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Polaron effects and electron correlations in two-electron systems: Arbitrary value of electron-phonon interaction

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The energy of two-electron systems [exchange-coupled pairs of paramagnetic centers (D^- centers) and bipolarons] is calculated for various distances between paramagnetic centers with regard to polaron effects for arbitrary coupling of electrons with a phonon field. Interaction of electrons with a phonon field is found by the Buymistrov-Pekar method. The calculations are made with a wave function (WF) in the form of expansion in Gaussians. Both the electronic correlations (direct dependence of the WF of a system on the interelectronic distance) and the permutation symmetry of the two-electron WF are taken into account. The lowest singlet $^1\Sigma_g^+$ and triplet $^3\Sigma_u^+$ terms are considered. Effects of electronic correlations are exemplified by the dependence of the energy and spatial distribution of the bipolaron WF on the distance between the centers of polaron polarization wells. A bipolaron corresponding to a two-center configuration is energetically unstable. The only minimum on the curve for the energy dependence of two polarons on the distance between the centers of their polarization wells corresponds to a one-center bipolaron configuration. For AgBr and AgCl we present the energies of the lowest singlet and triplet states of F_2 centers ($^1\Sigma_g$ and $^3\Sigma_u$ terms) and those for $1\sigma_g$ and $1\sigma_u$ terms of F_2^+ centers as a function of the distance between them (with a graph of various contributions into these energies). Control calculations performed for a hydrogen molecule with the use of a variational function suggested in the work yield the energies of the singlet and triplet states equal to -1.17416 and -0.78315 a.u. respectively, the equilibrium internuclear distance corresponds to $R_m = 1.4011$ a.u. The contribution of phonons into the exchange interaction between paramagnetic centers has antiferromagnetic character. The exchange interaction caused by phonons is comparable in the order of magnitude with Coulomb exchange.

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I. INTRODUCTION

Experimental studies of optical, photoelectric, magnetic properties, and impurity conductivity of semiconducting and ionic crystals show that along with local centers of the simplest type (shallow hydrogenlike centers in semiconductors and F centers in alkali-halide crystals) these systems contain more complicated formations. The simplest aggregate centers are exchange-coupled pairs of paramagnetic ones. The energy spectrum of shallow hydrogenlike centers and their complexes can be described in the framework of the continuum theory. In molecular physics, the nearest analog of this system is a hydrogen molecule. In solids, motion of electrons in such a "molecule" is a great deal complicated by interaction of electrons with oscillations of the crystal lattice. In a crystal, unlike in a molecular system, exchange-coupled pairs of paramagnetic centers can occur both in the ground singlet state $^1\Sigma_g^+$, and in the lowest triplet one $^3\Sigma_u^+$ and the distance between the centers is determined by the conditions of the crystal growth, the structure of the crystal lattice and impurity doping technology, but not by the minimum of the total energy which includes interaction between static Coulomb charges. In thermodynamic equilibrium, the population density of triplet states is governed by the temperature. We can get the simplest qualitative description of the energy spectrum of such a system by introducing effective atomic units instead of atomic ones, just as it is done for one-electron shallow hydrogenlike centers. More simple two-electron systems are bipolarons and F' centers in polar crystals and D^- centers in semiconductors (analog of an H^- ion in atomic physics).[1–9] The binding energy of D^- or F' centers is significant in crystals with strong electron-phonon interaction. The field of existence of bipolarons is confined to crystals with strong electron-phonon interaction (for $\eta = \varepsilon_\infty/\varepsilon_0 = 0$, $\alpha \geqslant \alpha_c = 6.8$),[10] where ε_∞ and ε_0 are high-frequency and static dielectric permittivities, respectively, and α is a dimensionless Fröhlich coupling constant of electron-phonon interaction.[11]

Aggregate color centers (exchange-coupled pairs of F centers or F_2 centers) in alkali-halide crystals were intensively studied in Kiev school in the 1950's.[12] Consideration of polaron effects reduced considerably the energy of two-electron states. Subsequently, an F_2 center served as a model to develop a theory of a two-center bipolaron.[13,14] In the framework of this model, it was proved theoretically that a stable autolocalized two-electron state can arise in crystals with strong electron-phonon interaction. Contribution of acoustical phonons into the ground-state energy of shallow impurity centers in crystals was studied by Deigen.[15]

Early works on the study of the energy spectrum of two-electron systems dealt with the lowest singlet states. Therefore effects concerned with exchange interactions (EIs), namely, polaron effects were out of consideration. Deigen *et al.*[16] were the first to show that phonon contribution into the exchange interaction of impurity centers in crystals can be comparable in the order of magnitude with direct Coulomb exchange. In their work, interaction between large-radius impurity centers via fields of optical and acoustical phonons was constructed by methods of perturbation theory. Kashirina and Suslin[17] dealt with polaron effects in an exchange interaction of two-electron systems in polar crystals with strong electron-phonon coupling. These authors[18] used Green functions to study temperature dependence of phonon contribution into the exchange energy of shallow impurity centers in crystals. They showed that in systems with closely spaced electron levels, qualitatively new temperature dependencies can arise in EIs of impurity centers due to contribution of acoustical phonons into the isotropic exchange energy. These systems demonstrated resonance effects leading to occurrence of terms in EIs with exponential dependence on temperature.

Presently, interest in the study of exchange-coupled pairs of shallow impurities has regenerated in the context of an opportunity to use such two-electron systems as a basis for constructing quantum computers which could operate on both spin[19] and nuclear resonance.[20,21] In both the schemes EIs between impurities provides interaction between qubits. The results of Ref. 22 show that polarons and bipolarons are good candidates to logical switching in molecular circuits of conducting polymers. Therefore, theoretical studies of the energy spectrum of simplest two-electron systems, such as bipolarons (free and coupled) and exchange-coupled pairs in crystals are not only of purely academical interest, but of practical importance as well.

Up to now no consideration has been given to the energy spectrum of exchange-coupled pairs in crystals with arbitrary value of electron-phonon coupling. Arising of a nonlocal addition (concerned with inclusion of polaron effects) in the energy of a two-electron system makes the study of the system rather a complicated procedure, as compared with a hydrogen molecule (which presents the closest analog of an exchange-coupled pair of shallow impurities in a crystal). In the strong coupling limit, the energy of exchange pairs has been calculated in the framework of Heitler-London method, which enables only a qualitative description of the system.[12,17]

The necessity of considering electronic correlations (hereafter this implies direct dependence of the WF of a system on the interelectronic distance) imposes specific requirements upon the trial variational function of the system. The function should be flexible enough to properly describe the energies of simplest two-electron systems in molecular and atomic physics (hydrogen molecule, helium atom, negative hydrogen ion). At the same time, it should be rather convenient so that one could perform integration over the electron coordinates and present the functional of the system in the simplest way suitable for treatment by methods of multiparameter functional variation.

In this work we deal with the most general two-electron system in a crystal, namely, with an exchange-coupled pair of shallow impurity centers in crystals with ion coupling. Simpler systems, such as bipolarons and D^- centers can be obtained as its limit cases. We will analyze the dependencies of the ground-state energy of the system on the distance between the centers for an arbitrary electron-phonon coupling, identify phonon contribution into the total energy and discuss the problems concerned with inclusion of interelectronic correlations and their influence on the energy spectrum of an exchange-coupled pair. We will also give some examples of our calculations of EIs of large-radius paramagnetic centers in crystals with an arbitrary value of the electron-phonon interaction. The calculations have been performed by the Buymistrov-Pekar method which is valid for an arbitrary value of the electron-phonon interaction. The method is widely used to calculate the energy of both one-electron[23–25] and two-electron[5,9,26,27] states and gives the best (for rather a versatile system of variation functions) results in the calculation of the D^--center energy and the lowest values of the bipolaron energy[9,27] as compared with direct variational methods which imply variation of the WF of the system.[28]

II. MAIN RELATIONS

Let us consider a pair of shallow impurity centers in a crystal with ionic coupling. Interaction of the electron subsystem with a phonon field is Fröhlich coupling with LO phonons. Then, the exchanged coupled pair is described by the Hamiltonian[16]

$$H = T_{12} + H_Q + H_f + H_{ef}, \tag{1}$$

where T_{12} is the kinetic energy of the electrons, H_Q includes all Coulomb interactions in the system, H_f is Hamiltonian of the phonon field, and H_{ef} is Hamiltonian of the electron-phonon interaction.

