coupling J_i is determined by expression (19).

In a recent work [26] devoted to a two-center intermediate coupling bipolaron, the electron WF has been chosen as a symmetrized product of polaron functions centered at various points, i.e. it had a nonmultiplicative form (Heitler-London method as applied to a bipolaron). However, the author varied functional with J_i, determined by (20) which is valid only for the particular case when the WFs of a two-electron system are chosen as a product of one-electron ones. This fact has led the author [26] to varying of inappropriate functional and thus, resulted in erroneous numerical calculations.

5 Numerical calculations

Let us choose a two-electron WF as a linear combination of Gaussian orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{N_{12}}} \sum_{i=1}^{n} C_i (1 + P_{12}) \exp(-a_{1i} r_1^2 - 2a_{2i} (\mathbf{r}_1 \cdot \mathbf{r}_2) - a_{3i} r_2^2), \quad (21)$$

where P_{12} is the permutation operator interchanges the indices of the electrons (1 and 2), C_i, a_{1i}, a_{2i}, a_{3i} are variational parameters, $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the first and the second electrons in a bipolaron, N_{12} is a normalization multiplier.

The WF of a polaron is chosen in the form

$$\Psi_p(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{i=1}^{n} c_i \exp(-a_i r^2), \quad (22)$$

where c_i, a_i are variational parameters, $\mathbf{r}$ is the electron coordinate in a polaron, N is a normalization multiplier.

Fourier components and the normalization multiplier of the WF (22) are given by the expressions

$$J_1 = \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2) \exp(i\mathbf{k}\mathbf{r}_1) d\tau_{12} = \\ = \frac{1}{N_{12}} \sum_{i,j=1}^{n} C_i C_j \exp\left(-\frac{k^2}{4} \frac{\alpha_{ij}}{\alpha_{ij}\gamma_{ij} - \beta_{ij}^2}\right), \quad (23)$$

$$J_2 = \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2) \exp(i\mathbf{k}\mathbf{r}_2) d\tau_{12} = \\ = \frac{1}{N_{12}} \sum_{i,j=1}^{n} C_i C_j \exp\left(-\frac{k^2}{4} \frac{\gamma_{ij}}{\alpha_{ij}\gamma_{ij} - \beta_{ij}^2}\right), \quad (24)$$

$$J_{12} = \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2) \exp(i\mathbf{k}\mathbf{r}_1 + i\mathbf{k}\mathbf{r}_2) d\tau_{12} = \\ = \frac{1}{N_{12}} \sum_{i,j=1}^{n} C_i C_j \exp\left(-\frac{k^2}{4} \frac{\alpha_{ij} + 2\beta_{ij} + \gamma_{ij}}{\alpha_{ij}\gamma_{ij} - \beta_{ij}^2}\right), \quad (25)$$

$$N_{12} = \int \Psi^2(\mathbf{r}_1, \mathbf{r}_2) d\tau_{12} = \sum_{i,j=1}^{n} C_i C_j \exp \left(\frac{\pi}{\alpha_{ij}\gamma_{ij} - \beta_{ij}^2} \right)^{3/2}, \qquad (26)$$

where $\alpha_{ij} = a_{1i} + a_{1j}$, $\beta_{ij} = a_{2i} + a_{2j}$, $\gamma_{ij} = a_{3i} + a_{3j}$.

In the case when symmetrized WFs are varied, we can put $J_1 = J_2$.

The corresponding expressions for a polaron are

$$J_p = \int \Psi^2(\mathbf{r}) \exp(i\mathbf{k}\mathbf{r}) d\tau = \frac{1}{N} \sum_{i,j=1}^{n} C_i C_j \left(\frac{\pi}{a_{ij}} \right)^{3/2} \exp \left(-\frac{k^2}{4a_{ij}} \right), \qquad (27)$$

$$N = \int \Psi^2(\mathbf{r}) d\tau = \sum_{i,j=1}^{n} C_i C_j \left(\frac{\pi}{a_{ij}} \right)^{3/2}, \qquad (28)$$

where $a_{ij} = a_i + a_j$.

With the use of (23) - (26) expression (19) takes the form

$$J_i = -\sum_{\mathbf{k}} V_{\mathbf{k}}^2 \frac{\left(2(1 + J_{12}) - (J_1 + J_2)^2\right)^2}{2k^2 + 2(1 + J_{12}) - (J_1 + J_2)^2}. \qquad (29)$$

Table 1 lists the values for the minimum of the functional of a free ($\gamma = 0$) bipolaron calculated by us with the WFs (21) and obtained in paper [1] for various α and η.

In comparing various variational approaches, comparison should be made not between the coupling energies which are generally determined with respect to the polaron energy calculated in the framework of the same approximation, but between the ground state energies. The best values of the bipolaron energy for $\alpha \geq 8$ were obtained in [1]. The method of integration over trajectories [2] as applied to a bipolaron gives higher (than in [1]) values for $\alpha \geq 8$ which results from overestimation of the Coulomb repulsion between electrons. At the same time for $\alpha = 7$, $\eta = 0$, the authors of [1] obtained -16.067. The corresponding result in [2] is -16.27 (this value was restored from the graphic data presented in [2]). So, for $\alpha \leq 7$ the method of integration over trajectories gives the best results for the bipolaron ground state energy. The best value obtained by us for $\alpha = 7$, $\eta = 0$ was -16.23 which only slightly exceeds the result found by Feynman method of integration over trajectories.

A bipolaron is stable when the bipolaron ground state energy E_{Bp} is lower than the polaron double energy $2E_p$

$$E_{Bp} < 2E_p. \qquad (30)$$

So, the bipolaron coupling energy is determined by the expression

$$\Delta E = 2E_p - E_{Bp}. \tag{31}$$

The lowest value of the polaron energy was obtained in [27] by Feynman method of integration over trajectories. The authors used an iteration procedure where Feynman expression for the polaron energy served as an initial approximation. The estimates of the polaron energy obtained in [27] led to a small correction to the Feynman value of the polaron energy ($\leq 1\%$) and can be considered as the upper boundary of the polaron energy in the range of intermediate α values. Table 2 lists the values for the minimum of the functional of a polaron, calculated by us with the WFs (22) and those obtained in a number of any papers for various α.

Note, that in the limit $\alpha \to \infty$ the polaron energy tends to the exact value obtained in [28] as a result of numerical solution of the relevant Euler's equation $E_p = -0.108513\alpha^2\hbar\omega$. This value of the polaron energy was found by us with the help of the WF (22) for $n = 5$. To reproduce the energy of a hydrogen atom with a precision of 6 significant figures, more terms in expression (22) are required. Thus, for $n = 10$, the energy of a hydrogen atom is $E_H = -0.9999986$.

In order to assess the versatility of the functions used in our calculations of the energy of two-electron systems, we employed them to calculate the ground state energy of a negatively charged hydrogen ion H^- (which is the closest analog of a bipolaron in atomic physics). The energy was found to be -1.055470 ($n = 28$ in (22)), the exact value being -1.055502 [29]. As is seen, in describing atomic systems with the help of the WFs (21), (22) the desired accuracy is achieved with a greater number of the terms.

Table 3 lists critical values of the parameters α_c and η_c calculated by us with respect to the upper boundary of the polaron energy obtained in [27]. The quantities α_c and η_c determine the range of the bipolaron existence. Thus, a bipolaron is stable when $\alpha \geq \alpha_c$ and $\eta \leq \eta_c$. The Table also presents the relevant values obtained in [1]. So, in the whole range of α values the energy of the bipolaron ground state is lower and the range of its existence is wider than in [1]. Let us compare the parameter β_c for $\alpha = 9$. Our value, which was found in the same way as in [1] with respect to the polaron energy $E_p = -11.538$ made up $\beta_c = 19.27$. In [1] β_c was found to be 19.0 and in [2] $\beta_c = 18.68$ (the latter value was determined with respect to Feynman polaron energy $E_p = -11.486$ [21]).

To compare our values of β_c with those obtained in [2] for some other parameters of electron-phonon coupling, let us take advantage of the fact that near the critical value of α_c ($\eta = 0$), the quantity β_c can be linearly approximated by parameter α with good accuracy. In the case under consideration with the use of Feynman polaron energy, this linear dependence takes the form $\beta_c = 2.649\alpha - 4.529$ while in [2] $\beta_c = 2.305\alpha - 2.107$. So, for $\alpha \geq 7.05$ Buimistrov-Pekar method as applied to a bipolaron gives better results (lower values of the ground state energy and wider region of bipolaron existence for parameter β) than those found by Feynman method [2].