For a two-electron system consisting of two paramagnetic centers occurring at points (a) and (b) in a crystal:

$$T_{12} = -\frac{\hbar^2}{2m^*}(\Delta_1 + \Delta_2), \tag{2}$$

where m^* is an electron effective mass.

$$H_Q = \frac{e^2}{\varepsilon_\infty r_{12}} - \frac{Z_1 e^2}{\varepsilon_0 r_{a1}} - \frac{Z_2 e^2}{\varepsilon_0 r_{b1}} - \frac{Z_1 e^2}{\varepsilon_0 r_{a2}} - \frac{Z_2 e^2}{\varepsilon_0 r_{b2}} + \frac{Z_1 Z_2 e^2}{\varepsilon_0 R}, \tag{3}$$

where r_{ai} is the distance of the ith electron from the point (a), r_{bi} is the same for the point (b), r_{12} is the distance between the electrons, R is the distance between paramagnetic centers. This notation is traditional for two-center coordinate systems which are used for calculations of the molecular system energy.[29] We place the coordinate origin in midposition between the points (a) and (b).

$$H_f = \hbar\omega \sum_{\mathbf{k}} a^+_{\mathbf{k}} a_{\mathbf{k}}, \quad H_{ef} = H^{(1)}_{ef} + H^{(2)}_{ef},$$

$$H^{(i)}_{ef} = \sum_{\mathbf{k}} V_{\mathbf{k}}(a_{\mathbf{k}} - a^+_{-\mathbf{k}})\exp(i\mathbf{k}\cdot\mathbf{r}_i), \tag{4}$$

where $V_{\mathbf{k}} = -i(e_0/k)\sqrt{2\pi\hbar\omega/V\tilde{\varepsilon}}$, $1/\tilde{\varepsilon} = 1/\varepsilon_\infty - 1/\varepsilon_0$, e_0 is an electron charge, V is the crystal volume, ω is the frequency of optical phonons, $\mathbf{k}$ is the wave vector of phonons, $a^+_{\mathbf{k}}$ and $a_{\mathbf{k}}$ are the creation annihilation operator of phonons with the wave vector $\mathbf{k}$, ε_∞ is high frequency, and ε_0 is static dielectric permittivity $i=1,2$; $\mathbf{r}_1$, $\mathbf{r}_2$ are the electron coordinates.

Notice that the continuum consideration used in the work is valid only in the framework of adiabatic approximation. That is to say, we believe that nuclei of all the atoms and weakly coupled electrons under study move much slower than strongly coupled electrons of a dielectric. The latter present a quick subsystem and are in the ground state which belongs to a discrete level far removed from the electron levels of the system involved. Then we assume that the quick subsystem follows adiabatically the slow one. The adiabatic approximation has also motivated phenomenological introduction of screening of the interelectronic interaction potential by high-frequency dielectric permittivity representing the inertia-free part of the screening. If these conditions are not fulfilled, the effects of spatial and temporal dispersion of dielectric permittivities should be taken into account as early as at the stage of definition of electron-phonon interaction which would imply going outside the framework of the Fröhlich description.

In the early works devoted to consideration of two-electron systems in ionic crystals[2,3] one more restriction was imposed which was concerned with the assumption that weakly coupled electrons move much faster than the nuclei of atoms in the crystal cell. Later on, in the work by Buymistrov and Pekar[4] this restriction was removed. Additional aspects concerned with introduction of screening of the interelectronic interaction potential by high-frequency dielectric permittivity and passing on to the limit of weak electron-phonon interaction are discussed in Ref. 5.

The trial WF is chosen in the form

$$\Psi_S(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{N_{12}}}\sum_{i=1}^{n} C_i[1+(-1)^S P_{12}]\exp[-a_{1i}r_1^2 - 2a_{2i}(\mathbf{r}_1\cdot\mathbf{r}_2) - a_{3i}r_2^2 - 2a_{4i}z_1 - 2a_{5i}z_2], \quad (5)$$

where C_i, a_{1i}, a_{2i}, a_{3i}, a_{4i}, a_{5i} are variational parameters, $S=0$ for a singlet state of a two-electron system and $S=1$ for a triplet one, and P_{12} is an operator for permutation of electron coordinates.

The Hamiltonian of a singly ionized pair of hydrogenlike paramagnetic centers in ion crystals (analog of the H_2^+ ion) is written as

$$H^+ = T + H_Q^+ + H_f + H_{ef}^{(1)}, \quad (6)$$

$$T = -\frac{\hbar^2}{2m^*}\Delta, \quad (7)$$

$$H_Q^+ = -\frac{Z_1e^2}{\varepsilon_0 r_a} - \frac{Z_2e^2}{\varepsilon_0 r_b} + \frac{Z_1Z_2e^2}{\varepsilon_0 R}. \quad (8)$$

To minimize the Hamiltonian (6) we choose a trial WF in the form

$$\Psi_{g,u}^+ = \sum_{i=1}^{n} c_i[\exp(-a_ir^2 - 2b_iz) \pm \exp(-a_ir^2 + 2b_iz)], \quad (9)$$

where the upper index refers to the lowest $1\sigma_g$ term and the lower index to the lowest $1\sigma_u$ one.

The terms are denoted in conformity with Ref. 29. The WF Ψ_g^+ is symmetrical and Ψ_u^+ is asymmetrical around the inversion of the origin placed in between Coulomb centers.

III. USEFUL LIMIT TRANSITIONS

In order to prove flexibility of our functions we used WF (5) to calculate the energies of singlet and triplet terms of a hydrogen molecule, the ground state of a negative hydrogen H^-, and the energies of para-helium and ortho-helium and applied WF (9) to find the energy of two lowest ($1\sigma_g$ and $1\sigma_u$) terms of an ionized hydrogen molecule. For atomic and molecular systems we put $\varepsilon_0=\varepsilon_\infty=1$.

Our calculations with the use of variational WF (5) for $n=32$ at the equilibrium internuclear distance $R=1.4011$ a.u. yield a ground state energy of a hydrogen molecule equal to -1.17416 a.u. and a lowest triplet term equal to -0.78405 a.u. The result obtained by James and Coolidge[30] for the ground singlet state is -1.172 a.u. and experimental value is -1.174 ± 0.003a.u.[31,32] The latest calculations[33] based on 80-term wave functions in the Born-Oppenheimer approximation yielded the value -1.1744746 a.u. ($^1\Sigma_g$ term) and -0.7841501 a.u. ($^3\Sigma_u$ term for $R=1.4$ a.u.). New experimental data and references to the works concerned with the study of the energy spectrum of a hydrogen molecule are given in Ref. 34.

WF (5) can also be used to find the energies of one-electron states. If we omit in Eq. (3) the terms standing for interelectronic repulsion, Hamiltonian (1) will transform into a sum of two one-electron Hamiltonians corresponding to a molecular hydrogen ion H_2^+. Variation of the Hamiltonian with the use of WF (5) (which corresponds to the singlet term of a two-electron system) yields the double ground state energy of an ionized hydrogen molecule H_2^+. Averaging over the WF (5) corresponding to the triplet state gives a sum of the energies of the ground $1\sigma_g$ term and the repulsive $1\sigma_u$ term of H_2^+.

If we put $R=0$ in Eq. (3) and omit the terms corresponding to internuclear repulsion, we will get a limit transition to a helium atom. The energies of para-helium and ortho-helium obtained by us with the use of Eq. (5) are equal to -2.903723 and $--2.17515$ a.u., respectively. The energy of a negative hydrogen ion is calculated to be -0.5027742 a.u., while the exact value is -0.5027751 a.u.[35]

If we omit the terms corresponding to interelectronic and internuclear repulsion in Eq. (3) and put $R=0$, we will obtain a limit transition to the model one-center system consisting of two identical singly ionized helium atoms which do not interact with each other. Symmetrical WF (5) yields the double ground-state energy, the asymmetrical one gives a sum of the energies of the ground and the first excited states of He^+ atom. Calculation of the total energy of two identical noninteracting one-electron systems with the use of a two-electron WF is the simplest numerical illustration of how the

Pauli principle is realized and in what order energy levels in a two-electron system are populated. Thus, for the lowest triplet term of a system consisting of two noninteracting He^+ atoms located at one point, just the state at which one He^+ atom is in the ground state and the other is in the first excited one can be realized.

With the use of WF (5), we have succeeded to reproduce classical experimental distance dependencies of the ground state of a system consisting of two hydrogen atoms.[29] The trial functions (9) have enabled us to reproduce similar dependencies for an ionized hydrogen molecule.[29] Highly accurate values have been obtained for the energy and the equilibrium internuclear distance of a hydrogen molecule and for the energy and the equilibrium internuclear distance of a molecular ion H_2^+. Thus, for the WF (9) symmetrical about the inversion operation (for $R=2$ a.u.) we have -1.102605 a.u., and for the asymmetrical one the energy is equal to -0.667510 a.u., while the relevant exact values are -1.102625 and -0.667535 a.u., respectively.[29,36]

In view of the fact that in solids optical and ESR spectra of simplest one-electron and two-electron systems are a great deal broadened, an accuracy provided by WF (5) is well suited to the description of the energy spectrum of such systems.