At present, the bipolaron coupling energy is commonly determined with respect to the polaron energy calculated in the same approximation. It is believed that the region of a bipolaron existence determined parameters α_c and η_c defined in the framework of this procedure is closer to the true value of these parameters [1, 2, 25, 30] than if it would be determined with respect to the upper boundary of the polaron energy calculated not the same method. Paper [1] presents qualitative reasoning in favour of this state of affairs. Calculations were made with respect to the polaron energy by Buimistrov-Pekar method with the use of expressions (21), (22) for $n = 5$. The critical value of the coupling constant, calculated in this approximation is $\alpha_c = 5.31$.

Let us also compare our results with those obtained in [25]. In the strong coupling limit $\alpha \to \infty$ the value of bipolaron energy calculated by us with the WFs (21) ($n = 5$) tends to $-0.273024\alpha^2\hbar\omega$. In order to find the absolute value of the bipolaron energy for the two-parameter WF used in [25]

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = N(1 + \gamma r_{12}^2)\exp(-\mu^2(r_1^2 + r_2^2)), \tag{32}$$

where N is a normalizing multiplier, γ and μ are variational parameters, we reproduced calculations with this function. In the whole range of α values, the bipolaron energy calculated with the use of the WF in question runs higher than the energy found in [1] and in our work. In the strong coupling limit we calculated the bipolaron energy with the use (32) to be $-0.2588406\alpha^2\hbar\omega$. Despite the fact that the WF (32) suggested in [25] for the calculation of the polaron energy gives overestimated energy values, it is very suitable to get qualitative results since it does not require the use of tedious methods of minimization of manyparameter functionals.

6 Instability of a two-center bipolaron

The problem of the choice of a bipolaron spatial configuration was discussed in detail in [31]. It was shown that in the strong coupling limit the only energy minimum corresponds to the one-center configuration. The two-center configuration is unstable and is associated with inappropriate choice of the WF of the system. When a better WF is taken, the minimum will disappear. Numerical calculations performed by us for the case of intermediate coupling with the WFs chosen in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{N_{12}}}\sum_{i=1}^{n}C_i(1+P_{12})\exp(-a_{1i}r_{a1}^2-2a_{2i}(\mathbf{r}_{a1}\cdot\mathbf{r}_{b2})-a_{3i}r_{b2}^2),\quad(33)$$

where $\mathbf{r}_{a1}$, $\mathbf{r}_{b2}$ are coordinates of the first and the second electrons determined from the points a and b, respectively, the points a and b being separated by the distance R, have shown that for all the parameters of electron-phonon interaction at which a bipolaron is stable, the only energy minimum is one corresponding to the one-center bipolaron configuration ($R=0$).

Figure 1 shows relevant dependencies of the bipolaron energy on the distance between the centers of two polarization wells of two polarons for various values of the Fröhlich constant α at $\eta=0$. In order to show on one graph the dependencies of the energy of a two-polaron system on the distance between the centers of polarization wells for various α, Figure 1 shows the dependencies $E_{Bp}(R)/\alpha^2$. The upper curve corresponds to the $\lim_{\alpha\to\infty}(E_{Bp}(R)/\alpha^2)$ and coincides with the appropriate dependence obtained in [31](Fig. 1) for the functional $J_s(R)$, corresponding to the strong coupling limit. The energy units in Fig. 1 as in [31] is effective Hartree determined by $Ha^*=m^*e^4/\hbar^2\varepsilon_\infty^2$, because of $\hbar\omega/Ha^*=(1-\eta)^2/2\alpha^2$.