IV. BUYMISTROV-PEKAR METHOD AS APPLIED TO CALCULATIONS OF THE ENERGY OF TWO-ELECTRON SYSTEMS IN CRYSTALS WITH AN ARBITRARY VALUE OF THE ELECTRON-PHONON INTERACTION

The Buymistrov-Pekar method was applied to two-electron systems in ionic crystals with an arbitrary value of electron-phonon coupling in Ref. 4, where systems without translational invariance (F and F' centers) and autolocalized polaron and bipolaron states were considered. Later on Buimistrov and Pekar[37] analyzed a more general case when the WF of a polaron state was chosen with regard to translational invariance of the system. However, their numerical calculations were performed only for an approximate functional (in particular, they used an expansion in terms of the wave vector $\mathbf{k}$ which is valid only in the limit case of small $\mathbf{k}$). The general expressions derived in Ref. 37 for the functional of the ground state of a translationally invariant polaron are so complicated that even nowadays they cannot be minimized numerically without the use of some approximation. At the same time, calculations of the energy of a D^- center by the Buymistrov-Pekar method (the limit of lacking translational invariance) in combination with the Gaussian system of functions yield the lowest values for the minimum of the corresponding functional.[9] The same refers to the bipolaron energy obtained by a direct variation of the WF of the system.[27] Integration over trajectories as applied to the bipolaron problem is currently the only method which gives the lowest values of bipolaron energy with regard to translational symmetry. The region where this advantage holds is rather narrow ($6.8 \leqslant \alpha \leqslant 7.05$). For $\alpha \geqslant 7.05$ the lowest values of bipolaron energy were obtained by the Buymistrov-Pekar method for the case of lacking translational symmetry.[27] Numerous attempts to find translationally invariant solutions of the bipolaron problem by traditional methods via direct variation of the WF of an electronic system (see Ref. 38, and references therein[39,40]) yielded larger values of the bipolaron ground-state energy as compared to the works were WF corresponding to autolocalized states were used.[26–28,41–44] Amirkhanov *et al.*[45] obtained numerically translationally invariant solutions without variation of the electron WF, however, these authors have not succeeded to reduce the value of the bipolaron energy relative to the best results obtained for autolocalized WF. Combination of Feynman integration over trajectories with direct variational method also leads to larger energy values.[39]

In a modern presentation, the Buymistrov-Pekar method is reduced to canonical transformation of Hamiltonian (1) as $\exp(\alpha S) H \exp(-\alpha S)$ with unitary operator $S = \Sigma_{\mathbf{k}}[F_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) a_{\mathbf{k}} - F_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) a_{\mathbf{k}}^+]$, where $F_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)$ is a function of the electronic system co-ordinates. We choose a function $F_{\mathbf{k}}$ in the form

$$F_{\mathbf{k}} = \widetilde{C}_{\mathbf{k}} + \gamma_{\mathbf{k}} f(\mathbf{r}_1,\mathbf{r}_2), \tag{10}$$

where $\widetilde{C}_{\mathbf{k}}$, $\gamma_{\mathbf{k}}$ are variational parameters. In what follows we will use Feynman system of units where $\hbar=1$, $\omega=1$, and $2m^*=1$. Accordingly, the unit of energy is $\hbar\omega$, and the unit of length is $L_0=\sqrt{\hbar/2m^*\omega}$.

Variation over $\widetilde{C}_{\mathbf{k}}$ and $\gamma_{\mathbf{k}}$ yields the following expressions for the functional of the ground state of an exchanged-coupled pair:

$$E = V_s + V_{fi}, \tag{11}$$

$$V_{fi} = \sum_{\mathbf{k}} V_{\mathbf{k}}^2 \frac{\widetilde{U}_{\mathbf{k}}^2}{2k^2 + U_{\mathbf{k}}\omega}, \tag{12}$$

$$\widetilde{U}_{\mathbf{k}} = \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) L_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle - \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle \times \langle \Psi_{12} | L_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle, \tag{13}$$

$$L_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) = \exp(-i\mathbf{k}\cdot\mathbf{r}_1) + \exp(-i\mathbf{k}\cdot\mathbf{r}_2), \tag{14}$$

$$U_{\mathbf{k}} = \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) f_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle - \langle \Psi_{12} | f_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle \times \langle \Psi_{12} | f_{\mathbf{k}}^*(\mathbf{r}_1,\mathbf{r}_2) | \Psi_{12} \rangle, \tag{15}$$

where V_{fi} is an addition which has appeared for intermediate coupling and V_s corresponds to the functional of the system in the limit of strong electron-phonon interaction

$$V_s = \overline{T}_{12} + \beta V_{ee} - \gamma V_{Ze} + \sum_{\mathbf{k}} V_{\mathbf{k}}^2 |\langle \exp(-i\mathbf{k}\cdot\mathbf{r}_1) + \exp(-i\mathbf{k}\cdot\mathbf{r}_2) \rangle|^2, \tag{16}$$

$$\alpha = \frac{e^2}{2\hbar\omega}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)\frac{1}{L_0}, \quad L_0 = \sqrt{\hbar 2m^*\omega},$$

$$\beta = \frac{e^2}{\hbar\omega\varepsilon_\infty L_0} = \frac{2\alpha}{1-\eta}, \quad \gamma = \frac{e^2}{\hbar\omega\varepsilon_0 L_0} = \frac{2\alpha\eta}{1-\eta},$$

$$\eta = \varepsilon_\infty/\varepsilon_0,$$

$$\overline{T}_{12} = -\int \Psi_{12}(\Delta_1 + \Delta_2)\Psi_{12}^{*} d\tau, \tag{17}$$

$$V_{ee} = \int \frac{|\Psi_{12}|^2}{r_{12}} d\tau, \tag{18}$$

$$V_{ze} = \int \left(\frac{Z_1}{r_{a1}} + \frac{Z_1}{r_{a2}} + \frac{Z_2}{r_{b1}} + \frac{Z_2}{r_{b2}} - \frac{Z_1 Z_2}{R}\right)|\Psi_{12}|^2 d\tau. \tag{19}$$

Ψ_{12} is the wave function of a two-electron system.

In the subsequent discussion we will only be interested in the electronic part of the two-electron system energy, therefore the term in Eq. (19) corresponding to the interaction of static Coulomb charges occurring at points (a) and (b) will be omitted. Then we put $Z_1 = Z_2 = 1$, $f_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) = L_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2)$.

The use of WF (5) enables easy integration over electronic coordinates. So, the problem is reduced to variation and finding a minimum for the function of many variables $E_{Bp}(R, C_i, a_{ki})$, where $k = 1,2,3$, $i = 1, \ldots, N$.

V. POLARON EFFECTS AND ELECTRONIC CORRELATIONS IN TWO-ELECTRON SYSTEMS

The role of electronic correlations in two-electron systems is clearly demonstrated by the study of a bipolaron spatial configuration. Hamiltonian of a system consisting of two electrons interacting with phonons in an ionic crystal can be obtained from the general Hamiltonian (1) if we put $H_Q = e^2/\varepsilon_\infty r_{12}$. Within the Buymistrov-Pekar method, the functional of a bipolaron is derived from functional (11) for $\gamma = 0$ in Eq. (16) in the form

$$E_{Bp} = \overline{T}_{12} + \beta V_{ee} + V_f, \tag{20}$$

$$V_f = V_{fs} + V_{fi},$$

$$V_{fs} = \sum_{\mathbf{k}} V_{\mathbf{k}}^2 |\langle \exp(-i\mathbf{k} \cdot \mathbf{r}_1) + \exp(-i\mathbf{k} \cdot \mathbf{r}_2)\rangle|^2, \tag{21}$$

where V_f is just responsible for the phonon contribution into the bipolaron ground-state energy, V_{fs} is the part corresponding to strong coupling, and V_{fi} is an addition for intermediate coupling determined by Eqs. (12)–(15).

A one-center (OC) bipolaron or Pekar bipolaron was first considered in Ref. 2 in the strong coupling limit. There the term "bipolaron" was first introduced to mean a stable state of two polarons.[1,2] The WF of a two-electron system was chosen in the multiplicative form

$$\Psi_{Bp}(\mathbf{r}_1, \mathbf{r}_2) = a(1)a(2), \tag{22}$$

where $a(1)$ is a polaron wave function.

For this WF, a bipolaron functional V_s is equal to the sum of two polaron functionals. Therefore a bound state of a bipolaron is lacking. Multiplicative form of the WF was also used in Ref. 4.