Note, also, that the parameter R involved in the WF (33) ($r_a=r-R/2$, $r_b=r+R/2$ for the origin chosen in the half of the distance between points a and b) does not enter into the initial Hamiltonian and can be treated as a distance between the centers of polarization wells only in view of the choice of the WF (33) in the form similar to the WF of a hydrogen molecule in the Heitler-London method [32]. It can easily be shown that a more general form of a two-electron WF corresponds to the expression

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{N_{12}}}\sum_{i=1}^{n}\widetilde{C}_i(1+P_{12})\times$$
$$\times\exp(-a_{1i}r_1^2-2a_{2i}(\mathbf{r}_1\cdot\mathbf{r}_2)-a_{3i}r_2^2-2a_{4i}z_1-2a_{5i}z_2),\qquad(34)$$

where $\widetilde{C}_i$, a_{1i}, a_{2i}, a_{3i}, a_{4i}, a_{5i} are variational parameters.

In a particular case when

$$\begin{gathered}\widetilde{C}_i = C_i \exp(-0.25(a_{1i} - 2a_{2i} + a_{3i})R^2), \\ a_{4i} = -0.5(a_{1i} - a_{2i})R, \qquad a_{5i} = -0.5(a_{3i} - a_{2i})R, \end{gathered} \tag{35}$$

expressions (33) and (34) coincide.

The use of (34) as a probe WF has shown that for all the parameters of electron-phonon interaction, the only energy minimum corresponds to spherically-symmetric spatial distribution of a two-electron WF, i.e. the variational parameters characterizing the "extent of nonsphericity" of the WF (34) are $a_{4i} = 0$ and $a_{5i} = 0$.

In control calculations of the energy of a hydrogen molecule, the choice of a WF in the form (34) has enabled us to reproduce with the good accuracy the experimental value of this energy. Thus, for $n = 28$ in (34) we calculated the hydrogen molecule energy to be -1.1733 a.u. for $R = 1.401$ which corresponds to the energy minimum. The result obtained by James and Coolidge [33] is -1.172, the experimental value of the energy in question is $-1.174 \pm 0.003 a.u.$ [34, 35]. The latest calculations [36], based on 80-term WFs in Born-Oppenheimer approximation has yielded the value -1.1744 a.u. The new experimental dates and the references on the works deal with the study of the energy spectrum of the hydrogen molecule are given in [37].

Note, that on account of considerable expenditure of computer time required for variation of manyparameter functional in the case of arbitrary coupling with phonons and the choice of the WF in the form (33), we derived the dependencies shown in Fig. 1 by substituting into functional (10) the parameters corresponding to the minimum of the strong coupling functional J_s. This procedure is justified in the study of qualitative dependencies shown in Fig. 1. More accurate expressions listed in the tables correspond to variation of the total functional (10) with the use of the WF (21) and the WF of more general form (34). Variation with the use of (34) has enabled us to reproduce completely the results obtained for the WF (21).

The calculations of the lowest triplet bipolaron term were fulfilled with the use of the antisymmetric with the respect to the permutation of the electron coordinates WF

$$\Psi^t(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{N_{12}}} \sum_{i=1}^{n} C_i (1 - P_{12}) \exp(-a_{1i} r_{a1}^2 - 2a_{2i}(\mathbf{r}_{a1} \cdot \mathbf{r}_{b2}) - a_{3i} r_{b2}^2), \tag{36}$$

Table 4 lists the values corresponding to a minimum of the functional (10) for the triplet bipolaron term for various parameters α (for $\eta = 0$), obtained with use WF (36) ($n = 5$) at $R = 0$. With the increasing of a distance R between the centers of polarization wells the relevant energies monotonically decrease going to a double polaron energy at $R \to \infty$. For all R the relation $E^t_{Bp}(R) > 2E_p$ (where $E^t_{Bp}(R)$ is a triplet term energy) is fulfilled. Thus, at $R = 0$ the triplet term has the maximum, and the bipolaron stability criterion is not fulfilled for any values of the distance between the centers of the polarization wells.

7 Conclusions

Numerical calculations of the bipolaron energy performed by us in the framework of Buimistrov-Pekar method have shown that the choice of Gaussian system of functions as applied to the bipolaron problem in combination with Buimistrov-Pekar method gives the best numerical results for the energy of two-electron systems in crystals with polar coupling, as compared to other methods using direct variation of the WF. The study of the WF of a more general form corresponding to the two-center configuration of a bipolaron in the case of an arbitrary electron-phonon interaction has demonstrated energy instability of the two center formation which was investigated earlier in [26, 38]. Despite the fact that in the early papers devoted to the bipolaron continuum theory, the choice of the bipolaron WF was not appropriate, the papers [38] undeniably stand out of subsequent works on the bipolaron subject matter. The work [38] was the first to show the possibility of the formation of a stable bipolaron state. At the same time, it seems that the study of the oscillatory spectrum of a two-center bipolaron near a fictitious energy minimum [39] serves an example of the study of a phenomenon whose existence is impossible even in principle.

Parameter R involved in the WF (33) and treated as the distance between the centers of polarization wells is analogous, in physical meaning, to the variation parameter a in [2] which is determined as a mean distance on which electrons fluctuate. The method of integration over trajectories as applied to the bipolaron problem [2] has also suggested that $a = 0$, which is consistent with our conclusion about energetic instability of a two-center bipolaron. At the same time the dependencies $J_{Bp}(R)$ shown in Fig. 1 which we obtained for the first time as a result of numerical calculations with due regard for the effects of interelectron correlations have also an independent meaning as a curves describing the dependence of the energy of two polarons on the distance between the centers of polarization wells. Our dependencies have qualitatively different character as compared to those presented in [40](Fig. 2) being based on qualitative reasoning on the character of interaction between polarons.

We suppose, that the deduction about the lack of the bound triplet bipolaron state, which we made as a result of the variation calculations with the use of an extremely flexible WF (36), illustrates that for continual bipolaron the bound excited states are absent in complete analogy with the Hill‘s theorem about the absence of any bound excited states for an ion H^- [3].

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Table 1: The values of the bipolaron energy in units $\hbar\omega$ calculated by Buimistrov-Pekar method (E_{Bp}) and the method of optimized canonical transformation (E_{Bp}^A) [1] for various parameters of electron-phonon interaction.

	The energy of the bipolaron ground state for various α values									
	5.5		6		7		9		20	
η	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A
0	-11.161	-11.086	-12.703	-12.601	-16.234	-16.067	-24.927	-24.652	-111.928	-110.504
0.01	-11.075	-11.002	-12.595	-12.487	-16.053	-15.910	-24.650	-24.354	-110.497	-109.064
0.1					-14.598	-14.500	-22.068	-21.756	-96.878	-95.335

Table 2: The values of the polaron energy calculated by the method of optimized canonical transformation (E_p^A) [1], functional integration (E_p^{AGA}) [27], Feynman‘s method (E_p^F) [21], Pekar‘s strong coupling method (E_p^P) [9], the strong coupling method with using wave functions (22) for $n = 5$ (E_p^{St}), Buimistrov-Pekar method with using wave functions (22) for $n = 5$ (E_p^{Bp}), for various parameters of electron-phonon interaction in units $\hbar\omega$. The bold font style indicates the lowest polaron energy in this range.

α	7	9	11	20	30	35	40	50
E_p^A	-7.2500	-10.653	-14.947	-44.997	-98.886	-133.91	-174.33	-271.34
E_p^{AGA}	**-8.1374**	**-11.538**	**-15.827**	**-45.334**	-98.524	-133.22	-173.37	-269.70
E_p^F	-8.1127	-11.486	-15.710	-45.283	-98.328	-132.81	-172.60	-266.01
E_p^P	-5.3171	-8.7896	-13.130	-43.405	-97.662	-132.93	-173.62	-271.28
E_p^{St}	-6.9740	-10.475	-14.830	-45.127	-99.389	-134.66	-175.35	-273.01
E_p^{Bp}	-7.1302	-10.564	-14.900	-45.144	**-99.400**	**-134.66**	**-175.350**	**-273.02**

Table 3: Estimated critical values of the electron-phonon coupling constant and the ratio of optical to static dielectric constants calculated by Buimistrov-Pekar method (η_c) with using the lowest upper bound of polaron energy (E_p^{AGA} for $\alpha \leq 20$ and E_p^{Bp} for $\alpha \geq 30$) and the method of optimized canonical transformation with using polaron energy E_p^{AGA} [1]. In the strong coupling limit ($\alpha \to \infty$) the Buimistrov-Pekar method gives $\eta_c = 0.1432$.