Vinetskii and Giterman[13] calculated the energy of bipolaron in ionic crystals with the use of the method and analytical expressions derived by Deigen[12] for the functional of an F_2 center (strong coupling). In their model a bipolaron was considered as an analog of a hydrogen molecule or a two-center (TC) bipolaron. The possibility of the formation of a stable bipolaron state was proved in the framework of the TC bipolaron model.[13,14] A two-electron WF was constructed in the framework of Heitler-London method by complete analogy with the WF of a hydrogen molecule:

$$\Psi_{Bp}(\mathbf{r}_1, \mathbf{r}_2) = N[a(1)b(2) + a(2)b(1)], \tag{23}$$

where

$$a(1) = (\lambda^3 \pi)^{1/2} \exp(-\lambda r_{a1}),$$

$$b(1) = (\lambda^3 \pi)^{1/2} \exp(-\lambda r_{b1}),$$

$$N = 1/\sqrt{2(1+S^2)}, \quad S = \int a(1)b(1) d\tau.$$

Table I lists the energies of the bipolaron ground state obtained with the use of this function and the values of the relations $E_{Bp}^{\mathrm{HL}}/2E_P$ and $\widetilde{E}_{Bp}^{\mathrm{HL}}/2E_P$, where E_{Bp}^{HL}, $\widetilde{E}_{Bp}^{\mathrm{HL}}$ are the energies of the bipolaron ground state for $\lambda = \lambda_m$ and $\lambda = \widetilde{\lambda}_m$ respectively. The variational parameter λ_m minimizes the polaron functional for a hydrogenlike WF $a(1)$, while $\widetilde{\lambda}_m$ (our calculations) minimizes the bipolaron functional for the WF (23). In Vinetskii's later work[14] one-electron WF were chosen in a more complicated form $a(1) = \varphi(1) = (1 + \lambda r_{a1})\exp(-\lambda r_{a1})$. The value of the relation $E_{Bp}^{\mathrm{HL}}/2E_P$, where E_P is the polaron energy for WF $\varphi(1)$, was calculated to be 1.08 (Ref. 14), as for the simplest hydrogenlike function.

The necessity of considering electronic correlations (namely, electronic correlations concerned with direct dependence of the electron WF on the interelectronic distance) was demonstrated in Larsen's work where the energy of D^- centers in crystals with ionic coupling was calculated.[5] The calculations were performed for an arbitrary value of electron-phonon interaction in the framework of Buymistrov-Pekar method. The electron WF was chosen in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (1 + bs)(1 + cu)\cosh(\gamma t)\exp(-\delta s), \tag{24}$$

where $s = r_1 + r_2$, $t = r_1 - r_2$, $u = |\mathbf{r}_1 - \mathbf{r}_2|$ are Hylleraas coordinates, and b, c, γ, δ are variational parameters.

Larsen[5] reported a giant growth of the coupling energy of a D^- center when the WF was chosen with regard to interelectronic correlations in semiconductors with ionic coupling and in ionic crystals. Interelectronic correlations were taken into account by the multiplier $(1 + cu)$. In crystals with relatively large value of electron-phonon interaction he used the approximation with $\gamma = 0$ in Eq. (24). Larsen did not consider the coupling energy of a free bipolaron, though the application of the WF (24) to the bipolaron problem must have led to one of the lowest values of the ground-state energy for an arbitrary value of electron-phonon interaction. In Ref. 43 the WF of a one-center bipolaron was taken in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (1 + ar_1)(1 + ar_2)(1 + \beta u)\exp(-as). \tag{25}$$

TABLE I. Energies (for $\eta=0$) and domains of existence of bipolarons obtained by various methods in the strong coupling limit. HL, MO, Heitler-London method, and the method of molecular orbitals accordingly [without variation over λ in WF (23) and (28)], HL*, MO*—the same with variation over λ. TC(C), OC(C) are two-center and one-center configurations of a bipolaron with regard for electronic correlations. E_p, E_{Bp} are the energies of a polaron and a bipolaron, respectively. R_m is the equilibrium state between the centers of polarization wells of two polarons, $E_{Lp}=-25/512$, $E_p^M=-0.0542564$ is the exact value of the polaron energy in the strong coupling limit (in the strong coupling limit effective atomic energy units $Ha^*=e^2/\tilde{\varepsilon}a^*$ and lengths $a^*=\hbar^2\tilde{\varepsilon}/m^*e^2$ were used), η_c, η_c^* are critical values of the parameter η, calculated with respect to E_{Lp} and E_p^M accordingly, $Q=E_{Bp}/2E_P$, and $Q^*=E_{Bp}/2E_P^M$.

Method, Ref.	HL, Ref. 12	HL*	MO	MO*	Ref. 46	Ref. 48	Ref. 48
WF	TC	TC	TC	TC	OC(C)	TC(C)	TC
$-E_{Bp}$	0.10612	0.10784	0.10024	0.10071	0.134624	0.136512	0.11503
R_m	4.5518	4.1155	2.5149	2.5538	0	0	5.0225
$-E_p$	E_{Lp}	E_{Lp}	E_{Lp}	E_{Lp}	0.05351	E_p^M	E_p^M
η_c	0.0535	0.0542	0.0142	0.0150	0.1392	0.1432	0.016
η_c^*	0	0	0	0	0.1322	0.1432	0.016
Q	1.0866	1.1043	1.0265	1.0313	1.2579	1.2581	1.0602
Q^*	0.9779	0.9938	0.9238	0.9281	1.2406	1.2581	1.0602

Calculations were performed by the strong coupling method. Earlier the same function was used in Ref. 3 to calculate the energy of an F' center in the strong coupling approximation. There bipolaron states were not treated either. In view of the fact that Suprun and Moyzhes[43] figured only the bipolaron energy dependence on the parameter η but the value of the bipolaron ground-state energy obtained with the use of the WF (25) was not given, we have carried out these calculations independently. Table I lists the energy of the bipolaron ground state calculated with the WF (25). Figure 1 illustrates fundamental difference of the multiplicative WF [$\beta=0$ in Eq. (25)] from the two-electron WF chosen with regard to interelectronic correlations. Both the WF correspond to parameters which minimize the bipolaron functional. One electron is placed in the coordinate origin. For the other we put $z_2=0$ and coordinates x_2 and y_2 vary along horizontal axes. The vertical axis represents the WF density. The density of the two-electron WF in the coordinate origin chosen as a product of polaron WF $(1+\lambda r_1)(1+\lambda r_2)\exp[-\lambda(r_1+r_2)]$ is taken to be unity. It is seen that the multiplicative approximation (22) [Fig. 1(a)] corresponds to the maximum density of the WF at the point where both the electrons occur ($\mathbf{r}_1=\mathbf{r}_2=0$), on the contrary, the density of the WF (25) at this point [Fig. 1(b)] has a deep minimum.

Generally, multipliers in a two-electron WF taking into account interelectronic correlations reduce a relative role of the regions where the electrons are closely spaced and raise the role of the regions where the electrons are spaced apart. In this case the bipolaron WF can have a maximum at the point $\mathbf{r}_1=\mathbf{r}_2=0$. As an example we refer to the WF of a one-center bipolaron such that

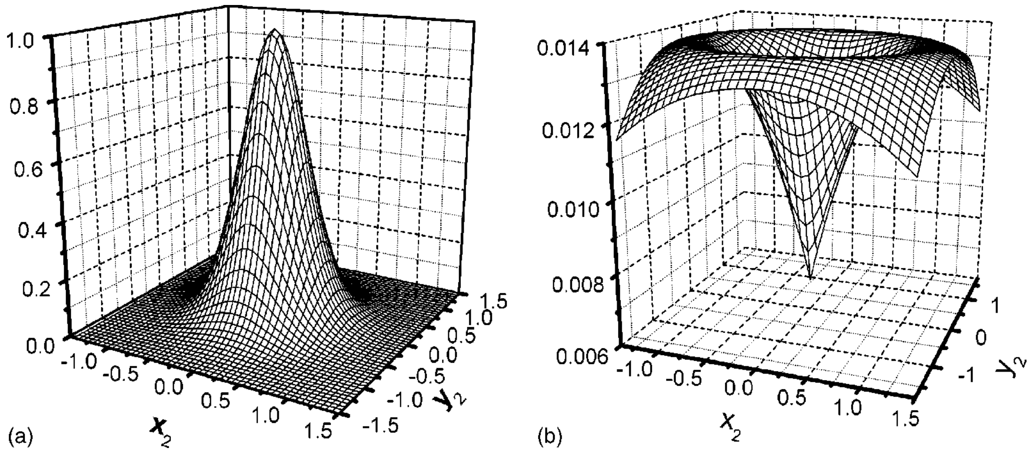

FIG. 1. (a) Density of the WF of a one-center bipolaron without regard for interelectronic correlations [$\beta=0$ in WF (25)]. (b) The same for the case of WF (25), chosen with regard to interelectronic correlations. One electron is placed in the coordinate origin ($\mathbf{r}_1=\{0,0,0\}$) and the radius vector of the other electron is $\mathbf{r}_2=\{x_2,y_2,0\}$. The density of the two-electron WF in the origin chosen as a product of polaron WF is taken to be unity.

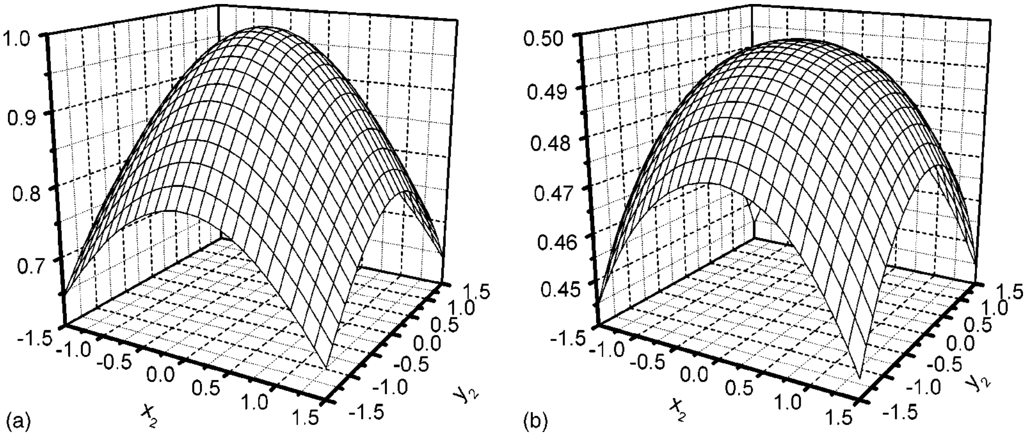

FIG. 2. (a) Density of the WF of a one-center bipolaron without regard to interelectronic correlations [WF (26) for $a_{1i}=a_{3i}$, $a_{2i}=0$]. (b) The same for WF (26) of the most general form ($a_{1i}\neq a_{3i}$, $a_{2i}\neq 0$).

$$\Phi(\mathbf{r}_1,\mathbf{r}_2)=\sum_{i=1}^{n} C_i \exp[-a_{1i}r_1^2-2a_{2i}(\mathbf{r}_1\cdot\mathbf{r}_2)-a_{3i}r_2^2]. \tag{26}$$

This choice of the WF provides the lowest bipolaron energies in the strong coupling limit.[44,46] Table I lists relevant characteristics of a bipolaron. Electronic correlations are taken into account by the multipliers $\exp[-2a_{2i}(\mathbf{r}_1\cdot\mathbf{r}_2)]$.

Figure 2 shows the densities of the WF (26) (vertical axis) corresponding to the parameters which minimize the bipolaron functional (20) in the strong coupling limit for the case when correlation terms are lacking in the trial WF (i.e., $a_{2i}=0$, $a_{1i}=a_{3i}$) [Fig. 2(a)] and relevant figures for the WF of the most general form for which the lowest values of the ground-state functional were obtained [Fig. 2(b)]. The meanings of the electron coordinates are the same as in Fig. 1. The scale of the graphs along the vertical axis is taken such that unity corresponds to the density of a WF chosen without regard for correlation terms [Fig. 2(a)] at the point $\mathbf{r}_1=\mathbf{r}_2=0$. It is seen that the profile of the bipolaron WF which takes electronic correlations into account has a larger width and a shallower maximum at zero as compared to the WF in which electronic correlations are neglected. Note also that minimization of the polaron functional with the WF

$$\Psi_p=\sum_{i=1}^{n} C_i \exp(-a_i r) \tag{27}$$

leads to an exact numerical value of the polaron energy in the strong coupling limit as early as at $n=5$ in Eq. (27). We obtained for the polaron energy in this case $E_p=-0.054256401Ha^*$ (where $Ha^*=m^*e_0^4/\hbar^2\tilde{\varepsilon}^2$, $\tilde{\varepsilon}^{-1}=\varepsilon_\infty^{-1}-\varepsilon_0^{-1}$). This value completely coincides with the exact polaron energy $E_p^M=-0.0542564$ which was found in Ref. 47 for the strong coupling limit as a result of numerical solution of a relevant Eiler equation.

Sahoo and Mitra[48] reported the lowest energy values for the spatial configuration corresponding to a TC bipolaron (strong coupling limit). There the electron part of the bipolaron trial WF was chosen in the framework of a molecular orbital (MO) method without regard for configurational interaction:

$$\Phi_{12}=\Psi(r_1)\Psi(r_2)=N_{12}[a(1)+b(1)][a(2)+b(2)], \tag{28}$$

where

$$a(1)=(\lambda^3/\pi)^{1/2}\exp(-\lambda r_{a1}),$$

$$b(1)=(\lambda^3/\pi)^{1/2}\exp(-\lambda r_{b1}),$$

$$N_{12}=1/\sqrt{2(1+S)}, \quad S=\int a(1)b(1)d\tau.$$

The results of Ref. 48 obtained at $\eta=0$ and R_m equal to the bipolaron functional minimum, are the following: $E_{Bp}(Z_m)/2E_{Lp}=1.22$, $Z_m=\lambda_m R_m=4.720$, where $\lambda_m=5/16$, $E_{Lp}=-25/512$ (in the strong coupling limit effective atomic energy units $Ha^*=e_0^2/\tilde{\varepsilon}a^*$ and lengths $a^*=\hbar^2\tilde{\varepsilon}/m^*e_0^2$ were used). The critical value $\eta_c=\varepsilon_\infty/\varepsilon_0$ below which bound bipolaron states exist, was found to be 0.14. A simplest qualitative analysis suggests that these calculations contain a numerical error. As is known, with no regard for configurational interaction, the MO method yields overestimated values of the ground-state energy of a hydrogen molecule as compared with the Heitler-London method.[29] The reason is overestimation of the role of OC configurations in a molecular system. If a OC configuration corresponding to the bound state of a negative hydrogen ion leads to overestimation of the total energy of a hydrogen molecule, the lack of a bound OC bipolaron state corresponding to the WF chosen in multiplicative form [for a one-center configuration $a(1)=b(1)$, $\Psi(1,2)=a(1)a(2)$] all the more must lead to overestimated results of the bipolaron ground-state energy as compared with relevant values obtained by Heitler-London method.

With the use of the MO method we can find a bipolaron functional for the WF given by Eq. (28), from a relevant functional of a hydrogen molecule [see Ref. 29, p. 87, Eq. (4.7) for H_{11}]. For this purpose we should omit the terms corresponding to interaction of electrons with protons and protons with each other. The part of the functional corresponding to electron-electron interaction should be multiplied by $(\varepsilon_\infty^{-1} - 2\tilde{\varepsilon}^{-1})$. Sahoo and Mitra[48] varied a functional which contained an error in the part corresponding to the bipolaron kinetic energy. Table I lists the energy values of the TC bipolaron ground-state and critical values of η_c obtained by Heitler-London method as well as the relevant values obtained by us by the MO method. The values of η_c and $Q = E_{Bp}/2E_p$ (where E_{Bp}, E_p are the energies of bipolaron and polaron, respectively) were calculated with respect to the polaron energy E_p found within the same approximation as the bipolaron energy, the values of η_c^* and Q^* were calculated with respect to the exact value of the polaron energy in the strong coupling limit E_p^M. As would be expected, by complete analogy with a hydrogen molecule, the MO method as applied to the bipolaron, yields higher values of the ground-state energy, than the HL method. Discussion of an overestimated value of the ground-state energy of a OC bipolaron obtained in Ref. 49 as a result of variation of an erroneous functional is given in Refs. 28 and 39.

So, bipolaron states were considered in the framework of two models, i.e., OC and TC ones. The OC model yielded a deeper minimum, therefore most of the works on bipolaron subject matter that came out after Suprun and Moizhes' publication[43] dealt with just the OC bipolaron configuration.[26,28,38,41,50,51] However, the drawback of the OC model as compared to the TC one lied in the fact that the trial OC WF were chosen in the form which did not enable researchers to get an appropriate limit transition to spaced-apart polarons. They could not construct a dependence of the energy of the interaction between two electrons on the distance between the centers of the polarization wells either. In addition, the studies cited did not touch upon the question of the kind of the extremum corresponding to a one-center configuration. If an additional parameter corresponding to the distance between the polarons had been entered into a trial function, the OC configuration might have appeared to correspond not to the minimum but to the maximum on the energy-vs-distance curve and, despite the fact that the necessary condition of the existence of a bound bipolaron is fulfilled $(E_{Bp} < 2E_p)$, this configuration may appear unstable. This problem can be solved with the trial WF of the form

$$\Phi(\mathbf{r}_1,\mathbf{r}_2) = \sum_{i=1}^{N} C_i'(1 + P_{12}) \times \exp[- a_{1i}r_{a1}^2 - 2a_{2i}(\mathbf{r}_{a1} \cdot \mathbf{r}_{b2}) - a_{3i}r_{b2}^2]. \tag{29}$$

Note that since the bipolaron functional (20) does not contain any terms depending on the distance R between the centers of polarization wells, the WF of the most general form (5) cannot be used to calculate the bipolaron energy. The distance R can be entered there artificially, by applying additional restrictions to the function. Thus, with the choice

$$C_i = C_i' \exp[- 0.25(a_{1i} - 2a_{2i} + a_{3i})R^2], \tag{30}$$

$a_{4i} = -0.5(a_{1i} - a_{2i})R$, $a_{5i} = 0.5(a_{3i} - a_{2i})R$, the WF (5) changes to the WF (29). The WF (29) provides (for $N = n^2$, $n = 1, 2, \ldots$) appropriate limit transitions to both OC and TC configurations as well as to polarons infinitely distant from each other. To pass on to the one-center configuration, we put $R = 0$ in Eq. (29) and get the WF (26). For $R \to \infty$, variation of a bipolaron functional with the WF (29) $(a_{2i} = 0,\ a_{1i} = a_{3i})$ leads [for $N = n^2$, $n = 1, 2, \ldots$, in Eq. (29)] to double polaron energy, calculated with the use of WF (27).

Table I also lists the values of the ground-state energy of a OC bipolaron (which we independently reproduced within the strong coupling method relying on the results of Ref. 43) and the data which were obtained in Ref. 44 in the strong coupling limit with the WF (29) for OC and TC configurations corresponding to equilibrium distance between the centers of polarization wells for a WF of a less general form without electronic correlations $(a_{2i} = 0,\ a_{1i} = a_{3i})$. Note that in order to compare various calculation methods realized within the variational approach, we should compare just the energy of the bipolaron ground-state but not the values of $Q = E_{Bp}/2E_p$ and η_c, where the polaron energy is generally calculated in the framework of the same approximation as the bipolaron energy E_{Bp}, e.g., Refs. 26 and 43.

Figures 3(a) and 3(b) illustrates the dependencies of the bipolaron energy [and various contributions into this energy, Fig. 3(b)] on the distance between the centers of polarization wells for $\alpha = 9$ and $\eta = 0$. These dependencies correspond to minimization of the bipolaron functional (20) with WF (29) for $N = 5$. Curve C in Fig. 3(a) and all the dependencies shown in Fig. 3(b) were obtained with the trial WF (29) of the most general form $(a_{2i} \neq 0,\ a_{1i} \neq a_{3i})$. Figure 3(b) shows the dependencies of various contributions (T, V_q, V_f are kinetic, Coulomb energies and phonon contributions) into the bipolaron energy E_{Bp} on the distance between the centers of polarization wells. The curve V_{fs} corresponds to the strong coupling contribution of phonons to the total energy determined by the equation $E_{Bp} = T + V_q + V_f$.

Within Buymistrov-Pekar method, the use of Eq. (27) for $N = 5$ and $\alpha = 9$ yields the polaron energy to be $E_p = -10.564$. Having performed variational calculations with the WF (29) of a less general form $(a_{2i} = 0,\ a_{1i} = a_{3i})$, we model a two-center bipolaron configuration [curve A Fig. 3(a)]. In this case the distance between the centers of polarization wells can be considered as a variational parameter. At the point $R = 0$ this distance has a maximum which coincides in size with double polaron energy calculated in the framework of this approximation. The results of calculations carried out in the strong coupling limit (minimization of the bipolaron functional with $V_{fi} = 0$, $a_{2i} = 0$, $a_{1i} = a_{3i}$) are listed in Table I. Thus, for $\eta = 0$ the minimum of the functional is reached for $R = R_m = 5.0225a^*$ and is equal to $-0.11503Ha^*$. As is seen from Table I, this minimum is the deepest of all the results obtained by now with the use of the TC bipolaron model. Figure 4 (strong coupling) demonstrates lines of equal density of the WF for a two-center [Fig. 4(a)] bipolaron configuration $R = R_m$, and for two polarons spaced at a considerable distance [Fig. 4(b)] $R = 10$. Note that for the distance R_m corresponding to a TC configuration [less general form of the WF (29), $a_{2i} = 0$, $a_{1i} = a_{3i}$] the shape of the bipolaron WF resembles an ellipsoid of revolution rather than a dumbbell as it is generally believed. A visual separation of the WF into the system with two maxima corresponding to spaced away

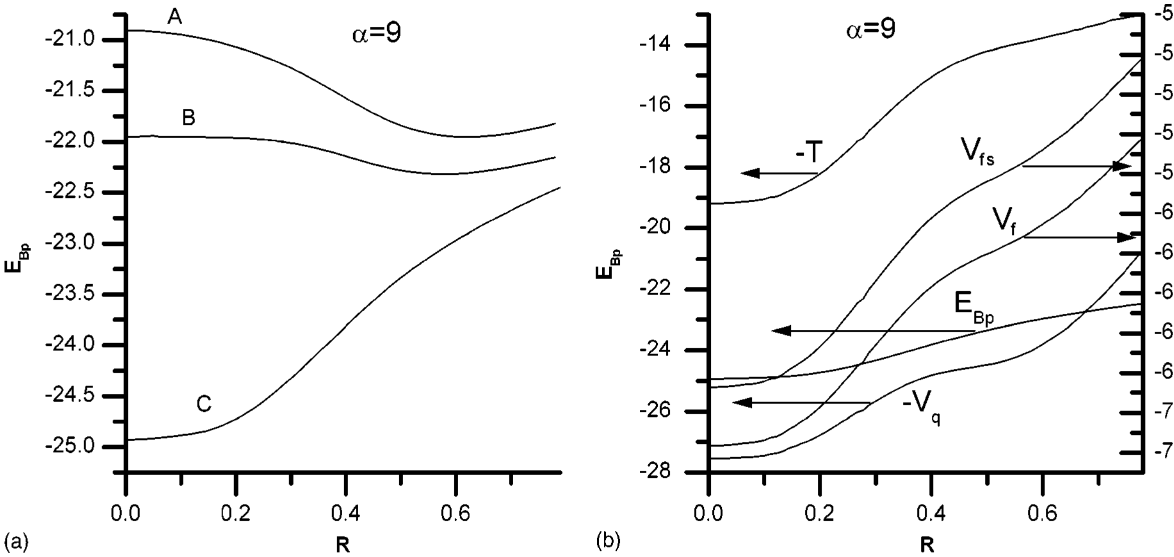

FIG. 3. (a) Dependence of the bipolaron energy on the distance between the centers of polarization wells of two polarons ($\eta=0$, $\alpha=9$). Curves A, B, C correspond to variation of the functional of the bipolaron ground-state with the use of WF (29) with ($a_{1i}=a_{3i}$, $a_{2i}=0$), ($a_{1i}\neq a_{3i}$, $a_{2i}=0$), ($a_{1i}\neq a_{3i}$, $a_{2i}\neq 0$), respectively. (b) Dependencies of various contributions into the bipolaron energy on the distance between the centers of polarization wells of two polarons for WF (29) of the most general form $a_{1i}\neq a_{3i}$, $a_{2i}\neq 0$. T is the kinetic energy, V_q is the Coulomb interelectronic repulsion, V_{fs} is the contribution of the terms corresponding to strong coupling in Eq. (21), and $V_f=V_{fs}+V_{fi}$ is the total phonon contribution into the ground-state energy of a bipolaron $E_{Bp}=T+V_q+V_f$.

polarons takes place at much larger R as compared with the equilibrium distance R_m. This behavior is also typical for the bipolaron WF chosen in the framework of Heitler-London method with the use of a hydrogenlike WF.

If we choose the WF (29) with $a_{2i}=0$, $a_{1i}\neq a_{3i}$ we will get a curve B in Fig. 3(a) which also corresponds to the bipolaron configuration. For this WF, (direct dependence of the WF on the interelectronic distance is lacking) the OC configuration corresponds to a maximum. Therefore, despite the fact that the necessary condition of the bipolaron existence $E_{Bp}<2E_p$ is fulfilled, the OC configuration appears unstable.

With the most general choice of the WF in the form (29), the minimum corresponding to the TC bipolaron configuration disappears, and only one minimum holds at $R=0$ [Fig. 3(a), curve C]. This behavior of the functional shows that a stable TC bipolaron configuration appears due to the choice of insufficiently flexible WF which does not take account of electronic correlations concerned with direct dependence of

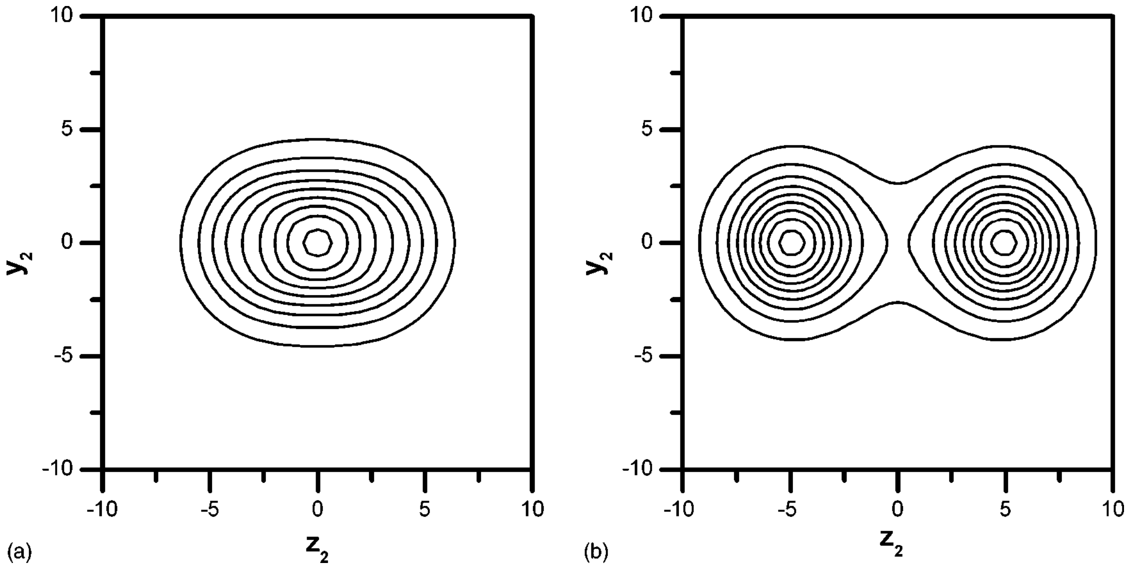

FIG. 4. (a) Lines of equal density for a two-center bipolaron [interelectronic correlations are lacking and $a_{1i}=a_{3i}$, $a_{2i}=0$ in WF (29)] in the case of equilibrium distance between the centers of polarization wells R_m, corresponding to the minimum of the ground-state energy. (b) The same for two polarons separated by a distance $R=10$. The axis OZ is chosen along the line joining the centers of polarization wells of two polarons. The coordinate origin is chosen in the middle of the fragment joining these centers.

TABLE II. Energy values of the ground state of D^- ($S=0$) and D^0 centers, E^- and E^0 calculated for crystals of AgBr and AgCl, respectively. The coupling energy is designated as E_B. All the energies are expresses in $\hbar\omega$ units. The upper indices L and A mark the values obtained in Refs. 5 and 6, respectively. The number of terms in the WF (26) and (27), used to calculate the energy of D^- and D^0 centers is equal to 12.

	α	R	$\hbar\omega$, (meV)	E^-	E_0	E_B^-	E_B^0	E_B^-/E_B^0
AgBr	1.64	1.68	15.4	−5.656	−3.818	0.198	2.178	0.091
				-5.637^L	-3.817^L	0.180^L	2.177^L	0.083^L
						0.132^A	2.166^A	0.061^A
AgCl	1.9	1.9	24.4	−6.668	−4.483	0.285	2.583	0.110
				-6.643^L	-4.482^L	0.261^L	2.582^L	0.101^L
				-6.662^A		0.202^A	2.560^A	0.078^A

the electron WF on the interelectronic distance.

So, taking account of the direct dependence of the WF on the interelectronic distance gives rise to a single minimum corresponding to a OC configuration. This energy pattern of a two-electron system (namely, only one minimum on the curve for the distance dependence of the energy of a two-electron system in a polar crystal) holds for the whole region of the bipolaron existence with respect to the parameter α.

Notice that the variation parameter $a=\langle r_1-r_2\rangle$ which is treated in Ref. 10 as the mean distance at which electrons fluctuate is analogous to the variation parameter R used in this paper. Our results correlate well with the fact that the only energy minimum of a bipolaron corresponds to $a=0$.[10] However, the dependencies of the bipolaron energy on the parameter a are not given in Ref. 10 because for any $a>0$ the criterion of the existence of a stable bipolaron state $E_{Bp} < 2E_p$ is not fulfilled in the cited work.

Table II illustrates energy values of the ground state of D^- ($S=0$) and D^0 centers E^- and E^0, respectively, calculated by us for crystals of AgBr and AgCl. The coupling energy is designated as E_B. All the energies are expresses in $\hbar\omega$ units. The upper indices L and A mark the values obtained in Refs. 5 and 6, respectively. The number of terms in the WFs (26) and (27), used to calculate the energy of D^- and D^0 centers is equal to 12. As is seen from Table II, Buimistrov-Pekar method in combination with the WF (26) yields the lowest values for the ground-state energy of a D^- center (or bound bipolaron).

VI. PAIRS OF LARGE-RADIUS PARAMAGNETIC CENTERS

While the TC configuration of a free bipolaron has appeared energetically unstable, the bound two-center bipolaron corresponds to a stable state. We mean pairs of large-radius paramagnetic centers in crystals with ionic coupling. Since Hamiltonian (1), used in this work is based on the continuum approach, we cannot expect that it would correctly describe the energy spectrum of F_2 and F' centers in alkali halides. However, in semiconductors with ionic coupling (for example, in II-VI and III-V semiconducting compounds) and, e.g., in high-purity silver halides (AgBr and AgCl) there exist shallow donorlike centers for which our model is accurate enough.[5,24,25] Therefore we will illustrate our approach by computations of the energy of F' (or D^-), F_2 and F_2^+-centers.

Figure 5(a) and 5(b) shows the ground-state energy, kinetic, Coulomb energies, and contribution of phonons into the total energy of a pair of shallow hydrogenlike centers and those for a singly ionized pair in AgBr for various distances between paramagnetic centers. Figures 6(a) and 6(b) demonstrates relevant distance dependencies in AgCl. Polaron effects in an exchange interaction are to be treated in an individual paper. Note only that the energy of a triplet state can be calculated with the WF (5), corresponding to the WF antisymmetrical about electron coordinates. In this case the exchange energy corresponds to the difference between the energies of a singlet and triplet states. Figure 7 illustrates the energy dependence of triplet terms of a pair of shallow hydrogenlike centers in AgBr and AgCl, calculated by us for various distances between the centers and the same for a $1\sigma_u$ term of singly ionized pairs. For all the distances between paramagnetic centers the phonon contribution into the EI has antiferromagnetic character and is comparable in the order of magnitude with direct Coulomb exchange. The EI of two polarons has antiferromagnetic character too.[46]

VII. CONCLUSION

Variational calculations performed with the use of a Gaussian system of functions (5) with regard to interelectronic correlations has enabled us to get spectroscopically accurate results for the energies of the singlet and lowest triplet states of simplest two-electron systems in atomic physics and a hydrogen molecule. The use of the proposed system of variational functions in solids has allowed us to obtain the energies of a two-electron system in crystals with account of polaron effects for a an arbitrary value of electron-phonon coupling. The system of functions that we have applied to calculate the energy of the most complicated two-electron system, namely, an exchange-coupled pair of paramagnetic centers in isotropic crystals can also be used to find the energy spectrum of exchange-coupled pairs and more simple two-electron systems (bipolarons and D^- cen-

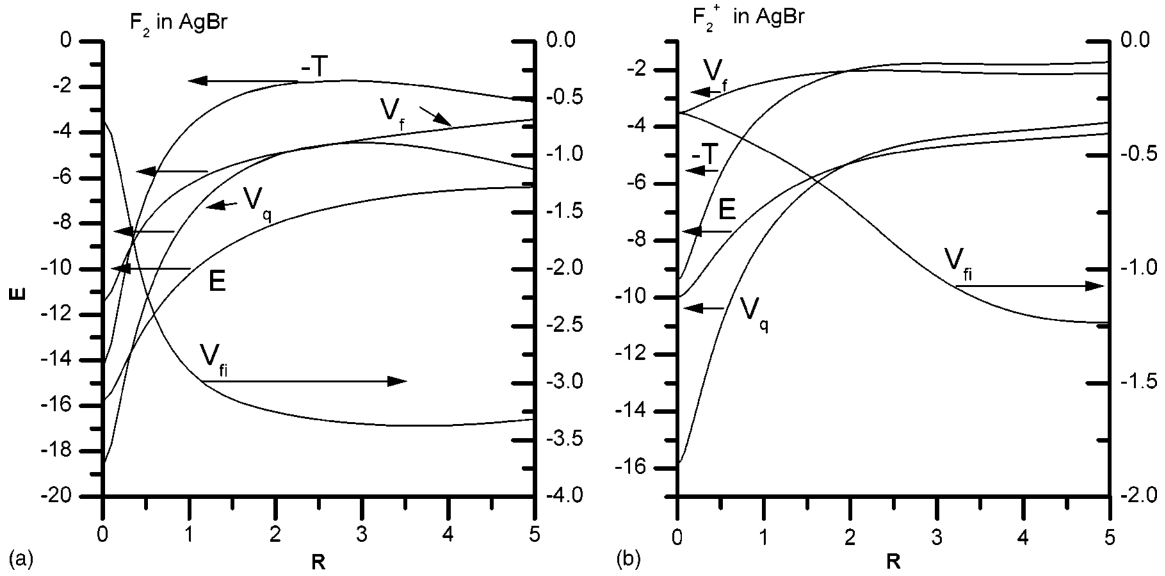

FIG. 5. (a) Dependencies of various contributions into the ground-state energy of an F_2 center ($^1\Sigma_g$ term) in AgBr on the distance between the centers of polarization wells of two polarons for WF (5). T is the kinetic energy, V_q corresponds to Coulomb interactions in the system, V_{fi} is the phonon contribution of the terms corresponding to intermediate coupling in Eq. (21), and $V_f = V_{fs} + V_{fi}$ is the total phonon contribution into the ground-state energy of an F_2 center, determined by minimization of functional (11) ($E = T + V_q + V_f$). (b) The same for the $1\sigma_g$ term of an F_2^+ center in AgBr.

ters) in crystals with anisotropic effective masses and dielectric permittivities and in low-dimensional systems. The Buymistrov-Pekar method used in our calculations yields the lowest values of the ground-state energy of two-electron systems as compared to other approaches implying direct variation of the WF of the system.[9,27]

The energy of electron coupling in an exchange coupled pair can be calculated as a difference between the sum of energies of a polaron and a singly ionized pair ($1\sigma_g$ term) and the ground-state energy ($^1\Sigma_g$ term). The energy spectrum of the neighboring pairs of shallow hydrogenlike centers more closely resembles a helium atom than a molecular system. In a singlet state, interelectronic interaction enhances the electron energy of a molecular formation as compared with the coupling energy of an isolated donor. In a triplet state the opposite situation occurs.

Using the graphic dependencies of Figs. 5 and 6 we can calculate coupling energies of such formations. The polaron

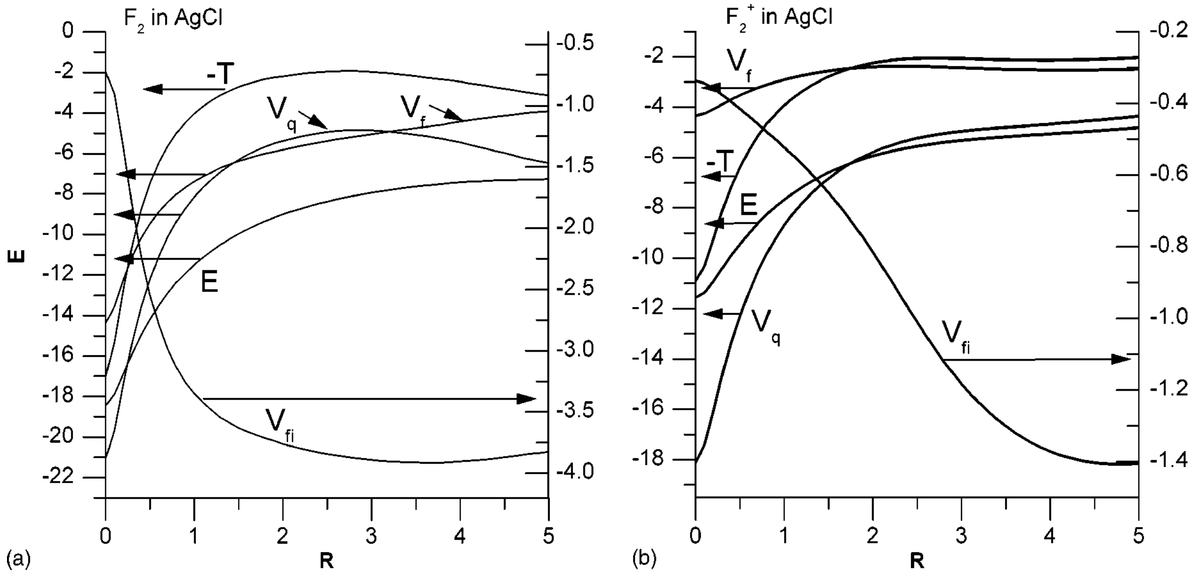

FIG. 6. (a) Dependencies of various contributions into the ground-state energy of an F_2 center ($^1\Sigma_g$ term) in AgCl on the distance between the centers of polarization wells of two polarons for WF (5). T is the kinetic energy, V_q corresponds to Coulomb interactions in the system, V_{fi} is the phonon contribution of the terms corresponding to intermediate coupling in Eq. (21), and $V_f = V_{fs} + V_{fi}$ is the total phonon contribution into the ground-state energy of an F_2 center, determined by minimization of the functional (11) ($E = T + V_q + V_f$). (b) The same for the $1\sigma_g$ term of an F_2^+ center in AgCl.

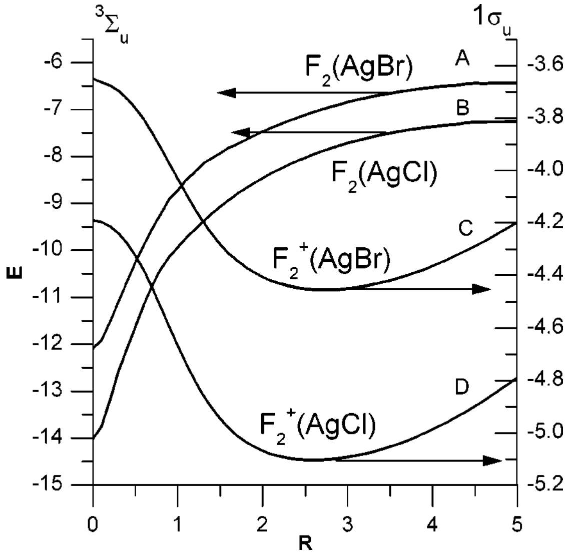

FIG. 7. Energy dependencies of $^3\Sigma_u$ terms of F_2 centers and $1\sigma_u$ terms of F_2^+ centers in AgBr and AgCl on the distance between the F centers. Curves A, B represent the energies of the $^3\Sigma_u$ term in AgBr and AgCl, respectively. Curves C, D correspond to the energy of the $1\sigma_u$ term in AgBr and AgCl, respectively.

energy of the studied crystals is given by $(-\alpha)$ with a good accuracy. The energies of the ground state of isolated donors and corresponding coupling energies in AgBr and AgCl calculated by the intermediate coupling method are presented in Table II. For example, for $R=0.5$, the coupling energies of an electron in donor pairs in singlet and triplet states are equal to 2.594 and 0.35102 in AgBr and 2.8589 and 0.29551 in AgCl. All the energies are in units of $\hbar\omega$ (=15.4 and 24.4 meV in AgBr and AgCl, respectively).

By way of illustration, in this work we have calculated relaxed $^1\Sigma_g$ and $^3\Sigma_u$ terms of exchange pairs of shallow hydrogenlike centers as a function of distance between the centers. The $^1\Sigma_u$ term can also be calculated in a similar way. The spectra of infrared absorption by neutral molecules consisting of donor pairs in III-V semiconducting compounds, associated with optical transitions between $^1\Sigma_g$ and $^1\Sigma_u$ terms were observed by Stradling *et al.*[52] and Bajaj *et al.*[53] and considered theoretically (without regard for polaron effects) by Golka.[54]

The spectrum of isolated F centers of AgBr and AgCl was studied by Sakuragi and Kanzaki.[55] According to their results, the lines in AgBr corresponding to the $1s$-$2p$ transition of a bound polaron fall (for various impurities) in the range of 19.8–22.4 meV. For AgCl the corresponding range is 30.5–35 meV. The energy of this transition was calculated by Buimistrov[24] and subsequently by Brandt and Brown.[25] The quantities under consideration are extremely sensitive to the parameters of the theory. With the parameters of the AgBr used by Buimistrov for the transition in question the energy difference was found to be $\Delta E=15$ meV. We have reproduced Buimistrov's calculations for the parameters used in our work and also in Refs. 5 and 6 and obtained the energy difference between self-consistent $1s$ and $2p$ states in AgBr to be $\Delta E=22.7$ meV. If it is remembered that no fitting parameters were used in the theory, the agreement with the experimental results should be assessed to be very good. The parameter which is the most difficult to determine is the effective mass of a band electron because here we need to invoke the polaron theory. We can choose just this parameter as fitting. Thus, according to our estimates, for the maximum of the absorption band corresponding to the transition between self-consistent $1s$ and $2p$ states in a pure AgCl to coincide with the experimental value of 33.5 meV, we should put $m^*=0.25$ instead of $m^*=0.3$, used in our work. In Ref. 25 the effective mass in AgCl was calculated by Buimistrov-Pekar method with the use of hydrogenlike trial functions to be $m^*=0.22$. In Ref. 23 the Buimistrov-Pekar method was used to determine this parameter in GaN from an experimentally found coupling energy of a shallow donor.

Formation of nearby pairs of impurity centers is observed as the concentration of alloying impurities in a crystal grows. At low concentrations, interaction between impurity centers leads to widening of absorption bands due to exchange interaction. This effect shows itself even at relatively low concentrations of alloying impurity, when, according to Bates' assessments[56] the distance between impurities is $R \cong (20-25)a^*$, where a^* is the effective Bohr radius. As the impurity concentration further increases, small-scale fluctuations of the charge density $(R \leqslant a^*)$ take on significance. This is especially true for exchange pairs of impurity centers (in greatly compensated materials—singly ionized pairs analogous to an H_2^+-molecule ion).[57,58]

Consideration of interelectronic correlations considerably decreases the energy of a two-electron system for one-center configurations and for neighboring pairs of hydrogenlike centers in crystals with strong electron-phonon interaction. As the distance between the paramagnetic centers grows, the role of interelectronic correlations decreases. We believe that our results obtained in relation with the problem of spatial configuration of a free bipolaron are proof that the two-center configuration of a free bipolaron is unstable as compared to the one-center configuration.

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