α	7.1	7.3	7.5	8	9	11	20	30	40	50
η_c	0.002	0.011	0.020	0.039	0.065	0.095	0.1375	0.1420	0.1429	0.1430
η_c^A	0	0	0.010	0.029	0.056	0.086	0.130	0.138	0.1385	0.140

Table 4: The values of the triplet term of the bipolaron energy E^t_{Bp} in units $\hbar\omega$ calculated by Buimistrov-Pekar method with using wave functions (36) for $n = 5$ at $R = 0$ for various parameters of electron-phonon interaction for $\eta = 0$. At $\alpha \to \infty$ $E^t_{Bp}/2\alpha^2 = -0.076021$.

α	7	9	11	20	30	35	40	50
E^t_{Bp}	-13.993	-18.458	-24.402	-66.656	-142.648	-192.057	-249.069	-385.903

Figure captions

Fig. 1. The dependencies of the bipolaron energy from the distance R between the centers of polarization wells of two polarons for different parameters of electron-phonon coupling constant α calculated by Buimistrov-Pekar method for $\eta = 0$ in effective atomic units ($m^*e^4/\hbar^2\varepsilon_\infty^2$ for the energy and $\hbar^2\varepsilon_\infty/m^*e^2$ for the distance).

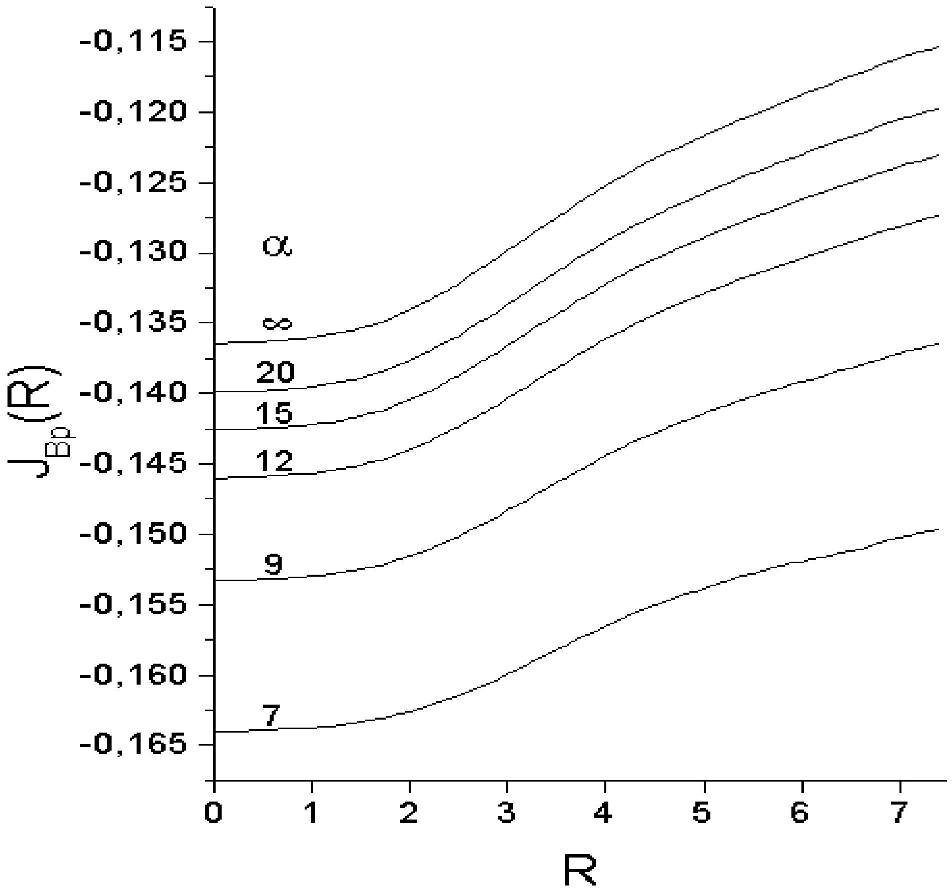
-0,115
-0,120
-0,125
-0,130
-0,135
-0,140
-0,145
-0,150
-0,155
-0,160
-0,165
$J_{B\rho}(R)$
α
∞
20
15
12
9
7
0
1
2
3
4
5
6
7
R

Figure 1: