

Large-radius bipolaron and the polaron–polaron interaction

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DOI: 10.3367/UFNe.0180.201005a.0449

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Abstract. Research on the polaron–polaron interaction and the theory of large-radius bipolarons are reviewed. The difference between the two-center and one-center continuum bipolaron models in isotropic and anisotropic crystals is discussed. It is shown that the inclusion of electron–electron correlations can significantly reduce the bipolaron and D^- -center energies as well as the energies of exchange-bound pairs of shallow hydrogen-like centers. The two-center bipolaron configuration corresponds to a shallow secondary minimum and is unstable. The phonon-mediated exchange interaction between Pekar polarons has an antiferromagnetic nature and exceeds the ferromagnetic interaction due to the Coulomb interaction of electrons localized in polaron potential wells. The possibility that the superfluidity of bipolarons can give rise to high-temperature superconductivity is discussed and problems related to the Wigner crystallization of a polaron gas are examined.

1. Introduction

Electron–phonon interactions or polaron effects are currently among the central topics of solid-state physics. Investigations of various effects in which electron–phonon interactions (EPIs) play a key role have been carried out since the 1940s and have remained in the focus of attention throughout the entire period of the development of modern physics. Bipolaron research is of primary importance for solving basic problems related to electron–phonon interactions. Of special interest are attempts to explain the phenomenon of superconductivity (SC) based on Bose condensation of a bipolaron gas. The possibility of superfluidity of Bose condensate of charged particles with integer spin (bosons) had been discussed in the papers of Ginzburg [2] and Schafroth [3] before the microscopic theory of superconductivity was developed by Bardeen, Cooper, and Schrieffer (BCS theory) [1] and later analyzed in many other publications [4–8].

The problem of the possibility of occurring high-temperature superconductivity (HTSC) was addressed by Ogg [9, 10], who tried to explain this phenomenon by the existence of bound two-electron states; this author observed abnormally high conductivity in metal–ammonia solutions frozen in liquid nitrogen. Ogg had postulated the possibility of superconductivity at temperatures above the nitrogen boiling point 40 years before Bednortz and Müller discovered HTSC (1986) [11, 12] in copper oxide, lanthanum, and barium-based ceramic, $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, with the superconducting transition temperature $T_c = 30$ K. Ogg maintained in his sensational report [9] that the current induced in a ring of a sodium solution frozen in ammonia persists for a few minutes, which

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Received 19 August 2009

Uspekhi Fizicheskikh Nauk **180** (5) 449–473 (2010)

DOI: 10.3367/UFNr.0180.201005a.0449

Translated by Yu V Morozov; edited by A Radzig

corresponds to a decrease in solution resistance by 17 orders of magnitude from its value in a liquid solution. The author suggested that a drop in temperature in cavities between polar NH_3 molecules due to Bose condensation and superfluidity of paired electrons gives rise to SC. That is how the notion of bound electron pairs in a polar medium came into being. However, later researchers failed to reproduce the results of Ogg's experiments and gradually lost interest in them.

In 1973, Dmitrenko and Shchetkin [13] reported observation of unstable SC in a frozen sodium–ammonia solution. Pashitskii [14] proposed a new theoretical interpretation of these experimental data and considered the anomalous conductivity of metal–ammonia solutions, emphasizing that all experimental findings available up to then had suggested an abnormally high but finite conductivity of $\text{NH}_3:\text{Na}$ solutions for $T < 80$ K, rather than HTSC.

Investigations into the formation of the stable two-electron state in a crystal, or a bipolaron (BP), are directly related to determination of the pairwise interaction potential between two polarons as a function of distance between them. The region of existence of large-radius BPs is restricted by the relatively high value of the EPI Fröhlich constant [15]

$$\alpha = \left(\frac{e^4 m^*}{2\hbar^3 \omega_{\text{LO}}} \right)^{1/2} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right), \quad (1)$$

where e and m^* are the charge and effective mass of the band electron, respectively, ω_{LO} is the frequency of the longitudinal optical phonon in an ionic crystal, ε_∞ and ε_0 are high-frequency and static permittivities, respectively, and $\alpha > \alpha_c = 6.8$ [16]; for $\alpha < \alpha_c$, the bound BP state is nonexistent. In Ref. [16], computation was performed by Feynman trajectory integral method [17, 18] allowing for translation-invariant solutions of polaron and BP problems. Methods using direct variation of the BP wave function (WF) give slightly higher critical values of EPI parameter, $\alpha_c = 7.3$ [19, 20] and $\alpha_c = 6.9$ [21]. These values were obtained alongside determination of BP binding energy $\Delta E_{\text{BP}} = 2E_{\text{P}} - E_{\text{BP}}$ (where E_{P} and E_{BP} are the polaron and BP ground state energies, respectively) relative to polaron energy evaluated with a high accuracy by the trajectory integral method in the limit of $\eta = \varepsilon_\infty/\varepsilon_0 \rightarrow 0$; they can be considered with an equally good accuracy as the upper boundary of the existence of bound BP in terms of α .

The BP problem was theoretically considered by Pekar and Tomasevich [22] (strong coupling) in 1951 by the variational method in the framework of continuous approximation, with probe WFs being chosen in the multiplicative form, without regard to correlation effects. The authors demonstrated the lack of energy gain in this approximation; in other words, the bound state of two large-radius polarons in the common spherically symmetric polarization well turned out to be energetically disadvantageous. The situation was further complicated by a computational error (incorrect normalization factor) made in Ref. [23], where the binding energy of F' -center, i.e., a system of two electrons (holes) trapped in a positively (negatively) charged point defect (vacancy or nonisovalent impurity) in an ionic crystal, was calculated using the two-electron variational WF of a more general form, taking account of the Coulomb correlations. The error resulted in a significant decrease in the phonon polarization part of the adiabatic functional responsible for efficacious electron–electron attraction (owing to the exchange of virtual optical phonons). As the central charge

tended to vanish, i.e., upon transition from F' -center to BP, the bound state proved energetically unfavorable. Hence, the general (wrong, as it has turned out) conclusion was drawn by S I Pekar in his monographs [24, 25], with reference to Tomasevich [23], that a spherically symmetric BP cannot exist due to strong Coulomb repulsion. This conclusion was also repeated in the work of Buimistrov and Pekar [26], who proposed a variational method for calculating the energy spectrum of one- and two-electron systems, including BP, for an arbitrary binding force between electrons and a phonon field.

In 1955, Moskalenko [27] considered a two-center (TC) axially symmetric BP, i.e., the bound state of two polarons, like a hydrogen molecule or Deigen's F_2 -center [28]. In such a BP, the role of positively charged nuclei is played by polaron wells, the centers of which do not coincide, while Coulomb repulsion between electrons is substantially weakened by exchange interactions in the singlet spin state, as in the Heitler–London model of the hydrogen molecule. However, the author of paper [27] chose for variational calculations too large a distance R between polarons, at which repulsion overrides attraction and increases with decreasing R . Due to this and possibly to relatively small Fröhlich coupling constant involved, neither a bound nor even a metastable BP state was obtained in Ref. [27].

In 1957, Vinetskii and Gitterman [29] considered the TCBP variational problem for any distance R and showed the possibility of forming a bound state under certain conditions. This problem was later addressed in greater detail in a paper by Vinetskii [30]. Specifically, it was demonstrated that the energy of a BP minus double polaron energy has an absolute negative minimum at $\alpha_{\text{F}} \approx 7.5$ if the parameter $\mu = 1 - \varepsilon_\infty/\varepsilon_0 > 0.97$, and a relative (metastable) minimum if $\mu > 0.94$ (see Ref. [31]). As shown later [32, 33], the binding energy of a TCBP increases considerably in crystals with uniaxial anisotropy of band effective masses of carriers of the light-plane or light-axis type and with anisotropic permittivity of the lattice. This observation refers, inter alia, to layered (quasi-two-dimensional) and chain-like (quasi-one-dimensional) crystals, including metal-oxide compounds (MOC) such as $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, in which HTSC was discovered [11, 12]. It is worth noting that the variational WF of two electrons in Refs [30–33] was chosen in the symmetric form, taking into account indistinguishability (exchange interaction) of the particles, but without regard to Coulomb correlation effects related to the direct dependence of the WF on the interelectron distance. The distance between centers of polarization wells of two polarons being $R = 0$, the energy gain for BP states also tended toward zero, in accordance with the results reported in Ref. [22].

In 1982, Suprun and Moizhes [34] proposed a new solution to the Pekar BP variational problem, taking into consideration Coulomb correlations in the framework of the simplest approximation [23]. They showed that correct numerical calculation leads to a substantial energy gain (up to 25% of the double polaron energy as $\varepsilon_\infty/\varepsilon_0 \rightarrow 0$); this suggests stability of a spherically symmetric large-radius bipolaron at a sufficiently large ionic bond ($\varepsilon_\infty/\varepsilon_0 \leq 0.14$). Later studies of one-center BPs (OCBPs) with account of interelectron correlations [35, 36] demonstrated a much greater energy gain than in Refs [32, 33] dealing with two-center BPs (TCBPs) in anisotropic crystals.

An earlier paper by Larsen [37] reported “a huge binding energy” of small D^- -centers in ionic semiconductors. The intermediate-coupling method of Buimistrov and Pekar [26] was used in calculations and the Slater type WF was chosen as a trial taking into account electron correlations. The author of Ref. [37] was not interested in BP states, although the BP functional could be obtained from the explicit limiting transition to a simpler system (Coulomb center charge $\rightarrow 0$), while BP bound states for the chosen functions appeared at somewhat larger coupling constants ($\alpha \geq 7.5$). The study reported in paper [34] was conducted in the framework of the strong-coupling notion; only in Ref. [38] was the Buimistrov–Pekar method applied to calculating OCBP energy for Gaussian functions taking into account electron correlations.

Anderson [39, 40] showed in the framework of the Hubbard model with negative correlation energy $U < 0$ at sites (U^- -centers) the possibility of transition of a metal with a half-filled conduction band (one electron per site) to the charge-ordered dielectric state in which vacant sites alternate with those occupied by bound electron pairs. Anderson speculated that attraction between electrons at a single site overruns Coulomb repulsion and is due to adiabatic interaction between electrons and local atomic vibrations. In other words, one can actually speak here about localized small-radius BPs. Anderson’s findings were soon confirmed in experiments designed to study metal–insulator transitions in Ti_4O_7 single crystals [41]. A similar problem of local electron pairs with account of interaction (attraction or repulsion) between the neighboring sites was considered in 1980 by Kulik and Pedan [42]. These authors demonstrated formation of a delocalized (conducting and probably superconducting) state of local pairs under the proper conditions. The possibility of electron pairing at sites with negative correlation energy was also considered in papers [43, 44]. The large strength of electron–phonon interactions, the high temperature of transition to the superconducting state unusual for semiconductors and semimetals, along with some other behavioral features in superconducting state for such compounds as $BaBi_xPb_{1-x}O_3$, $PbTe(Tl)$, and $SrTiO_3$ have led to the suggestion that the traditional BCS mechanism of superconductivity does not operate in these conditions [44, 45].

The small-radius BP model in narrow-band metals in the strong-coupling approximation and their superconductivity conditioned by Bose condensation were also considered by Alexandrov and Ranninger [46–48].

A review by Mott [49] was devoted to small-radius spin BPs and the possibility of explaining HTSC in terms of the model of the spin BP in the triplet state. In an earlier study [50], Nagaev considered the behavior of a spin polaron in antiferromagnetic crystals with low Néel temperatures. Lakhno [54, 55] discussed the possibility of appearing autolocalized states in high-temperature antiferromagnets (analogs of condensons in covalent crystals [51–53]).

In 1975, Vinetskii and Pashitskii [56] addressed the problem of the BP mechanism of SC in ionic crystals exemplified by Nb-doped $SrTiO_3$ pseudoferritelectrics [57] owing to the superfluidity of quasi-ideal BP Bose gas. Due to abnormally high permittivity of $SrTiO_3$ at low temperatures ($\epsilon_0 > 2 \times 10^4$), the condition $n_0^{1/3} a_B^* \gg 1$ (where n_0 is the concentration, $a_B^* = \epsilon_0 \hbar^2 / 4e^2 m_{BP}^*$ is the effective Bohr radius of BP with mass m_{BP}^* and charge $2e$) of high density (ideality) of charged Bose gas for $m_{BP} \geq 10m_0$ (where m_0 is the free electron mass) is fulfilled for $n_0 \geq 10^{18} \text{ cm}^{-3}$, when the mean

distance between BPs, $\bar{r} \approx n^{-1/3} \approx 10^{-6} \text{ cm}$, is much greater than intermediate-coupling BP radius $r_0 \geq 3a \approx 10^{-7} \text{ cm}$ (a is the lattice constant). Notice that the macroscopic approximation is still applicable to such BPs because the effects of spatial dispersion of permittivities ϵ_0 and ϵ_∞ , associated with crystal lattice discreteness, are manifest in full measure for distances $r \leq a$, when $\epsilon_0 \approx \epsilon_\infty$. These ideas, including the idea of enhanced binding energy of large-radius BPs in systems with reduced dimension, have been developed in a number of publications that followed the discovery of HTSC [16, 58].

According to Bogoliubov’s microscopic superfluidity theory [59] for a weakly nonideal Bose gas, the spectrum of quasiparticles has a finite energy gap given by BP effective plasma frequency $\omega_p^* = (16\pi e^2 n_0 / \epsilon_0 m_{BP}^*)^{1/2}$ owing to long-range Coulomb interaction; therefore, it meets the Landau superfluidity criterion [60]. Bose condensation temperature $T_0 = 3.31 \hbar^2 n_0^{2/3} / k_B m_{BP}^*$ that in the present case can be identified with critical temperature T_c of transition to the superconducting state varies at $m_{BP}^* \approx 10m_0$ depending on BP concentration n_0 in a broad range from $T_0 \approx 3 \text{ K}$ at $n_0 \approx 10^{18} \text{ cm}^{-3}$ to $T_0 \approx 300 \text{ K}$ at $n_0 \approx 10^{21} \text{ cm}^{-3}$. In the latter case, BP concentration is so high that, both in the case of a BP gas and in the case of Cooper pairs, the composite nature of a BP becomes apparent and it stops behaving like an ideal Bose particle; at yet higher concentrations, BP dissociates into separate polarons.

The possibility of HTSC with $T_c \geq 100 \text{ K}$ was demonstrated in principle [61] based on the mechanism of large-radius BP superconductivity in the framework of continuous approximation [56] for ionic crystals. Investigations into this mechanism are overviewed in paper [62]. Similar ideas were put forward by Alexandrov [47] based on the small-radius BP model [48].

Of special interest are copper-containing metal-oxide compounds with the layer [e.g., $La_2(Sr, Br)CuO_4$ and $(Bi, Tl)_2(Sr, Ba)_2CaCuO_8$] or the layer-chain-like ($YBa_2Cu_3O_7$) structure by virtue of their HTSC. The reduced dimension (strong anisotropy) of the electronic spectrum in such crystals has to manifest itself in their superconducting properties. Quasi-two- or quasi-one-dimensionality of the electronic spectrum has a noticeable influence on the BP binding energy due to the quantum-mechanical effect of enhancing attraction with a decrease in dimensionality of space. This accounts for the possibility of carrier (electron, hole) pairing in the real (as opposed to momentum) space, i.e., formation of BP rather than Cooper pairs, in the layer and layer-chain MOC single crystals. One-dimensional BPs in polymer chains of organic compounds like polyacetylene were theoretically considered in Refs [63, 64]. Experimental evidence of BP conductivity for such low-dimensional systems was obtained in Ref. [65], where the authors assumed that the absence of an electron paramagnetic resonance (EPR) signal correlated with conductivity in pyrrolic polymers was due to the formation of mobile BPs. A review of theoretical and experimental studies of soliton states and BPs in conducting polymers can be found in Ref. [66].

A fierce dispute between P Anderson and N Mott concerning the description of HTSC in terms of the BP mechanism erupted in *Physics World* [67–69]. Anderson refuted not only arguments in favor of BPs but also the very possibility of polaron formation in metal-oxide ceramic. In contrast, Mott alluded to one of his studies done jointly with Alexandrov and Bratkovsky [70] and emphasized experimental data suggesting that the BP mechanism related to Bose

condensation of small-radius BPs in cuprate MOCs is responsible for HTSC. There was an equally tense debate over the applicability of the BP mechanism to HTSC between Ranninger and Alexandrov et al. [71–73]. De Mello and Ranninger [71, 73] agreed that the BP mechanism can account for SC in a number of compounds whose properties had been studied in Refs [46, 48] but rejected the possibility of explaining HTSC in the framework of this mechanism.

The polaron and BP theory originally designed to apply to SC and HTSC phenomena is widely used in describing many physical, chemical, and biological processes proceeding not only in solids but also in organic compounds and polar liquids, including water and aqueous solutions. The polaron theory of charge transfer in proteins developed in Refs [74–80] was used in paper [81] to describe the hydrated electron. A S Davydov [82, 83] used the main provisions of the translation-invariant theory of the continual polaron developed by Bogolyubov [84] and Tyablikov [85] as a basis for the soliton concept applied to biological molecules. This aspect of the polaron theory continues to be extensively developed [86–88]. The dynamic theory of soliton formation and soliton transfer in DNA is elaborated in Refs [89–95].

The present review concerns studies developing the large-radius BP theory (continuous approximation) in the framework of TC- and OC-models of BP; it considers the role of electron correlations in the formation of bound BPs and conditions for fulfillment of the virial theorem with respect to the systems of interest. The relationship between BPs and HTSC is also briefly discussed.

2. Two models of the large-radius bipolaron

2.1 General relations

In the continuous approximation, electron–phonon interaction is described by the Fröhlich Hamiltonian that has the following form for two electrons in a phonon field:

$$H_{\text{BP}} = -\frac{\hbar^2}{2m^*}(\Delta_1 + \Delta_2) + \frac{e^2}{\varepsilon_\infty |\mathbf{r}_1 - \mathbf{r}_2|} + \hbar\omega \sum_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{k}} V_{\mathbf{k}} \left\{ \exp(-i\mathbf{k}\mathbf{r}_1) + \exp(-i\mathbf{k}\mathbf{r}_2) \right\} a_{\mathbf{k}}^+ + \text{h.c.}, \quad (2)$$

where ε_0 and ε_∞ are static and high-frequency permittivities, respectively, $V_{\mathbf{k}} = (e/k)\sqrt{2\pi\hbar\omega/(V\varepsilon)}$, $1/\varepsilon = 1/\varepsilon_\infty - 1/\varepsilon_0$, V is the crystal volume, ω is the optical phonon frequency, \mathbf{k} is the phonon wave vector, $a_{\mathbf{k}}^+$ and $a_{\mathbf{k}}$ are the operators of creation and annihilation of phonons with the wave vector \mathbf{k} , \mathbf{r}_1 and \mathbf{r}_2 are coordinates of the first and second electrons, and m^* is the electron effective mass.

Although the first successful studies designed to calculate the energy of strong-coupling BPs [29, 30] were based on the analogy with the hydrogen molecule, the BP Hamiltonian has an important feature distinguishing it from the hydrogen molecule Hamiltonian; namely, Eqn (2) does not contain a parameter analogous to the distance between two protons in the molecule. Two forms of the dependence of hydrogen molecule energy on the distance between protons are equally frequently used in molecular physics: one takes into account interproton repulsion, and the other does not. Both forms were considered in the monograph by Slater [96, Figs 3.3 and 3.4, respectively]. The energy dependences disregarding internuclear repulsion are especially convenient for variational calculations of the energy of a two-hydrogen-atom system

with closely located protons and accomplishing the limiting transition corresponding to the ‘fusion’ of two hydrogen atoms into helium atom. In this case, the internuclear distance dependence of the hydrogen molecule energy has a sole minimum corresponding to the helium atom configuration at point $R = 0$ (see Ref. [96, Fig. 3.3]). Thus, the dependence of the hydrogen molecule WF on the interproton distance does not by itself lead to the energy minimum at point $R = R_m \neq 0$ due to the presence of the term describing repulsion between protons in the Hamiltonian of the hydrogen molecule.

Bearing in mind that the Hamiltonian (2) of two electrons in a phonon field does not depend on the distance between the centers of the polarization wells of two polarons, it is natural to conjecture that potential dependences on the interpolaron distance, describing the total energy of the system, must correspond to potential dependences of the hydrogen molecule energy on the distance between protons without accounting for proton–proton repulsion; also, the BP ground state exhibits spherical symmetry.

2.2 The one-center bipolaron — analog of the helium atom

Hamiltonian (2) is different from the Hamiltonian describing the helium atom in the presence of electron–phonon interaction and the absence of Coulomb electron–nucleus interaction. When a Coulomb potential appears, whose field contains moving electrons, the similarity with the helium atom and the negative H^- ion becomes more explicit. It is natural to suggest that the spherically symmetric WF should correspond to the ground bound state of a two-electron system, if any. As mentioned above, the first large-radius BP model was constructed in complete analogy with the helium atom. The two-electron WF in this model was chosen to be sufficiently simple but to take into account interelectron correlations related to the direct dependence of WF on interelectron distance. Such a WF had the form [23, 24]

$$\Psi(r_1, r_2) = N(1 + \alpha r_1)(1 + \alpha r_2)(1 + \beta r_{12}) \times \exp(-\alpha r_1) \exp(-\alpha r_2), \quad (3)$$

where N is the normalization factor, \mathbf{r}_1 and \mathbf{r}_2 are coordinates of the first and second electrons, respectively, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the first and second electrons, $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$, and α and β are variational parameters.

The wave function of a simpler multiplicative form (the product of WFs of noninteracting polarons) was utilized in Ref. [22]. This WF can be obtained by assuming $\beta = 0$ in formula (3). Calculations of the energy of BPs or F' -centers bound by single-charge Coulomb potential were performed in the framework of this model by O F Tomasevich [23]. This model is a mathematical analog of a negative H^- ion in a phonon field. Errors in the calculation of the normalization factor in the WF of the form (3) and minor numerical errors in the part corresponding to the phonon contribution in the BP functional (see Ref. [23]) resulted in the underestimation of the F' -center energy and an erroneous conclusion about unimportance of electron correlations related to the direct dependence of WF on the distance between electrons. Later on, the author of monograph [24] arrived at the conclusion (with reference to work [23]) of the impossibility of formation of a stable BP state in the framework of the one-center model.

The same function (3) was applied in calculating the BP energy in a metal–ammonia solution by A S Davydov [97]. He repeated the erroneous conclusion about OCBP instability.

2.3 The two-center bipolaron — analog of the hydrogen molecule

The failure to find the bound BP state in the framework of the OC configuration led to appearing the TCBP model [29, 30]. Before that, polaron effects in ionic crystals for a pair of F-centers (F₂-centers) had been investigated by Deigen [28]. The employment of the continuous approximation allowed this model to be regarded as a complete analog of the hydrogen molecule resided in a phonon field. This latter work provided a basis for the BP model [29] with the electron WF chosen by perfect analogy with the WF of the H₂ molecule:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Phi(\mathbf{r}_1, \mathbf{r}_2) + \Phi(\mathbf{r}_2, \mathbf{r}_1). \quad (4)$$

Wave function $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ was chosen in the form of the product of hydrogen-like WFs centered at different points coinciding with the centers of polarization wells of two polarons:

$$\Psi_{\text{BP}}(\mathbf{r}_1, \mathbf{r}_2) = N(a(1)b(2) + a(2)b(1)), \quad (5)$$

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

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

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

An alternative method for computation of BP energy was used in Ref. [98] where a model Hamiltonian was proposed to calculate OCBP energy by trajectory integral method. In this study, a variational parameter was introduced to be treated as the distance between the centers of polarization wells of two polarons. The author of paper [98] undertook qualitative consideration of the model and noticed the possibility of appearing a stable BP state; however, he did not make numerical calculations.

Over 30 years elapsed between the first reports on the calculation of the energy of a strong-coupling BP [29, 30] and publication of the paper by Suprun and Moizhes [34] in which the authors corrected the erroneous estimates of OCBP energy presented in Refs [23, 97]; they studied the TC model of the BP despite the low value of binding energy.

After the publication of Ref. [34], different research groups reproduced results of computation by a variety of methods. The OC configuration of BPs having been found to be energetically advantageous compared with the TC configuration, further studies of the latter model were virtually discontinued.

In direct analogy with the hydrogen molecule, a continuum TCBP in an isotropic ionic crystal had to vibrate and rotate about a minimum corresponding to the equilibrium distance between the centers of polaron polarization wells. It will be shown in Section 3 that the TC configuration of a BP corresponds to a secondary minimum that disappears in the case of a more flexible choice of trial WF, taking into account electron correlations arising from the direct dependence of the WF on the distance between electrons.

Because this review is concerned with the work developing the theory of large-radius continual BPs, it does not encompass the problems of small-radius polarons or BPs studied in Refs [99, 100] with the use of the intersite BP model.

3. The inclusion of electron correlations and spatial configuration of a bipolaron

3.1 The strong-coupling bipolaron

In the continuous approximation in the strong-coupling limit, polaron and bipolaron functionals take the form [24, 34]

$$J_{\text{P}} = \frac{T_1}{N_{\text{P}}} - \frac{e^2 C}{2N_{\text{P}}^2} \int \frac{\Psi_1^2 \Psi_2^2}{r_{12}} d\tau_{12}, \quad (6)$$

$$J_{\text{BP}} = \frac{T_{12}}{N} + \frac{e_0^2 J_{\text{C}}}{\varepsilon_{\infty} N} - \frac{2e^2 C}{N^2} \int \frac{\Psi_{12}^2 \Psi_{34}^2}{r_{13}} d\tau_{12} d\tau_{34}, \quad (7)$$

where N_{P} , N are the normalization factors of the polaron and BP WFs, respectively, and

$$T_i = -\frac{\hbar^2}{2m^*} \int \Psi_i \Delta_i \Psi_i d\tau_i, \quad i = 1, 2,$$

$$\Delta_i = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}, \quad T_{12} = T_1 + T_2,$$

$$J_{\text{C}} = \int r_{12}^{-1} \Psi_{12}^2 d\tau_{12}, \quad C = \varepsilon_{\infty}^{-1} - \varepsilon_0^{-1},$$

$$\Psi_i \equiv \Psi_i(\mathbf{r}_i), \quad \Psi_{12} \equiv \Psi_{12}(\mathbf{r}_{12}),$$

with m^* and e being electron effective mass and charge, respectively. The second term on the right-hand side of formula (7) corresponds to the Coulomb repulsion.

Let us introduce effective hartree, $\text{Ha}^* = e^2/\varepsilon_{\infty} a^*$, as the unit of energy, and effective Bohr radius $a^* = \hbar^2 \varepsilon_{\infty}/m^* e^2$ as the unit of length.

Functional (7) is obtained in the strong-coupling approximation for a two-center WF symmetrized with respect to interchange of the electron coordinates. The presence of interelectron correlations is a necessary condition for the appearance of the bound BP state because the BP functional identically decays into two polaron functionals if the electron WF is chosen in the multiplicative form, even in the strongest-coupling limit, when $\eta \rightarrow 0$. For TCBPs, electron correlations are taken into account by the choice of WF in the form of a symmetrized product of polaron functions centered at different points; correlation effects for the OC model (Pekar BP) are taken into consideration by introducing the direct dependence of the WF on the distance between electrons. A more complicated WF generalizing the two models takes into account both forms of electron correlations and permits obtaining OC- and TC-models of BPs as limiting cases.

Interelectron correlations related to the direct dependence of the electron WF on the distance between electrons were taken into consideration in many studies. Here are a few examples:

$$\Psi_{12} \sim (1 + Cr_{12})[1 + b(r_1 + r_2)] \times \exp[-\delta(r_1 + r_2)] \cosh(cr_{12}) [37],$$

$$\Psi_{12} = \sum_i (1 \pm P_{12}) \exp(-a_{1i}r_1 - 2a_{2i}r_{12} - a_{3i}r_2) [19, 20, 101],$$

$$\Psi_{12} \sim \left\{1 - k \exp[-\epsilon(r_1 - r_2)^2]\right\} \exp[-\delta(r_1^2 + r_2^2)] [102],$$

$$\Psi_{12} \sim (1 + kr_{12}^2) \exp[-\delta(r_1^2 + r_2^2)] [103],$$

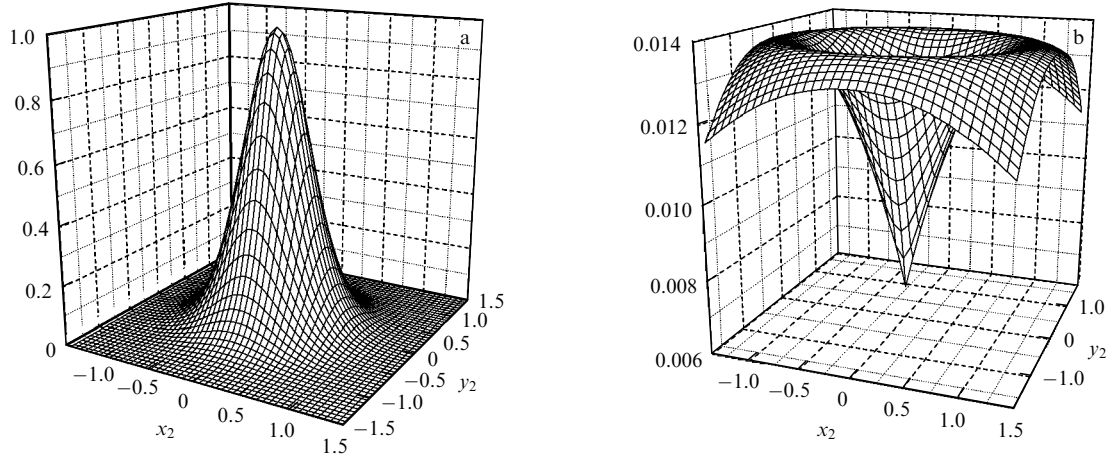


Figure 1. (a) Electron density for a one-center BP without account of interelectron correlations ($\beta = 0$) in WF (3). (b) The same for WF (3) taking account of interelectron correlations.

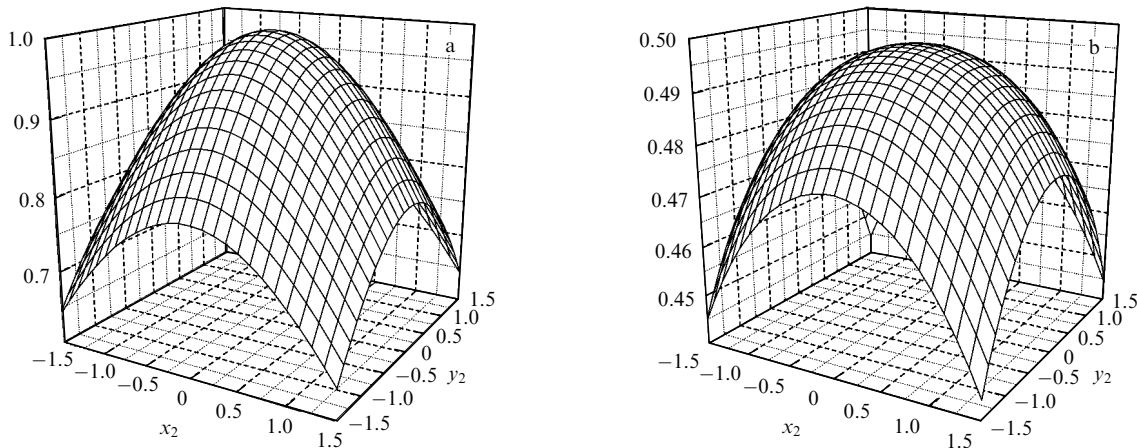


Figure 2. Electron density for WF (8) at $n = 5$ (a) without ($a_{1i} = a_{3i}$, $a_{2i} = 0$) and (b) with ($a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$) account of interelectron correlations. Variational calculations were performed in the strong-coupling limit for $\eta = 0$.

where C , b , δ , ϵ , a_{1i} , a_{2i} , a_{3i} , and k are variational parameters, and P_{12} is the interchange operator for coordinates of the first and second electrons.

3.1.1 Interelectron correlations and the spatial distribution of the two-electron wave function. Various two-electron functions were utilized to find the OCBP energy. The correct Pekar BP functional in the strong electron–phonon interaction limit, obtained using WF (3), is reported in Ref. [104]. Changes in BP wave functions, when interelectron correlations are taken into consideration, can be deduced from the comparison of the spatial distribution of probability density of electron positions given by the WF squared in the ground state for a BP with and without account of electron correlations.

Figure 1 displays the electron density spatial distribution for a Pekar BP wave function obtained in Ref. [105] without and with account of electron correlations, respectively. One electron is placed in the origin of coordinates ($\mathbf{r}_1 = \{0, 0, 0\}$); the radius vector of the second electron is $\mathbf{r}_2 = \{x_2, y_2, 0\}$. The electron density in the origin of coordinates without account of correlation additions is assumed to be unity. It can be seen that for WF (3), after finding the BP functional minimum, the region of small interelectron distances characterized by strong

electron–electron repulsion is practically excluded from consideration. The Gaussian basis utilized in Refs [21, 105, 106], namely

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^n C_i \exp(-a_{1i}r_1^2 - 2a_{2i}(\mathbf{r}_1\mathbf{r}_2) - a_{3i}r_2^2), \quad (8)$$

leads to a different WF density distribution, but the tendency toward lowering the contribution from close interelectron distances persists.

Figure 2 illustrates the electron density distribution for the Gaussian WFs of the form (8) without ($a_{1i} = a_{3i}$, $a_{2i} = 0$) and with ($a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$) account of electron correlations.

The wave function of two polarons located at a distance R between the centers of polarization wells can be chosen in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^n C_i (1 \pm P_{12}) \exp(-a_{1i}r_{a1}^2 - 2a_{2i}(\mathbf{r}_1\mathbf{r}_2) - a_{3i}r_{b2}^2), \quad (9)$$

where P_{12} is the interchange operator for coordinates of the first and second electrons, r_{a1} and r_{b2} are radius vectors of the first and second electrons in the two-center system of coordinates with the centers at points a and b coinciding

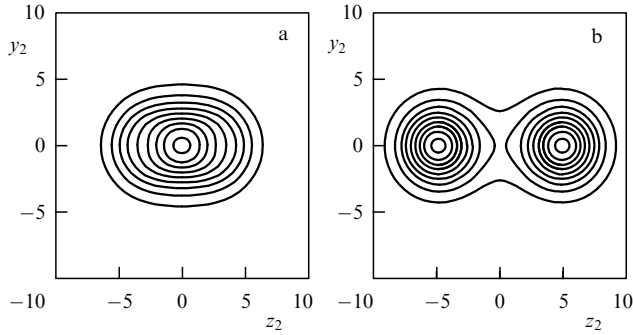


Figure 3. (a) Electron density isolines for equilibrium distance R_m between the centers of TCBP polarization wells (interelectron correlations in WF (9) are absent, so $a_{1i} = a_{3i}$, $a_{2i} = 0$). (b) The same for two polarons spaced apart at distance $R = 10$. The z -axis is directed along the line connecting the centers of polarization wells of the two polarons. The origin of coordinates is halfway between these centers.

with the centers of polarization wells of polarons located at a distance R from each other; the upper sign (+) refers to a singlet state, and the lower one (−) to a triplet state of the two-polaron system.

When polarons that form BPs are spaced far apart, the Gaussian WFs of the form (9) permit obtaining the correct limiting transition to the functional represented by the sum of functionals of two noninteracting polarons. Wave function (3) possesses no such property. Figure 3 displays electron density isolines obtained in the absence of electron correlations ($a_{1i} = a_{3i}$, $a_{2i} = 0$) [105] using the Gaussian WFs of the form (9). Figure 3a illustrates the spatial distribution of electron density for the equilibrium distance between the centers of polarization wells of strong-coupling TCBPs for $\eta = \varepsilon_\infty/\varepsilon_0 = 0$. Figure 3b corresponds to the density of a system comprising two polarons spaced far apart ($R = 10$). Taking account of interelectron correlations in the wave function (9) ($a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$) barely changes the electron density distributions at large distances between polarons. However, in the case of a spherically symmetric WF, the bipolaron energy drops down to a minimal value at point $R = 0$.

3.1.2 Comparison of energy minima for one- and two-center bipolarons.

Let us compare the depth of energy minima

obtained in Ref. [106] for TC- and OC-configurations with the help of the most general WF (9) allowing the two models to be integrated. For the OC configuration, when WF (9) goes over into WF (8) at $R = 0$, the minimal BP energy $E_m = -0.136512 \text{ Ha}^*$, i.e., BP binding energy is 25.8% of the exact double strong-coupling polaron energy $E_P^M = -0.0542564 \text{ Ha}^*$. The corresponding value for the TC configuration (interelectron correlations related to the direct dependence of the WF on the distance between electrons are totally absent) is $E_m = -0.11503 \text{ Ha}^*$ (the BP binding energy is 6.02% of the double polaron energy) for the equilibrium distance $R_m = 5.0225 a^*$ between the centers of polarization wells of two polarons.

Table 1 lists energy values of the BP ground state obtained by different methods in the strong-coupling limit at $Q = E_{BP}/2E_P$ and $Q^* = E_{BP}/2E_P^M$, where E_P is the polaron energy obtained in the same approximation as BP energy, and $E_P^M = -0.0542564$ is the exact value of polaron energy in the strong-coupling limit [107].

In Vinetskii's study [30] developing the TCBP theory, polaron functions were chosen in a more general form compared with those in earlier work [29], and the BP wave function represented the symmetrized product of Pekar polaron functions: $(1 + \alpha r_{a1}) \exp(-\alpha r_{a1})(1 + \alpha r_{b2}) \exp(-\alpha r_{b2})$ [where traditional notations for the TC-coordinate system are used: $\mathbf{r}_{a1}(\mathbf{r}_{a2})$ is the radius vector of the first (second) electron counted from the center a ; $\mathbf{r}_{b1}(\mathbf{r}_{b2})$ is the same for the center b]. As follows from calculations in Ref. [30], the ratio $E_{BP}^{HL}/2E_P$, where E_{BP}^{HL} is the BP energy obtained in the framework of the Heitler–London approximation, and E_P is the polaron energy for Pekar WF $(1 + \alpha r) \exp(-\alpha r)$, was equal to 1.08; in other words, it barely changed compared with the value obtained in Ref. [29] for the simplest hydrogen-like WF $a(1)$. Table 1 also contains evaluated TCBP energies obtained by the molecular orbital (MO) method for WFs:

$$\Phi_{12} = \Psi(r_1)\Psi(r_2) = N_{12}(a(1) + b(1))(a(2) + b(2)), \quad (10)$$

where $a(1)$ and $b(1)$ are hydrogen-like WFs [see formula (5)], and N_{12} is the normalization factor.

It follows from the above consideration that disregarding electron correlations related to the direct dependence of a WF on the interelectron distance results in the emergence of an extremely small energy minimum for a nonzero distance R_m between the centers of polarization wells of two polarons.

Table 1. BP energies and regions of existence, obtained by different methods in the strong-coupling limit (for $\eta = 0$).

Method	HL [29]	HL* [105]	MO [105]	MO* [105]	[34]	[106]	[106]
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

Note. HL, MO — Heitler–London method and molecular orbital method, respectively [without variation of the parameter λ in WFs (5) and (10)]; HL*, MO* — the same with variation of λ ; TC(C), OC(C) — two- and one-center WFs taking account of electron correlations; E_P , E_{BP} — polaron and BP energies, respectively; R_m — equilibrium distance between the centers of polarization wells of two polarons; $E_{LP} = -25/512$ — polaron energy obtained with the use of a hydrogen-like WF; $E_P^M = -0.0542564$ — exact value of polaron energy in the strong-coupling limit [107] (effective hartree $\text{Ha}^* = e^2/\tilde{\epsilon}a^*$ is used as the unit of energy, and effective Bohr radius $a^* = \hbar^2\tilde{\epsilon}/m^*e^2$ as the unit of length); η_c , η_c^* — critical values of parameter η calculated with respect to polaron energies E_{LP} and E_P^M , respectively; $Q = E_{BP}/2E_P$ and $Q^* = E_{BP}/2E_P^M$.

Such spatial configuration corresponding to TCBP was first considered in Refs [29, 30]. When the TCBP binding energy was calculated with respect to the exact numerical value of double polaron energy reported by Miyake [107], the depth of the energy minimum for the TC configuration obtained with the use of WFs (5) and (10) proved too low for the existence of the bound state, even in the strong-coupling limit, when $\eta \rightarrow 0$. As seen from Table 1, $Q^* < 1$ and $\eta_c^* = 0$ held for both the Heitler–London and molecular orbital methods. In other words, the computation error for polaron energy was of the same order of magnitude as the depth of the BP energy minimum. This fact called into question the existence of bound BPs because the above minimum could be the consequence of an insufficiently flexible choice of bipolaron WF.

In the strong-coupling limit, energy minima calculated in paper [106] using the WF of the most general form (9) for both OC- and TC-configurations are the deepest of all those obtained thus far. These values are given in Table 1.

Because the exact value of strong-coupling polaron energy is reproduced with an accuracy up to six decimal places even for the polaron WF chosen as the sum of five Gaussian terms, namely

$$\Psi(r) = \sum_{i=1}^5 C_i \exp(-a_i r^2), \quad (11)$$

where C_i and a_i are variational parameters, the error related to inexact determination of polaron energy for a BP with WF (9) is altogether absent [109]. Due to this, quantities Q and Q^* , η_c and η_c^* characterizing the lower and upper boundaries of BP energy and the region of BP existence in η here coincide.

The strong-coupling polaron as a particle with a hydrogen-like spectrum was studied by the variational method in Ref. [24]. In Refs [108–110], self-consistent excited states were found by numerical solution of the corresponding Euler equation. This problem was discussed at greater length in review [111] considering the structure of the large-radius polaron. Recently, a variational function for the first excited self-consistent state of a polaron and F-center has been found [112], which made it possible to exactly reproduce numerical solutions of appropriate Euler equations obtained in the strong-coupling limit for the 2p-state:

$$\Psi_{2p} = \sum_i^5 C_i \sinh(b_i z) \exp(-a_i r^2), \quad (12)$$

where C_i , a_i , and b_i are variational parameters. The use of five terms in expression (12) improves numerical solution $E_{2p} = -0.022867$ (see Ref. [109]) and gives a smaller energy of the self-consistent state for the first excited level of polaron, $E_{2p} = -0.022967$. As reported by Gabdullin [109], the accuracy of the energy calculation did not exceed three significant figures, meaning that the lower polaron energy obtained by the variational method was unrelated to numerical errors that occurred in work [109]. Numerical examples were given for $\eta = 0$. Any further increase in the number of exponents does not lead to the lowering of the energy of the polaron self-consistent 2p-state. Variational function (12) allows the first excited state of both polaron and hydrogen atom to be reproduced with an accuracy up to six decimal places. Therefore, this function can be employed to find the variational WFs of BP and F'-center excited states at an arbitrary electron–phonon coupling.

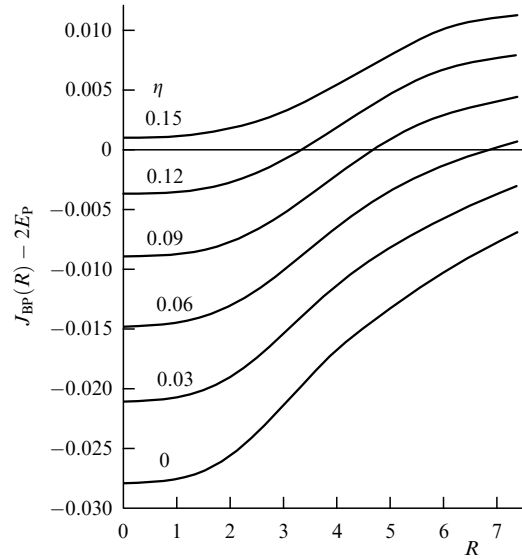


Figure 4. Dependence of the energy of a two-polaron system on the distance between the centers of polarization wells for different parameters η of ionic bond. Calculations were made for five terms in WF (9) in the strong-coupling limit. $J_{BP}(R)$ is the BP energy for the distance R between the centers of the polarization wells of the two polarons, and E_P is the polaron energy.

3.1.3 Polaron interaction energy as a function of distance between the centers of polarization wells. As shown in Table 1, the utilization of WF (9) allows both TC- and OC-configurations of BPs to be reproduced. The former is reproduced in the total absence of electron correlations for a less general form (9) of WF, when additional limitations, e.g., $a_{1i} = a_{3i}$, $a_{2i} = 0$, are imposed on variational parameters. In variational calculations, only the lowest energy value makes physical sense, whereas the remaining minima are secondary ones and should be discarded. In other words, TC configuration of BPs corresponds to a secondary minimum and appears as a result of the inflexible choice of WF. This situation is illustrated by Fig. 4 showing BP energy dependences as functions of distance between polarons at different values of parameter η , studied in Ref. [106] and obtained using WF of the most general form (9) ($a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$). The double polaron energy is taken as the reference point. The curves in Fig. 4 can be interpreted as the interaction energy between two polarons. Its dependence on the distance between the polarons has an analog in the form of the dependence of interaction energy between two hydrogen atoms on the internuclear distance, without account of proton–proton repulsion (see monograph [96], Fig. 3.3).

At large distances between polarons, the BP energy tends toward double polaron energy. As shown in Fig. 4, the BP binding energy, i.e., the positive value of $2E_P - J_{BP}(R)$ for bound states, vanishes at $\eta = \eta_c = 0.143$ and becomes negative thereafter. Because the interaction energy tends toward double polaron energy (toward zero in Fig. 4) at large distances between the centers of the polarization wells of two polarons, the distance dependences of their energy have maxima. This necessitates consideration of the possibility of occurrence of BP metastable states when passage to the large inter-polaron distance region requires that the potential barrier be overcome. Such a possibility was discussed earlier by Vinetskii and Semenets [31] for TCBP.

A large number of OCBP studies made by different methods were published after issuing paper [34].

Feynman trajectory integral method was applied in Ref. [113] to consider OCBPs in polar and covalent crystals. Results in the strong-coupling limit for ionic crystals coincide with calculated Pekar BP energies obtained by the traditional variational method with the use of the trial WF in the form $\Psi(\mathbf{r}_1, \mathbf{r}_2) = \exp[-\delta(r_1^2 + r_2^2) - k\mathbf{r}_1\mathbf{r}_2]$, taking into account interelectron correlations. Such a simple function leads to less accurate magnitudes of binding energy compared with those reported in Ref. [34].

In paper [114], the OCBP was considered using the Feynman–Haken method. As proposed by Haken [115], the effective action S_{eff} is chosen to correspond to the trial Hamiltonian

$$H_{\text{eff}} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + \frac{1}{2} C^2 r_1^2 + \frac{1}{2} C^2 r_2^2 + \frac{1}{4} D'^2 (\mathbf{r}_1 - \mathbf{r}_2)^2, \quad (13)$$

where C and D' are the variational parameters. Thereafter, the Jensen–Feynman inequality [17, 18] is utilized to find the upper boundary of the BP energy:

$$E_0^{\text{exact}} \leq E_{\text{FH}} \equiv E_0^{\text{eff}} + \lim_{\beta \rightarrow \infty} \frac{\langle \langle S - S_{\text{eff}} \rangle \rangle}{\beta}, \quad (14)$$

where E_0^{exact} is the exact BP energy, E_0^{eff} corresponds to H_{eff} , $\langle \langle \rangle \rangle$ stands for statistical averaging with the weighting factor $\exp(S_{\text{eff}})$, $\beta = 1/k_B T$, and k_B is the Boltzmann constant.

Results in the strong-coupling limit are compared with the results of calculations by the standard variational method using different WFs. Application of the Feynman–Haken method to the calculation of the OCBP energy gave the same values as in Ref. [113]. However, the possibility of more exact reproduction of strong-coupling data [34] by methods related to the choice of trial action remains to be clarified.

This problem was further covered in paper [116]. In the beginning, the author performs canonical transformation of Hamiltonian (2) corresponding to strong coupling:

$$H_{\text{BP}} \rightarrow \tilde{H}_{\text{BP}} = \exp(-S) H_{\text{BP}} \exp S, \quad (15)$$

where $S = \sum_{\mathbf{k}} [(\xi_{\mathbf{k}1} + \xi_{\mathbf{k}2}) a_{\mathbf{k}}^+ - \text{h.c.}]$. Quantities $\xi_{\mathbf{k}1}$ and $\xi_{\mathbf{k}2}$, unlike analogous quantities in the standard strong-coupling scheme, are not variational parameters; they are chosen in the form of the matrix elements $\xi_{\mathbf{k}1} + \xi_{\mathbf{k}2} = \langle P | \exp(i\mathbf{k}\mathbf{r}_1) + \exp(i\mathbf{k}\mathbf{r}_2) | P \rangle$ of the two-electron variational function $|P\rangle$.

Furthermore, the Feynman–Haken procedure was followed. Hamiltonian corresponding to effective action is chosen in a form equivalent to expression (13) with the effective potential

$$V_{\text{eff}}(\mathbf{r}_1, \mathbf{r}_2) = \lambda^4 r_1^2 + \lambda^4 r_2^2 + 2\beta^4 \mathbf{r}_1 \mathbf{r}_2, \quad (16)$$

where λ and β are variational parameters. The third term in the effective potential V_{eff} makes it possible to take account of electron correlations. The energy of the BP ground state is evaluated by a perturbation theory method up to the second order. The basis is chosen as the system of eigenfunctions corresponding to the solution of Schrödinger equation with the trial Hamiltonian. The wave function $|P\rangle$ corresponds to the ground state. Variational parameters in the effective

potential are found by varying the system's energy obtained in the first order of the perturbation theory. The author of Ref. [116] thus used an alternative method to reproduce the result for the OCBP energy reported earlier in Ref. [34]. Because the BP binding energy in paper [116] was found based on the underestimated polaron energy ($E_P = -0.05385$ instead of the exact numerical value $E_P^M = -0.0542564$), the region of η values at which the BP exists was unjustifiably extended ($\eta_c = 0.165$).

The ground state of strong-coupling OCBPs in the center-of-mass system was investigated in Ref. [117]. Because center-of-mass coordinates and interelectron distance cannot be separated, the authors proposed a scheme of iterative numerical solution for two coupled equations written down in these coordinates. The BP variational wave function found in Ref. [118] was taken as the initial approximation in Ref. [117]. Laborious numerical calculations gave $\eta_c = 0.123$ for the lower boundary of existence of the bound BP. This value was computed with respect to the exact double BP energy in the strong-coupling limit. Results of calculations employing the numerical solution of a set of two integro-differential equations suggest a few percent decrease in BP ground state energy compared with the corresponding value obtained in Ref. [118]. The authors of Ref. [119] proposed convenient series expansions of BP energy in the electron–phonon interaction parameter, which allow comparing BP energy values obtained by trajectory integral method and other methods and to determine trustworthy BP energies and regions of existence in η_c at an arbitrary Fröhlich coupling constant.

Regardless of the method, each computation of BP energy represents a laborious numerical experiment requiring cumbersome calculations. The region of BP existence can be extended far from always. The data on BP energy and the region of η values at which a BP exists, obtained in the strong-coupling limit by variational calculations with the use of multiparameter WFs in Refs [105, 106], appear to be reliable and will hardly be improved in further studies. However, more precise determination of BP energy spectrum characteristics is not the main objective of such calculations; rather, they are designed to develop computational methods for the study of electron system energy in the fields of different elementary excitations of the crystal lattice.

The axially symmetric TCBP, whose energy was calculated by Vinetskii and Gitterman [29], could rotate and vibrate about a minimum corresponding to the equilibrium distance between the centers of polarization wells of two polarons. The hydrogen molecule served as a natural analog in deriving the vibrational–rotational spectrum of such a structure in Ref. [30]. After the publication of paper [34], V L Vinetskii, one of the authors of TCBP studies [29, 30], recognized the failure of this model; his last study was devoted to OCBPs [120].

Nevertheless, studies of the TCBP vibrational–rotational spectrum near the physically senseless secondary minimum gave rise to an erroneous line of BP research that still continues to develop. We thoroughly analyzed such erroneous work in Ref. [121].

3.1.4 Long-range interactions between polarons. In the strong-coupling approximation, the autolocalized polaron exhibits a discrete spectrum and in this sense can be regarded as an analog of the hydrogen atom [24, 111]. It was shown in Ref. [106] that, at large interpolaron distances, electron

correlations related to the direct dependence of the BP WF on the distance between electrons do not play significant role. At such distances, the WF of two polarons (Fig. 3b) can be approximated with a high accuracy by the symmetrized (singlet state) or antisymmetrized (triplet term) product of WFs of isolated polarons. The terms corresponding to the kinetic energy can be eliminated in the same way as in the Heitler–London method for the hydrogen molecule [96]. The energy of two noninteracting polarons can be regarded as the ground state. Then, the energy of the two polarons can be represented with an accuracy up to the terms quadratic in overlap integral in the following form

$$E_{\text{int}} = E_1 - J_{\text{ex}} \mathbf{S}_1 \mathbf{S}_2, \quad (17)$$

where \mathbf{S}_1 and \mathbf{S}_2 are spins of the first and second polarons, and

$$E_1 = \frac{1}{\varepsilon_0} \int \frac{a(1)^2 b(1)^2}{r_{12}} d\tau_{12}, \quad J_{\text{ex}} = \frac{1}{\varepsilon_{\infty}} K_1 - \frac{4}{\varepsilon} K_2 K, \quad (18)$$

$$K_1 = \int \frac{a(1)b(1)a(2)b(2)}{r_{12}} d\tau_{12}, \quad K_2 = \int \frac{a(1)b(1)b(2)^2}{r_{12}} d\tau_{12},$$

$$K = \int a(1)b(1) d\tau_1.$$

Here, notations generally accepted for the coordinates of two-center systems were introduced: $a(1)$, and $b(1)$ are polaron WFs centered at points a and b , respectively [$a(1) \equiv \Psi_{\text{P}}(r_{a1})$, $b(1) \equiv \Psi_{\text{P}}(r_{b1})$]. Variational function (11) can be used as a polaron WF; this function permits reproducing, accurate to six decimal places, the polaron energy value obtained by Miyake [107] by numerical solution of the appropriate Euler equation. In expression (18), the first term of exchange energy J_{ex} corresponds to ferromagnetic Coulomb exchange, while the second one describes the antiferromagnetic interaction between polarons due to the phonon contribution.

Thus, polarons repulse each other at large distances, while the spin-dependent part of the interaction energy (total exchange) has an antiferromagnetic (AF) nature (as $\eta \rightarrow 0$, $E_1 \approx 1/\varepsilon_0 R$, $J_{\text{ex}} \approx -3K^2/\varepsilon_{\infty} R$). This also means that the potential barrier needs to be overcome if the bipolaron state is to be formed.

Because polarons repulse each other at large distances, a polaron system can behave analogously to an electron gas with Coulomb repulsion between the particles. In this system, as in the electron gas [122], transition to the Wigner crystal is possible at sufficiently low concentrations, provided condition $k_{\text{B}}T < e^2/\varepsilon_0 a$ is satisfied (where a is the interparticle distance). Wigner crystallization of polaron gas has been considered in a series of studies. By way of example, it was shown in Refs [123, 124] that a system of polarons (continuous approximation) is subject to crystallization into a hexagonal lattice with a period determined by polaron concentration, as in the Wigner theory. The authors of paper [125] assessed the stability of polaron Wigner crystals and provided theoretical substantiation of the possibility of insulator–superconductor transition in polaron lattice breakdown. It should be emphasized, without going into the details of this phenomenon, that AF-exchange interaction between polarons may lead to AF-ordering in the polaron system, provided Wigner crystallization conditions are fulfilled [106]. Antiferromagnetism in electron Wigner crystals was considered in Refs [126, 127].

AF interaction between polarons may diminish the paramagnetic constituent of magnetic susceptibility in a

polaron gas at an elevated polaron concentration, even if bipolaron bound states fail to form.

3.2 The continual bipolaron in anisotropic crystals

Hamiltonian (2) can be generalized for the case of crystals with anisotropic effective masses and permittivities. BP energy in anisotropic crystals was calculated for the first time for the two-center BP model in Refs [32, 33]. The main purpose of calculations in such systems was to confirm the authors' conjecture that bipolaron binding energy in anisotropic systems, expressed in units of double polaron energy, must increase compared with the corresponding values of binding energy in isotropic crystals. Accordingly, the region of η values at which a BP exists must extend. Crystals with an axially symmetric effective mass of charge carriers ('light-plane' and 'light-axis' type symmetries) were chosen as concrete objects. The assumption of expanding the bipolaron region of existence over parameter η was confirmed.

In later studies [35, 36], the BP Hamiltonian considered earlier in Refs [32, 33] was utilized to determine the OCBP binding energy. The trial WF was chosen, taking into account electron correlations, in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i=1}^n C_i \exp(-a_{1i} z_1^2 - 2a_{2i} z_1 z_2 - a_{3i} z_2^2) \times \exp(-b_{1i} \rho_1^2 - 2b_{2i} \rho_1 \rho_2 - b_{3i} \rho_2^2), \quad (19)$$

where ρ_1 and ρ_2 are radii vectors in the xy plane of the first and second electrons, respectively: $\rho = (x, y)$, with C_i , a_{1i} , a_{2i} , a_{3i} , b_{1i} , b_{2i} , and b_{3i} being variational parameters.

The energy minimum for OCBPs in anisotropic systems considered in Refs [35, 36], as for an isotropic crystal, was much deeper than for TCBCPs. Therefore, the TCBCP corresponds to the secondary minimum in the case of anisotropic crystals, too.

Figure 5 shows the dependences of BP energy on the parameter η for different anisotropy parameters of electron effective masses m_{xy}^*/m_z^* in a crystal with an anisotropic effective mass of the 'light-plane' type. The region of existence of anisotropic BP significantly extended. Calculations were made with five terms entering into expression (19). Permittivities were assumed to be isotropic.

The example of the calculation of BP energy in Ref. [35] refers to a crystal where both permittivities and electron effective masses are anisotropic. The authors analyzed, as a case in point, the BP energy in La_2CuO_4 . Experimental permittivities for these crystals are well known: $\varepsilon_0 = 50$, $\varepsilon_{\infty} = 4$ in a plane of CuO_2 layers, and $\varepsilon_0 = 23$ in the perpendicular direction. For isotropic effective masses, the BP binding energy calculated in work [35] comprises 15.6% in units of polaron energy, and increases to 25.2% in the $m_{xy} \ll m_z$ limit, which makes the emergence of bound BPs in this HTSC crystal highly probable, especially taking into account that this material constitutes a system with well-apparent anisotropy of the 'light-plane' type.

3.3 The continual intermediate-coupling bipolaron

Free BPs and F' -centers in ionic crystals for the case of electron–phonon interaction with an arbitrary strength were considered in paper [26]. Because the BP trial function was chosen in the form of the product of polaron WFs, electron correlations were absent and the BP bound state could not be found. The Buimistrov–Pekar method [26] was successfully

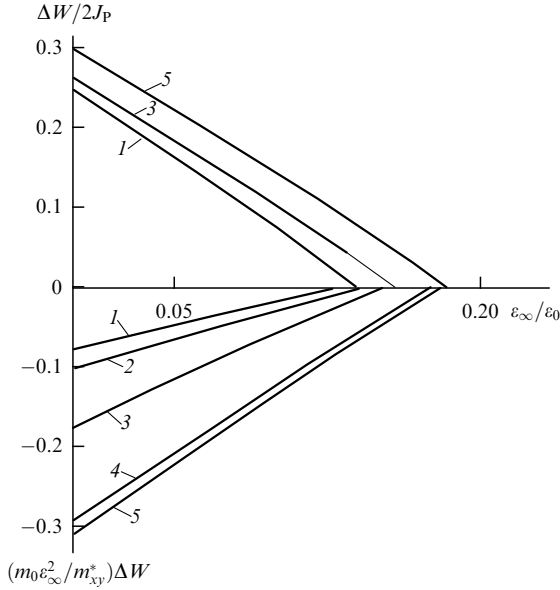


Figure 5. Dependences of BP energies $\Delta W = J_{BP} - 2J_P$ (double polaron energy is taken as zero) and quantity $\Delta W/2J_P$ on the $\varepsilon_\infty/\varepsilon_0$ ratio for different anisotropy parameters of the electron effective mass and isotropic permittivities. Lines 1–5 correspond to the parameter m_{xy}^*/m_z^* equaling 1, 2^{-2} , 2^{-4} , 2^{-15} , and 2^{-20} , respectively.

applied in a later study by Larsen [37], where the D^- -center was considered in polar crystals.

3.3.1 Canonical transformation method applied to systems with electron–phonon interaction. The Buimistrov–Pekar method reduces to the choice of the trial function for a two-electron system in a phonon field in the form

$$\Phi_{12} = \Psi(\mathbf{r}_1, \mathbf{r}_2) \exp(-S_1) \exp(-S_2)|0\rangle, \quad (20)$$

$$S_1 = \sum_{\mathbf{k}} F_{\mathbf{k}}(a_{\mathbf{k}}^+ - a_{\mathbf{k}}),$$

$$S_2 = \sum_{\mathbf{k}, i=1,2} g_{\mathbf{k}} [\exp(-i\mathbf{k}\mathbf{r}_i) a_{\mathbf{k}}^+ - \text{h.c.}],$$

where $F_{\mathbf{k}}$ and $g_{\mathbf{k}}$ are variational functions corresponding to static (strong coupling) and dynamic polarization of the phonon field, respectively. $F_{\mathbf{k}}$ and $g_{\mathbf{k}}$, determined by varying the effective Hamiltonian over these functions, are defined as follows:

$$g_{\mathbf{k}} = \frac{V_{\mathbf{k}}(1 + \chi(k))}{1 + k^2 + \chi(k)}, \quad F_{\mathbf{k}} = -(g_{\mathbf{k}} - V_{\mathbf{k}})U_{\mathbf{k}},$$

$$U(k) = \langle \cos(\mathbf{k}\mathbf{r}_1) + \cos(\mathbf{k}\mathbf{r}_2) \rangle, \quad (21)$$

$$\chi(k) = \langle \cos(\mathbf{k}\mathbf{r}_{12}) \rangle - \frac{1}{2} U^2(k).$$

The canonical transformation proposed by Adamowski and Bednarek [20] to find the energy of the free BP and D^- -center differs from the Buimistrov–Pekar transformation (20) in the absence of variation over $g_{\mathbf{k}}$ and $F_{\mathbf{k}}$, and these functions are chosen in the form

$$g_{\mathbf{k}} = V_{\mathbf{k}} \frac{\lambda_1}{\rho_1^2 k^2 + 1}, \quad F_{\mathbf{k}} = V_{\mathbf{k}} \frac{\lambda_2}{(\rho_2^2 k^2 + 1)^2}, \quad (22)$$

where $\lambda_{1,2}$ and $\rho_{1,2}$ are variational parameters.

Table 2. The BP ground state energy for different parameters α and η . E_{BP} and E_{BP}^A are BP energies computed by the Buimistrov–Pekar [26] and Adamowski [19] methods in Refs [128] and [20], respectively.

α	η	E_{BP} [128]	E_{BP}^A [20]
6	0	−12.703	−12.601
	0.01	−12.595	−12.487
7	0	−16.243	−16.067
	0.01	−16.053	−15.91
	0.10	−14.598	−14.500
9	0	−24.927	−24.652
	0.01	−24.650	−24.354
	0.10	−22.068	−21.756
20	0	−111.928	−110.504
	0.01	−110.497	−109.064
	0.10	−96.878	−95.335

Table 2 lists values of the BP ground state energy for different parameters α and η obtained by the Buimistrov–Pekar method [26] in Ref. [128], and by the Adamowski canonical transformation method [19] in Ref. [20].

Results of the variational calculation of BP energy by different methods should be compared with the total ground state energy as in Table 2 rather than with the BP binding energy that is usually calculated with respect to polaron energy obtained in the same approximation as the BP energy, and may be different depending on the method applied.

For the entire BP existence region, the Buimistrov–Pekar method gives the lowest values of the ground state energy and the widest region of BP existence compared with the best results of direct variational methods, including variation of the WF system [19, 20].

The dependences of BP energy as functions of the distance between the centers of polarization wells of two polarons for different WFs are shown in Fig. 6. All values are expressed in Feynman units. In Ref. [21], such dependences are presented for different electron–phonon coupling constants. Calculations were made by the Buimistrov–Pekar method [26].

It is well known that the best results of polaron energy calculations for practically the entire range of the Fröhlich coupling constant are obtained by the trajectory integral method. However, this method loses its advantage for systems with Coulomb interactions, such as BPs, D^- -centers, and complexes of small impurity centers, compared with calculations done by variation of the system’s WF. For example, the Feynman method gives higher BP energy values than the Buimistrov–Pekar method for all $\alpha \geq 7.3$ [21, 105]. At the same time, the best BP energy obtained by the latter method for $\alpha = 7$ was −16.23 [21], i.e., greater than −16.27 arrived at using integration over trajectories (this value was reconstructed from the graphical data presented in Ref. [16]). However, the region in which such an advantage of the trajectory integral method holds true is very narrow; specifically, the critical value of the parameter obtained in Ref. [16] was $\alpha_c = 6.8$ compared with $\alpha_c = 6.9$ found in Ref. [105]. It should be noted that the two values were calculated with respect to the Feynman energy of the polaron.

Figure 6 illustrates an intermediate-coupling case: $\alpha = 9$ and $\eta = 0$ [105]. Feynman units are used as units of energy

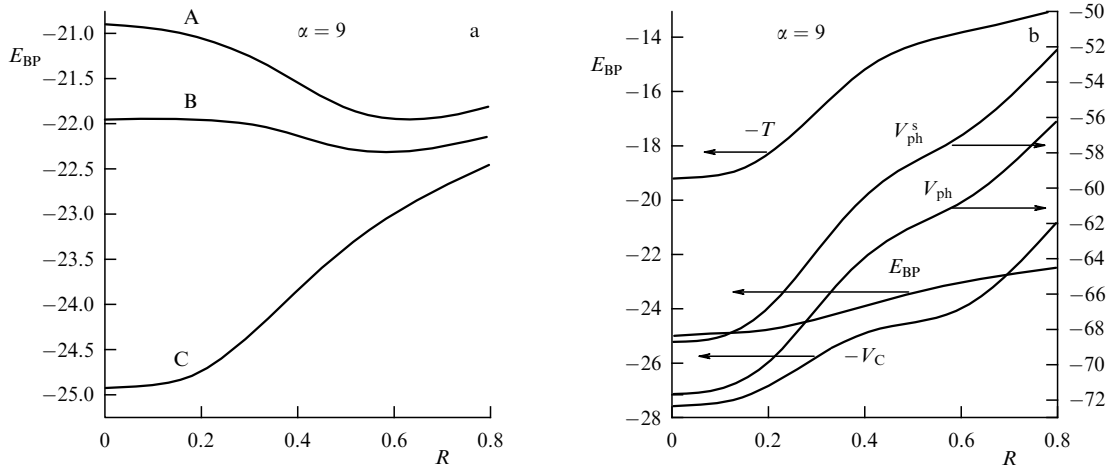


Figure 6. (a) Plots of BP energy vs. distance between centers of polarization wells of two polarons ($\eta = 0$, $\alpha = 9$). Curves A, B, C correspond to variations of total BP energy. Bipolaron WF is given by Eqn (9) for $a_{1i} = a_{3i}$ and $a_{2i} = 0$; $a_{1i} \neq a_{3i}$ and $a_{2i} = 0$, and $a_{1i} \neq a_{3i}$ and $a_{2i} \neq 0$, respectively. (b) Dependences of different contributions to BP energy on the inter-polaron distance for WF (9) of the most general form: $a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$. V_C is the Coulomb repulsion, T and V_{ph}^s are contributions corresponding to the addition of strong coupling to the kinetic energy and EPI energy, $V_{ph} = V_{ph}^s + V_{ph}^{int}$ is the total contribution of the EPI constituent to the BP ground state energy $E_{BP} = T + V_C + V_{ph}$, and V_{ph}^{int} is the addition of intermediate coupling to the EPI energy.

and length. In the simplest case of the absence of interelectron correlations ($a_{1i} = a_{3i}$, $a_{2i} = 0$), the sole minimum in the total energy vs. inter-polaron distance plot corresponds to nonzero $R = R_m$. The maximum occurs at $R = 0$. Increasing the flexibility of the trial WF and assuming $a_{1i} \neq a_{3i}$, $a_{2i} = 0$ gives two extrema as well (curve B in Fig. 6). Thus, the bipolaron has a nonzero binding energy at $R = 0$ and the maximum corresponds to this point, the same as in curve A. Energy dependences A and B in Fig. 6 describe the TC model of a BP. In the case of the most flexible WF ($a_{1i} \neq a_{3i}$, $a_{2i} \neq 0$) chosen with account of the direct interelectron distance dependence of the BP wave function, the BP energy for the OC configuration deepens significantly and the secondary minimum at point $R = R_m$ disappears (curve C in Fig. 6). Figure 6 demonstrates that the TC configuration of the BP results from the inexact choice of the system's WF, while the minimum corresponding to this configuration is a secondary one. Thus, the continual TCBP as a stable entity makes no physical sense whatever.

3.4 D^- -centers in ionic crystals

Reference [37] reported a giant rise in the binding energy of D^- -centers in polar crystals, related to taking account of interelectron correlations. Results of the calculation of the parameters corresponding to AgCl and AgBr crystals were discussed as concrete examples.

Consideration of BP bound on the Coulomb potential gives rise to an additional system's parameter describing the interaction of electrons with a static charge field. Let us define D^- -center energy as a function of two dimensionless parameters: the Fröhlich constant α of electron–phonon interaction, and the effective rydberg-to- $\hbar\omega$ ratio, $R = m^*e^4/2e_0^2\hbar^3\omega = (e^2/2r_0\hbar\omega\epsilon_0)^2$, where $r_0 = \sqrt{\hbar/2m^*\hbar\omega\epsilon_0}$.

Numerical values of the ground state energy and binding energy for D^- -centers in AgCl and AgBr crystals, obtained by canonical transformation methods in Refs [37, 101, 105], are listed in Table 3.

Figure 7 presents a ‘phase diagram’ of the D^- -center, borrowed from paper [101]. It can be seen that the properties of the D^- -center vary with changes in the parameters α and R .

Electron–phonon interaction can not only increase the binding energy of the D^- -center but also cause its instability (region I). Instability of the D^- -center is realized in TlCl, TlBr, PbS, and PbSe semiconductors. In the P region, the D^- -center for $\alpha \ll 1$ resembles a negative hydrogen atomic ion, and its binding energy increases as the parameter α increases. This parameter region is characteristic of semiconducting II–VI compounds. For $\alpha \geq \alpha_p \approx 7.2$, and $R \geq 2$, the binding energy of the D^- -center rapidly grows. This parameter region is characteristic of crystals with ionic bonding. In the case of strong electron–phonon interaction, the binding energy of the D^- -center becomes commensurate with that of the hydrogen-like D^0 -center and even exceeds it with a further rise in

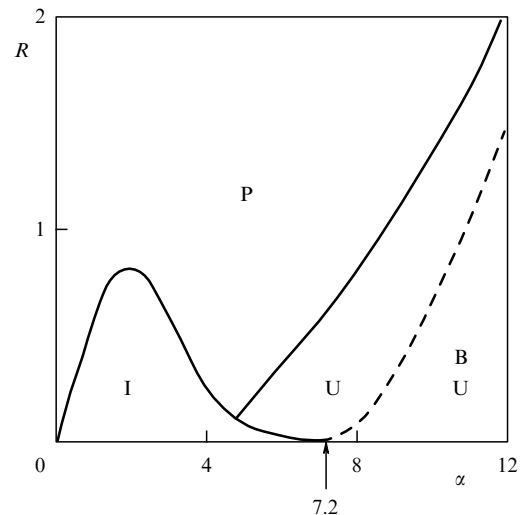


Figure 7. ‘Phase diagram’ of the D^- -center: α is the Fröhlich constant of electron–phonon interaction, and $R = R_D/\hbar\omega$ (the ratio of effective donor rydberg $R_D = m^*e^4/2\hbar^2e_0^2$ to the energy $\hbar\omega$ of longitudinal optical phonons). The D^- -center is unstable in region I; formation of polarons and D^0 -centers is energy-preferred in region P; in region U, the binding energy of the D^0 -center is lower than that of the D^- -center (U^- -centers with negative correlation energy); bipolarons are formed along with U^- -centers in region B. (Taken from Ref. [101].)

Table 3. Ground state energies of the D^- -center (bound on the BP Coulomb potential) taken from Refs [37, 101, 105].

Crystal	α	R	$\hbar\omega$, meV	E^-	E_0	E_b^-	E_b^0	E_b^-/E_b^0	Ref.
CdTe	0.272	0.657	21.08	-1.266	-0.965	0.029	0.693	0.042	[105]
CdS	0.529	0.783	38.0	-1.931	-1.363	0.039	0.834	0.047	[105]
ZnSe	0.45	0.924	31.4	-1.926	-1.428	0.048	0.978	0.049	[105]
AgBr	1.64	1.68	15.4	-5.656	-3.818	0.198	2.178	0.091	[105]
				-5.637	-3.817	0.180	2.177	0.083	[101]
						0.132	2.166	0.061	[37]
AgCl	1.9	1.9	24.4	-6.668	-4.483	0.285	2.583	0.110	[105]
				-6.643	-4.482	0.261	2.582	0.101	[101]
						0.202	2.560	0.078	[37]
CdF ₂	2.53	1.274	50.0	-7.357	-4.510	0.317	1.98	0.016	[105]

Note. E^- and E_0 are the ground state energies of D^- - and hydrogen-like D^0 -centers, respectively. E_b^- and E_b^0 are the binding energies corresponding to these centers.

electron–phonon interaction strength (region U). This region corresponds to alkali–haloid crystals. In region B, BPs form along with D^- -centers. Nevertheless, they tend to localize on positively charged donors because the binding energy of D^- -centers is higher than that of BPs.

3.5 Exchange-coupled pairs of paramagnetic centers in ionic crystals

If a TCBP as a self-contained structure is energetically unstable, then an exchange-coupled pair of paramagnetic centers (PCs) or BP bound on the TC Coulomb potential constitutes a stable system. The first work designed to study PCs and their complexes in a phonon field was carried out using alkali–haloid crystals in the framework of continuous approximation [28]. The F-centers of such crystals being deep, neither the continuous approximation used to describe electron–phonon interaction nor the effective mass approximation for an electron localized at a center can be a proper model. However, there are small hydrogen-like centers for semiconducting II–VI and III–IV compounds, as well as for crystals with ionic bonds (like AgBr and AgCl), for which the continuous approximation is fulfilled with a sufficiently high accuracy [37, 129, 130]. The distance between paramagnetic centers in an exchange-coupled pair is determined by the concentration of impurity centers, crystal growth conditions, and the technical process of defect formation in the crystal lattice rather than by the energy minimum. This makes possible, in principle, the appearance of exchange-coupled pairs in the entire range of distances between paramagnetic centers. The dependences of different contributions to the energy of such TC structures on the distance between PCs were presented in Ref. [105]. If the PCs have moved to great distances from each other, the role of electron correlations significantly decreases. Electron correlations are essential for PCs located at distances smaller than the PC Bohr radius and for one-center systems, such as F^- - and D^- -centers [37, 101, 105, 128].

At large distances between PCs, the energy of interaction between the centers can be regarded as a small addition to the ground state energy that includes the energy of interaction between isolated PCs and phonons. Then, the energy of interaction between the centers, including Coulomb interactions and indirect interactions via a phonon field (or other elementary excitations of crystal lattice), can be considered in terms of the perturbation theory. The problem in such a formulation was addressed in papers [131, 132], where the

contribution of phonons to the energy of nonrelativistic exchange interaction between PCs via the fields of optical and acoustic phonons was studied. The numerical calculations reported in Refs [131, 132] demonstrated that the phonon contribution to the energy of isotropic spin–spin interaction of PCs is of the same order of magnitude as direct Coulomb exchange. The temperature effects of exchange interaction associated with phonons were investigated in Ref. [132].

Today, interest in studying shallow exchange-coupled pairs and D^- -centers has greatly increased owing to the development of nanotechnologies and the possibility, in principle, of creating quantum computers embodying electron spin resonance effects [133–135], in particular, with the use of Ge–Si structures [136].

4. The virial theorem and inter-polaron interaction

Conditions for the fulfillment of the virial theorem (VT) for a polaron functional in the general form for an arbitrary coupling were investigated by Lemmens and Devreese [137], and in application to strong-coupling BPs by the authors of the present review in Ref. [104].

4.1 Scaling transformation and the virial theorem for the strong-coupling polaron and bipolaron

In the strong-coupling limit, the energy E_P of polaron ground state and BP energy E_{BP} are defined as the lower boundaries (absolute minima) of functionals (6) and (7): $E_P = \min J_P[\Psi_1]$ and $E_{BP} = \min J_{BP}[\Psi_{12}]$, respectively, the sole additional condition being normalizability of the trial WF [138, p. 156].

Let us substitute the function $\psi = \lambda^{3N/2} \Psi(\lambda \mathbf{r})$ for the trial function $\Psi(\mathbf{r})$ (where $\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$, N is the number of electrons) and consider the scaling transformation coefficient λ as a variational parameter. If the function $\Psi(\mathbf{r})$ leads to an extremum of the functional of interest, then ψ at $\lambda = 1$ turns into Ψ ; consequently, $J_{BP}[\psi]$ must have an extremum at $\lambda = 1$.

The variation of functional $J_{BP}[\psi(\lambda \mathbf{r})]$ over parameter λ gives

$$\frac{dJ_{BP}}{d\lambda} = 0. \quad (23)$$

Relation (23) represents a mathematical expression of the virial theorem associated with the scaling transformation of

coordinates of the system being considered and holds true for any extremum of the initial functional, including any secondary extremum.

In the strong-coupling limit, terms corresponding to the kinetic and potential energies of functionals (6) and (7) exhibit the property of homogeneity. Due to this, application of the scaling transformation allows for variation over parameter λ in the analytical form and leads to simple expressions for the ground state energy, for which the VT in the simplest form is fulfilled at extreme points, namely, the kinetic energy of the system equals the total energy taken with the opposite sign. The scaling factor and the energy of the self-consistent ground state for a normalized polaron and BP functions are defined by the expressions

$$\lambda = -\frac{V_{P(BP)}}{2T_{P(BP)}}, \quad E_{P(BP)} = -\min \left\{ \frac{V_{P(BP)}^2}{4T_{P(BP)}} \right\}, \quad (24)$$

where $E_{P(BP)}$, $V_{P(BP)}$, $T_{P(BP)}$ are the mean values of total, potential, and kinetic energies of the polaron (BP). In the general case, in the presence of additional Coulomb interactions in the system arising for bound polarons and BPs (e.g., F- and F'-centers in polar crystals), the mean potential energy $V_{P(BP)}$ includes phonon field energy, electron–phonon interaction energy, and the energy of all Coulomb interactions in the system.

It is worth noting that the property of homogeneity over parameter λ for the terms corresponding to mean kinetic and potential energies is lost for the polaron and BP functionals obtained by the Buimistrov–Pekar method; therefore, the VT in the simplest form related to the scaling transformation of electron coordinates cannot be fulfilled.

For a nonzero distance R between two polarons, the VT, even in the strong-coupling regime, has a more complicated form

$$R \frac{dE_{BP}(R)}{dR} + 2T_{BP}(R) + V_{BP}(R) = 0. \quad (25)$$

Naturally, condition (23) must be satisfied at any value of the electron–phonon interaction constant. However, it is impossible to vary the polaron and intermediate-coupling BP functionals over parameter λ and obtain the scaling transformation factor λ in the analytical form. Nevertheless, the VT at points corresponding to minima of polaron and bipolaron functionals must be fulfilled and can be checked numerically.

4.2 The Pekar 1 : 2 : 3 : 4 theorem for the strong-coupling polaron

The VT in application to polarons studied by Pekar [24, 25] was called the 1:2:3:4 theorem. The theorem states that the following relations hold in the strong-coupling limit:

$$T_P = -F_P, \quad E_{ph} = -2F_P, \quad E_{el} = 3F_P, \quad E_{int} = 4F_P, \quad (26)$$

where

$$F_P = T_P + \frac{1}{2} E_{int}, \quad E_{el} = T_P + E_{int}. \quad (27)$$

The ground state energy E_P and quantities T_P , E_{ph} , E_{int} (mean kinetic energy, phonon field energy, and electron–

phonon interaction energy, respectively) are described by the expressions

$$\begin{aligned} E_P &= \langle \Psi_P | H_P | \Psi_P \rangle, \quad T_P = \left\langle \Psi_P \left| -\frac{\hbar^2}{2m^*} \Delta \right| \Psi_P \right\rangle, \\ E_{ph} &= \left\langle \Psi_P \left| \sum_k \hbar \omega_k a_k^+ a_k \right| \Psi_P \right\rangle, \\ E_{int} &= \left\langle \Psi_P \left| \sum_k [V_k a_k \exp(i\mathbf{k}\mathbf{r}) + V_k^* a_k^+ \exp(-i\mathbf{k}\mathbf{r})] \right| \Psi_P \right\rangle. \end{aligned} \quad (28)$$

In the strong-coupling limit at minimum points, the total polaron energy $E_P = T_P + E_{int} + E_{ph}$ equals the kinetic energy taken with the opposite sign, and F_P defined by formula (27) coincides with the total energy of the self-consistent state that can be interpreted as the polaron thermal ionization energy.

4.3 The 1 : 3 : 4 theorem for electron systems at an arbitrary strength of electron–phonon interaction

Relations (26) can be obtained by application of the Hellmann–Feynman theorem [139, 140] to the polaron functional. According to this theorem, when quantity $E_0 = \langle \Phi_0 | H | \Phi_0 \rangle$ depends on a certain parameter β , the derivative with respect to β is expressed as

$$\frac{dE_0}{d\beta} = \left\langle \Phi_0 \left| \frac{dH}{d\beta} \right| \Phi_0 \right\rangle. \quad (29)$$

Electron charge, effective mass, phonon energy, etc. may be considered as the parameter β . Derivation of expressions (26) using the Feynman theorem (29) was implemented by Lemmens and Devreese [137]. This approach is not confined to the strong-coupling limit. Reference [137] provides proof that relations of the 1:3:4 theorem for polarons hold for the entire variation range of the electron–phonon interaction constant, whereas the 1:2 relation, similar to equality $F_P = E_P$, is satisfied only in the strong-coupling limit. The 1:2 relation ensues from the fact that the ground state energy must be proportional to α^2 and corresponds to the strong-coupling limit considered by Pekar [24, 25]. As shown in Ref. [141], the 1:2:3:4 theorem remains true for the terms proportional to α^2 , provided the polaron energy can be represented as a series expansion in the parameter $1/\alpha^2$.

The method employed in Refs [137, 142] for proving the VT for polarons is just as well applicable to an electron system with Coulomb interactions. The objects of interest can be polarons bound on Coulomb centers (shallow impurity centers in covalent crystals or F-centers in ionic crystals), free bipolarons and those bound by Coulomb centers (D⁻- or F'-centers, exchange-coupled pairs of shallow impurity centers, or F₂-centers), as well as more complicated systems of impurity centers in a phonon field. It is easy to show by means of simple transformations that the 1:3:4 theorem remains true for one-electron and two-electron (in the general case, many-electron) systems in a phonon field at an arbitrary strength of the electron–phonon interaction; in the case under consideration, this theorem is formulated in a more general form:

$$-T = \tilde{F}, \quad \tilde{E}_{el} = 3\tilde{F}, \quad \tilde{E}_{int} = 4\tilde{F}, \quad (30)$$

with the notations generalizing definitions (27) for systems with Coulomb interactions:

$$\tilde{F} = T + \frac{1}{2}\tilde{E}_{\text{int}}, \quad \tilde{E}_{\text{int}} = E_{\text{int}} + 2E_C, \quad \tilde{E}_{\text{el}} = T + \tilde{E}_{\text{int}}, \quad (31)$$

where T is the kinetic energy, E_{int} is the electron–phonon interaction energy, and $E_C = \langle \Phi_0 | H_C | \Phi_0 \rangle$ contains all Coulomb interactions in the system.

For the BP functional, one finds

$$\begin{aligned} E_{\text{BP}} &= \langle \Phi_{12} | H_{\text{BP}} | \Phi_{12} \rangle, \quad E_{\text{ph}} = \left\langle \Phi_{12} \left| \sum_k \hbar\omega_k a_k^+ a_k \right| \Phi_{12} \right\rangle, \\ T_{\text{BP}} &= \sum_{i=1,2} \left\langle \Phi_{12} \left| -\frac{\hbar^2}{2m^*} \Delta_i \right| \Phi_{12} \right\rangle, \quad E_C = \left\langle \Phi_{12} \left| \frac{e^2}{\epsilon_\infty r_{12}} \right| \Phi_{12} \right\rangle, \\ E_{\text{int}} &= \sum_{\mathbf{k}, i=1,2} \left\langle \Phi_{12} \left| \sum_k [V_k a_k \exp(i\mathbf{k}\mathbf{r}_i) + V_k^* a_k^+ \exp(-i\mathbf{k}\mathbf{r}_i)] \right| \Phi_{12} \right\rangle, \end{aligned} \quad (32)$$

where Φ_{12} is the WF of the system with Hamiltonian (2). Quantity $E_{\text{BP}} = T_{\text{BP}} + E_C + E_{\text{int}} + E_{\text{ph}}$ defines the total BP energy.

The problem of calculation of the quantities entering into expressions (30) and defined by formulas (31), (32) is worthy of special consideration.

By way of example, we shall discuss the calculation of polaron- and BP-state energies employing the Buimistrov–Pekar method [26]. BP trial function Φ_{12} is chosen in the form (20). In order to calculate mean values of quantities entering Eqns (32), it is convenient to use expressions relating phonon field and kinetic energy operators before and after canonical transformation:

$$\begin{aligned} U^{-1} a_k^+ U &= a_k^+ - F_k - [\exp(-i\mathbf{k}\mathbf{r}_1) + \exp(-i\mathbf{k}\mathbf{r}_2)] g_k, \\ U^{-1} \frac{1}{i} \nabla_{1,2} U &= \frac{1}{i} \nabla_{1,2} \\ &+ \sum_{\mathbf{k}} \mathbf{k} g_k [\exp(-i\mathbf{k}\mathbf{r}_{1,2}) a_k^+ + \exp(i\mathbf{k}\mathbf{r}_{1,2}) a_k], \end{aligned} \quad (33)$$

where $U = \exp(-S_1) \exp(-S_2)$.

In other words, when verifying fulfillment of the virial theorem defined by expressions (30), (31), it is first of all necessary to perform a canonical transformation and obtain expressions corresponding to the new (renormalized) values of kinetic energy and electron–phonon interaction operators. These operations should be followed by averaging over the electron WFs.

Numerical testing indicates that virial relations (30) are fulfilled for the BPs considered by the Buimistrov–Pekar method for an arbitrary strength of electron–phonon interaction. Similar to the strong-coupling limit, the VT is satisfied for both the OC-configuration of BPs and the TC-configuration corresponding to the shallow secondary minimum that disappears if the electron WF is chosen taking account of electron correlations associated with the direct dependence of the WF on the distance between electrons. Thus, the VT is automatically fulfilled at points corresponding to minimal functional values (including secondary minima). In conformity with the variational principle, preference should be given to lower energy values because greater ones may disappear upon choosing a more flexible WF.

5. Polaron–polaron interactions

5.1 Interpolaron interaction in the region of polaron negative binding energy

The consideration of problems pertaining to the study of the dependence of interpolaron interaction energy on the distance between polarons in previous Section 4 involved the region of crystal parameters corresponding to the BP positive binding energy. Analysis of the distinctions between TC BPs and OCBPs is of special importance for this region. Equally significant is the problem of finding the interaction potential between two polarons for the region of weak and intermediate coupling of electrons to a phonon field. In the case of strong coupling, the energy of polaron–polaron interaction as $R \rightarrow 0$ tends toward a finite value and does not diverge as in electron–electron interactions in crystals with a weak electron–phonon interaction. This property persists in the crystal’s parameter region in which no BP forms and a polaron can be regarded as a particle with internal degrees of freedom [24, 111].

The behavior of polaron–polaron interaction energy in the parameter region where repulsion prevails for all interpolaron distances can be illustrated by the dependence of BP energy on the distance between polaron well centers at $\eta = 0.15$, as shown in Fig. 4 (top curve). Evidently, polarons repulse each other but give rise to a common potential well as they draw closer together, the wall whereto both electrons become attracted; therefore, at such distances electron repulsion weakens.

In the literature, the term ‘polaron–polaron interaction potential’ is sometimes applied to different physical quantities. In this review, we define this potential as a quantity corresponding to the difference between the total energy of a two-electron system and the double energy of a free polaron. This is the most general definition that holds true for any EPI strength. Such a definition implies a contribution of all terms of the initial Hamiltonian to the polaron interaction energy, including the energy of electron interaction with the common potential well resulting from polarization of the crystal lattice by electrons.

Adamowski [19] applied the term ‘effective polaron–polaron interaction’ to that part of the effective BP Hamiltonian which depends on the distance r_{12} between electrons:

$$\begin{aligned} V_{12}(r_{12}) &= \frac{1}{r_{12}} \left\{ \beta + 2\alpha\lambda_1(\lambda_1 - 2) \left[1 - \exp\left(-\frac{r_{12}}{\rho_1}\right) \right] \right. \\ &\quad \left. - \frac{\alpha\lambda_1^2}{\rho_1} \exp\left(-\frac{r_{12}}{\rho_1}\right) \right\}, \end{aligned} \quad (34)$$

where $\beta = 2\alpha/(1 - \eta)$.

Potential (34) assumes the character of repulsion potential and increases the total BP energy; however, additional terms in the effective Hamiltonian that can be interpreted as the energy of electron interaction with lattice polarization compensate for repulsion and give rise to the formation of a bound state.

In the effective Hamiltonian obtained by the Buimistrov–Pekar method, a similar interaction can be distinguished:

$$V_{12}(r_{12}) = 2 \sum_{\mathbf{k}} (g_k^2 - 2V_k g_k) \cos(\mathbf{k}\mathbf{r}_{12}). \quad (35)$$

Nevertheless, in both cases such a distinction of pairwise electron–electron interaction potential in the BP functional

has a formal character since variational parameters λ_1 and ρ_1 entering into expression (34) and the variational function g_k entering expression (35) contain implicit information about the total BP functional and they can be found only by its minimization.

The Hamiltonian of the D^- -center differs from the BP Hamiltonian only in the additional Coulomb potential [37, 101]. For this reason, potentials (34) and (35) of effective electron–electron interaction can be extrapolated to the region of weak electron–phonon coupling. Such a passage to the limit was explored by Larsen [37]. In this limit, it is possible to neglect static polarization and put $F_k = 0$ and $g_k \approx V_k/(1+k^2)$ in formula (20). The effective electron–electron interaction potential obtained in this limit assumes the form

$$V_{12}(r_{12}) = \frac{e}{\epsilon_0 r_{12}} + \frac{e}{\tilde{\epsilon} r_{12}} \left(1 - \frac{1}{2} r_{12}\right) \exp(-r_{12}), \quad (36)$$

where $\beta = 2\alpha/(1-\eta)$.

Potential $V_{12}(r_{12})$ is much weaker than the Haken potential [115]

$$V_H(r_{12}) = \frac{e}{\epsilon_0 r_{12}} + \frac{e}{\tilde{\epsilon} r_{12}} \exp(-r_{12}); \quad (37)$$

therefore, the utilization of $V_{12}(r_{12})$ instead of $V_H(r_{12})$ leads to a greater binding energy of the D^- -center.

The energy spectrum of the D^- -center in semiconductors with weak electron–phonon interaction was studied by Shi et al. [143] in the context of perturbation theory.

Buimistrov and Pekar [26] also investigated the passage to the limit of weak coupling. They considered the F-center as an example. Putting the electron WF in the form $\Psi = \text{const} = V^{-1/2}$ (which corresponds to the absence of interaction with the potential of static Coulomb charge, $V_C(r) = 0$, and the limiting case of weak coupling, $V_k \rightarrow 0$) leads to

$$\overline{\exp(i\mathbf{k}\mathbf{r}_i)} = 0, \quad \overline{\exp(i\mathbf{k}\mathbf{r}_{ij})} = \frac{\delta_{ij}}{V}, \quad (38)$$

$$\overline{[\nabla_i \exp(i\mathbf{k}\mathbf{r}_i)]^2} = \frac{k^2}{V},$$

where subscripts $i, j = 1, 2$ label electrons, V is the crystal volume, and the function over-bars denote averaging over the electron WF. In this limit, the effective radius of the F-center tends toward infinity, the electron WF may be replaced by a constant quantity, and the effective functional of the F-center turns into the functional of a weak-coupling polaron with the energy $E_p = -\alpha\hbar\omega$. The Buimistrov–Pekar method [26] that takes no account of translational symmetry begins to give smaller values for the polaron energy than the above linear dependence only for $\alpha > 6$.

More exact values of the polaron energy were obtained by Buimistrov and Pekar [144], who took into consideration in the polaron's effective Hamiltonian the additional terms dependent on the total momentum, which arose from taking account of the translational invariance of the initial Hamiltonian. Expressions for the polaron energy taking into account translational invariance are rather cumbersome; for this reason, numerical calculations of the polaron energy using the translation-invariant Buimistrov–Pekar method remain to be completed. This method has not thus far been used to calculate BP energy, too. Approximate formulas allowing

polaron energy to be estimated in the case of intermediate coupling were presented in Ref. [144]; they make it possible to compare the above method with Feynman's trajectory integral method. By way of example, it was reported in Ref. [144] that the polaron energy estimated at $\alpha = 5$ is roughly 7% smaller than that assessed by the Feynman method [17, 18].

The primary goal in many studies covering electron interactions in crystals via a phonon field has not been to determine the total energy of a two-electron system but to examine the pair potential of electron–electron interactions, which weakens Coulomb repulsion. Tulub [145] has found the electron–phonon interaction potential taking into account relative momentum of electrons in the intermediate-coupling approximation. To begin with, BP Hamiltonian (2) is written in the center-of-mass system; then, coordinates of this center are excluded by applying canonical transformation of Lee, Low, and Pines (LLP) [146, 147]. The total momentum is assumed to be zero and the effective Hamiltonian is split into two parts, one of which, H_0 , includes only terms depending on the interelectron distance and describes 'free' motion of a polaron having effective mass $\mu = m^*/2$ in a phonon field with the frequency $\omega_k = \omega + k^2/(4m)$, while the other, H_1 , contains all the remaining terms of the initial Hamiltonian, plays the role of potential energy operator, and is considered as a correction. The energy correction obtained in Ref. [145] depends on the interelectron distance and has the form

$$\begin{aligned} \varphi_q(r_{12}) = & -\frac{e^2}{r_{12}\tilde{\epsilon}} \frac{a^2 - 2b^2}{a^2} + \frac{e^2}{r_{12}\tilde{\epsilon}} \exp[-(a^2 - b^2)^{1/2} r_{12}] \\ & \times a^{-2} [(a^2 - 2b^2) \cos(br_{12}) - 2(a^2 - b^2)^{1/2} b \sin(br_{12})], \end{aligned} \quad (39)$$

where $a^2 = 2m^*\omega$, $2b = q(1-\tilde{\eta})$, and \mathbf{q} is the relative momentum of two electrons. Quantities $\tilde{\eta}$ and \mathbf{q} depend on the total momentum \mathbf{P} of the center of gravity of interacting electrons; the explicit form of these functions can be found in Refs [146, 147]. Quantity $\tilde{\eta}$ can be determined numerically for each given value of total momentum \mathbf{P} .

When the intermediate-coupling LLP method yields satisfactory results for polaron energy at zero relative momentum \mathbf{q} , expression (39) can be regarded as an exact one. Phonon interaction itself in the intermediate-coupling region described by the LLP theory leads to electron–electron attraction, but the interaction strength is insufficient for BPs to form because the sum of Coulomb $e^2/\epsilon_\infty r_{12}$ and phonon $\varphi_q(r)$ potentials is always positive. As $r \rightarrow 0$, the potential $\varphi_q(r)$ remains finite, and as $r \rightarrow \infty$ the interaction between two electrons is described by the Coulomb law $e^2/(\epsilon_0 r_{12})$.

Bishop and Overhauser [148] used a perturbation theory method to explore indirect interaction between two electrons via optical and acoustic phonon fields. The main conclusion they arrived at is that the effective electron–electron interaction in ionic crystals gives rise to attraction between electrons and results in the screening of Coulomb repulsion. Due to this, taking into account electron–phonon interaction weakens 'priming' Coulomb repulsion $1/(\epsilon_\infty r_{12})$, which becomes equal to $1/(\epsilon_0 r_{12})$. It creates a background for oscillations of the electron–electron interaction potential. The oscillations are associated with the cutoff of the phonon spectrum by the Debye value q_D of the phonon wave vector. The asymptotic behavior of the total effective electron–electron interaction potential at large distances

between the particles has the form [148]

$$\left[\frac{e^2}{\varepsilon_\infty r_{12}} + V(r_{12}) \right]_{r_{12} \rightarrow \infty} \sim \frac{e^2}{\varepsilon_\infty r_{12}} \left[1 + \left(\frac{\varepsilon_\infty}{\varepsilon_0} - 1 \right) \left(1 - \frac{1}{2} \cos \frac{q_D r_{12}}{b_0} \right) \right], \quad (40)$$

where $b_0 = (\hbar q_D^2 / (2m^* \omega))^{1/2}$.

As follows from expression (40), the attractive potential may arise for $\varepsilon_0 > 3\varepsilon_\infty$ between weak-coupling polarons due to oscillating addition. For the parameters of LiCl crystal, the first potential well 28 meV in depth associated with oscillations appears for electrons spaced 33 Å apart. According to the authors of Ref. [148], such deep potential wells may provoke formation of bound electron states in an ionic crystal and Bose condensation in an electron system composed of such pairs.

Oscillating behavior of potential (40) of indirect phonon-mediated interactions and of the potential $V(r_{12})$ defined by expression (39) has essentially different nature. In the latter case, as well as in the derivation of formulas (36), (34), and all expressions for BP energy cited in this review, limits of integration over phonon variables tend to infinity, which corresponds to $q_D \rightarrow \infty$. In Ref. [146], such a scheme is explained by the fact that the contribution to all integrals of the phonon WF rapidly decreases with increasing wave vector.

Formula (40) was derived on the assumption that the WF of two electrons with opposite spins (spin variables are denoted by \uparrow and \downarrow) has the form $\exp(ik_\uparrow r_1)$ and $\exp(ik_\downarrow r_1)$, while electron momenta $k_\uparrow, k_\downarrow \approx 0$. In this case, the WFs of interacting electrons are constants, while interaction potential is spherically symmetric and depends on r_{12} alone. In order to obtain the interaction energy of two electrons, it is necessary to average the effective potential over the electron WF. Then, the contribution of oscillating terms to the polaron interaction energy will be significantly smaller than to the initial expression (40), and the role of oscillating terms averaged over the electron WF chosen in the form $\Psi_{12} = \text{const}$ reduces to addition $\sim V^{-1}$, which can be omitted in the $V \rightarrow \infty$ limit. There is no difficulty in understanding this fact if one makes use of the following relation in integration of potential (40) with respect to volume:

$$\frac{2\pi^2}{r_{12}} = \int \frac{\exp(i\mathbf{k}\mathbf{r})}{k^2} d\mathbf{k}$$

and of expressions (38).

If potential (36) is averaged using WF of the form $\Psi_{12} = \text{const}$, radius of D⁻-center $\rightarrow \infty$, and the second term in this expression vanishes; therefore, the effective polaron interaction energy will also correspond to $e^2/\varepsilon_0 r_{12}$.

5.2 Polaron gas with account of polaron–polaron interactions

De Filippis, Cataudella, and Iadonisi [149] studied the properties of a polaron gas, taking account of polaron–polaron interactions. The consideration was confined to the region of weak and intermediate (on the weak side) electron–phonon coupling. The scheme for obtaining the effective electron–electron interaction is essentially similar to that used by Tulub [145]. First, the coordinate of the BP center of mass is excluded by the LLP method, then the Hamiltonian

thus obtained is studied by the variational method as described in Ref. [146]. The trial function is chosen in the form

$$|\Psi(r_{12})\rangle = U_1(\mathbf{r}_{12}) |0\rangle \varphi(r_{12}),$$

where $\varphi(r) = Nr^\beta \exp(-\gamma r)$, N is the normalization factor, and operator U_1 is defined by the expression

$$U_1(\mathbf{r}_{12}) = \exp [f_{\mathbf{k}}(\mathbf{r}_{12})a_{\mathbf{k}} - f_{\mathbf{k}}^*(\mathbf{r}_{12})a_{\mathbf{k}}^\dagger].$$

Further on, the effective potential of pairwise interelectron interaction is considered as a function of the distance between electrons. Similar to Ref. [148], averaging over this distance is not performed, and the effective potential of interaction between two electrons in a phonon field is examined instead of the total energy of the system of two polarons.

The Bogolyubov–Tyablikov translation-invariant approach [84, 85] proposed by Bogolyubov for polarons was generalized by Solodovnikova and Tavkhelidze [150] for a two-particle system.

The peculiarities of the behavior of effective interaction energy of electrons in a phonon field are of importance for the elaboration of the theory of collective effects observed in a polaron gas. Apart from obvious analogies with collective effects in solid-state plasma, as well as in atomic and molecular gases, effects considered earlier in the work of Bogolyubov and Vlasov [151, 152], the specific dependences of polaron interaction in a phonon field may give rise to a number of special features lacking in the previously studied systems. For example, whole branches of the physics of nonequilibrium processes concerned with the description of gas and liquid properties can be, in the literal sense, ‘rewritten’ for the polaron gas. While fully retaining the problem formulation set in Refs [151, 152] for systems of interacting particles (atoms, molecules, electrons), it is necessary to substitute the potential for pairwise interaction between polarons into the relevant kinetic equations instead of the pairwise interaction potential of the aforementioned systems.

Assuming that polarons possess an internal structure similar to the atomic one, it is possible to consider by analogy the problem of finding solutions to a kinetic equation for the atomic system. The simplest kinetic equation for such a system has the form [152, Ch. 9]

$$\frac{\partial f(\mathbf{r}, \mathbf{v}, t)}{\partial t} + \text{div}_{\mathbf{r}} \mathbf{v} f + \text{div}_{\mathbf{v}} \langle \dot{\mathbf{v}} \rangle f = 0, \quad (41)$$

$$\langle \dot{\mathbf{v}} \rangle = -\frac{1}{m} \text{grad}_{\mathbf{r}} V, \quad (42)$$

$$V(r, t) = \int K(|\mathbf{r} - \mathbf{r}'|) f(\mathbf{r}', \mathbf{v}', t) d\mathbf{r}' d\mathbf{v}', \quad (43)$$

where $K(|\mathbf{r} - \mathbf{r}'|)$ is the interaction energy of the pair of particles at points \mathbf{r} and \mathbf{r}' . In a nondegenerate polaron gas, polarons in thermal equilibrium obey the classical Maxwell–Boltzmann distribution function, similar to atoms and molecules in gases and liquids. This property was used by Pekar [24] to develop a statistical theory of polaron gas in solids, by Deigen [153] to study anomalies related to magnetic susceptibility of metal–ammonia solutions, and by Krivoglaž and Pekar [154] to assess the polaron effect on conduction electron thermodynamics in semiconductors. In the state of thermal equilibrium, the distribution function of a polaron

system has the simplest form

$$f(\mathbf{r}, \mathbf{v}) = \rho(\mathbf{r}) \omega(\mathbf{v}^2), \quad (44)$$

where

$$\rho(\mathbf{r}) = \rho_0 \exp\left(-\frac{V(\mathbf{r})}{\theta}\right), \quad \omega = \left(\frac{mv^2}{2\theta}\right)^{3/2} \exp\left(-\frac{mv^2}{2\theta}\right); \quad (45)$$

here, $\theta = k_B T$, and ρ_0 is the normalization factor.

Substitution of expression (45) into formula (43) gives nonlinear integral equation

$$V(\mathbf{r}) = \int K(|\mathbf{r} - \mathbf{r}'|) \exp\left(-\frac{V(\mathbf{r}')}{\theta}\right) d\mathbf{r}'. \quad (46)$$

According to the main inference stated by Vlasov in his monograph [152, pp. 309–312], Eqn (46) describes both gaseous and crystalline phases depending on density and temperature of the medium, and interaction forces between particles. A specific feature of the crystalline phase is the spatial periodic structure of the distribution function determining the probability of particle location. In accordance with this assumption, the periodicity in question is due to peculiarities of statistical laws of particle motion that relate atomic displacements in a crystal to the stationary periodic structure of the distribution function rather than to the forbiddance imposed on the displacement of atoms from the equilibrium position.

Such a formulation of the problem was used by Iadonisi et al. [155, 156] in a theoretical consideration of the formation of a polaron crystal from a low-density polaron gas. Interaction between polarons was calculated in the framework of Pekar's continuous theory for TC-BPs. Because conjectured crystallization occurred in the case of a low-density polaron gas, the inter-polaron distances were much greater than the effective polaron radius. The difference in interaction potential between polarons at such distances for TC- and OC-models becomes smoothed out because the role of interelectron correlations decreases. The asymptotic behavior of long-range polaron–polaron interaction energy is described by expression (17) regardless of the choice of the model. An important characteristic of the interaction potential of two polarons in OC- and TC-models is its finite value at a zero distance, $R = 0$. In the low-density limit, the long-range polaron–polaron interaction reduces to Coulomb repulsion, $1/\epsilon_0 R$.

Nevertheless, the difference between TC- and OC-models of the bipolaron is smoothed only in case of traditional consideration of Wigner crystallization of polaron gas, when the criterion for the existence of a 'polaron crystal' is given by the amplitude of polaron oscillations about the equilibrium inter-polaron separation [157].

The possibility of periodic solutions to integral equation (46) identified in the Vlasov method with the realization of the crystalline state arises only on condition that attractive forces prevail over repulsive ones; in other words, a necessary condition is one in which the following integral inequality is satisfied:

$$\int K(s) s^2 ds < 0. \quad (47)$$

In this case, integral (47) must have a finite value.

Thus, it is not only the asymptotic behavior of the long-range polaron–polaron interaction potential that is essential for the consideration of polaron gas crystallization effects in the framework of Vlasov's model, but also the region near $R = 0$. At small distances between the centers of polaron polarization wells, electron correlations begin to play an important role and polaron–polaron interaction potential for the OC model has a much deeper potential well than for the TC model (see Fig. 4). For this reason, the value of integral form in the OC model may significantly alter the criteria for the appearance of periodic solutions and lattice parameters of the polaron crystal considered in Ref. [156].

5.3 Effects of static and dynamic screening of electron–electron interactions in a polaron gas

It should also be noted that a necessary condition in the consideration of polaron gas is the assumption of electro-neutrality of the system as a whole. To recall, consideration of Wigner crystallization implies the introduction of the evenly distributed background of positive charges, against which electrons are located uniformly. In Ref. [149], the background positive charge was taken into account, in that the region with $q = 0$ was excluded from the consideration when sums taken over wave vector q were calculated. The dependences of the interaction energy of the two polarons in Fig. 4 were deduced in the framework of traditional consideration of the BP Hamiltonian without regard for additional screening by the compensating charge field. Therefore, screening effects related to the condition of electroneutrality of the polaron gas must be taken into account before these dependences are utilized for substitution into Eqn (46). Moreover, such screening will ensure convergence of integral (46) computed in infinite limits. In this case, the criteria for the existence of BP bound states, polaron and BP effective masses, and distance dependences of pairwise polaron interaction energy (all being functions of polaron gas concentrations) may change.

In intrinsic semiconductors, conditions of electroneutrality are satisfied due to the presence of an electron–hole gas; in doped semiconductors, ionizing impurities functioning as the charged background should be taken into consideration. Because conditions of a crystal electroneutrality are not necessarily of local character and impurities can be nonuniformly distributed over the crystal lattice, experimental examination of Wigner crystallization of an electron gas in real three-dimensional crystals encounters difficulty. Therefore, those dimension-reduced systems in which the role of positive background is played by a system of positively charged ions or holes localized in the spatially remote region of the neighboring layer are preferred [158].

Besides static screening effects associated with the positively charged background, many-electron systems also exhibit dynamic effects attributable to the influence of plasma oscillations of current carriers on the properties of autolocalized electron states, as well as to shallow impurity centers and their complexes. Such effects, sometimes called dynamic screening effects, were considered in many studies. In Ref. [159], perturbation theory methods were applied to find the potential for indirect interactions between paramagnetic centers via a plasmon field in a covalent semiconductor; the authors brought to attention the fact that interactions between electrons of impurity centers and

plasmons lowered the ground state energy of the localized electrons, in perfect analogy with polaron effects in ionic crystals. Effects associated with interactions between electrons and plasma oscillations in the system of holes in a covalent semiconductor with hole conduction were considered in Ref. [160]. Taking into account interactions with plasma oscillations resulted in the appearance of a large-radius exciton (continual exciton), the energy of which was a function of hole concentration in the valence band. In addition, Ref. [160] considered the possibility of the formation of autolocalized one-electron (polaron) and two-electron (bipolaron) states associated with electron–plasmon interactions in covalent crystals. Iadonisi and colleagues [161, 162] considered bipolarons in an ionic crystal with plasma oscillations. Reference [162] focused on deriving the expression for the potential of effective electron–electron interaction via phonons and plasmons, examining asymptotic dependences of the potential in different limiting cases corresponding to (1) the complete absence of interaction with plasmons (electrons interact with phonons alone) and (2) zero EPI (electrons interact only with plasma oscillations), and studying the asymptotic behavior of the potential at large distances, depending on the concentration of the charge carriers. An important consequence of the introduction of the electron–plasmon interaction into the BP functional is also EPI screening since plasmons screen all electrostatic interactions.

Additional effects related to interactions between localized electrons and plasma oscillations manifested themselves in all systems studied in Refs [159–162]; they could reduce the total energy of the system. Plasma oscillations were considered as analogs of longitudinal optical phonons in ionic crystals.

Ionic crystals can exhibit the presence not only quasi-optical plasmons but also quasicoustic plasma oscillations. The possibility of Cooper pairing of current carriers by means of indirect interaction via plasmons was predicted by D Pines long before the discovery of HTSC [163]. Such a mechanism of superconductivity mediated through quasicoustic plasmons was considered by Fröhlich [164] and Pashitskii [165]. Studies on this effect were reviewed by Pashitskii and Pentegov [166]; these authors undertook a detailed analysis of numerical calculations of screened Coulomb and retarded electron–plasmon interactions in quasi-two-dimensional layered crystals with the quasicoustic plasmon dispersion law. It was also shown in Ref. [166] that the plasmonic mechanism of superconductivity ensures rather high temperatures of transition to the superconducting state in 2D-systems.

Expression (45) holds true for polaron gas at sufficiently high temperatures. At low temperatures, peculiarities related to the Fermi statistics of polarons should be taken into account. Brosens, Klimin, and Devreese [167] studied a multielectron system in a phonon field by the trajectory integral method, which allows the effects of translational invariance of many-particle systems to be considered. Analysis involved interparticle interaction in the degenerate polaron gas. Criteria for the formation of a stable multipolaron state corresponding to the ground state of a polaron gas were scrutinized at sufficiently strong EPI and small parameter η . In the limiting case of interaction between two polarons, the singlet term corresponds to the ground state, in excellent agreement with the antiferromagnetic character of polaron–polaron interaction (18).

6. Conclusions

A large number of publications concerning HTSC in materials with totally new chemical composition and structure have appeared since the discovery of HTSC in cuprate MOCs. These materials include bismuth and yttrium ceramics differing from cuprates in certain characteristics of crystalline structure and conductance behavior. Superconductivity and HTSC (with $T_c = 33$ K in $\text{RbCs}_2\text{C}_{60}$) were found in solid fullerenes formed by intercalation of alkali metal atoms into a crystalline structure of C_{60} in the stoichiometric ratio $X_3\text{C}_{60}$ or $XY_2\text{C}_{60}$ (where X and Y are alkali metal atoms) [168–170]. Observation of HTSC with critical temperature $T_c = 39$ K in the well-known material MgB_2 was reported in 2001 [171].

The majority of high-temperature superconductors constitute extremely complicated oxide compounds of variable composition that are highly sensitive to the conditions of synthesis and thermal treatment. Such compounds also demonstrate high instability during their further service. The physical nature and mechanism of HTSC in such materials remain to be elucidated. Controversy pertaining to this issue was most pronounced in the fierce debate between P Anderson and N Mott [67–69], with the active participation of K Müller, who continues to advocate the bipolaron mechanism of HTSC [172] as opposed to the ‘magnetic’ theory of Anderson, despite criticism aimed at him from the latter author. The bipolaron mechanism of HTSC with Jahn–Teller pairing is considered in Refs [172, 173]. Reference [174] contains a review of publications concerned with the relationship between HTSC and Jahn–Teller properties of divalent copper ions.

Bipolaron superconductivity at sufficiently high temperatures can also be expected to appear in other types of ionic compounds, metal–ammonia solutions, etc. Suffice it to say that the CuCl and CdS crystals widely known and used in semiconductor electronics attracted the close attention of researchers long before the discovery of HTSC. Putative observation [175] of HTSC in CdS uniformly compressed at the liquid-nitrogen temperature was reported 6 years before the discovery of HTSC with reference to the detection of the Meissner effect usually accompanying HTSC. It was maintained in Ref. [175] that the magnetic properties of CdS under uniform compression resemble in many respects those of low-temperature type II superconductors, such as TaNb , in which superconductivity was apparent at $T = 4.2$ K.

The anomalous magnetic properties of CuCl were explored over a long period [176, 177]. Diamagnetic anomalies were shown to develop during rapid freezing of CuCl at temperatures above 90 K. Soon, independent studies of this phenomenon [177] confirmed the anomalous enhancement of diamagnetism in a temperature range of 120–230 K. The authors attributed these anomalies and their instability in time to the appearance of HTSC in part of the crystal rather than in the bulk.

The diagnostics of HTSC transitions may be implemented with a highly sensitive electron paramagnetic resonance (EPR) technique. Specifically, transition to the HTSC state is recorded from the nonresonant signal of microwave absorption near zero magnetic fields. Nonresonant EPR signals dependent on the magnetic field and related to the Josephsonian character of superconductors were detected in HTSC materials almost simultaneously with the discovery thereof [178].

The EPR method allowed natural SQUID structures to be detected in monocrystalline HTSCs like $RBa_2Cu_3O_{7-x}$ (where $R = Y, Gd, Eu$) [179]. From angular dependences of microwave absorption, they were shown to be localized strictly in the ab plane of crystal layers and attributed to the direction of HTSC currents that most efficiently screen external magnetic fields, while the component of the screening current parallel to the c -axis is almost inapparent [180].

It can be concluded that EPR makes it possible not only to determine with high accuracy the superconducting transition temperature, but also to confirm (by a noncontact method) that the orientation of superconducting layers in HTSC single crystals coincides with their ab plane. This finding is in excellent agreement with the assumption accepted in the theory of the bipolaron HTSC mechanism that current carriers responsible for the transition to the HTSC state are localized in CuO_2 layers. According to the bipolaron theory, conductance between layers occurs through a hopping mechanism and behaves in layers like the conductance inherent in heavy particles (polarons and bipolarons) [68]. As shown in Section 3.2, the probability of bipolaron formation increases with decreasing dimension of the superconductor or weakening the crystal anisotropy effects.

Nonresonance microwave absorption in weak magnetic fields for $T \leq 280$ K was also detected in ferrielectric single crystals ($LiNbO_3$) characterized by marked anisotropy of static permittivity [181]. Lithium niobate single crystals were simultaneously doped with Mg (up to 8 mol %) and Fe or Cr. This phenomenon was interpreted in Ref. [181] as the emergence of signals from HTSC regions inside the single crystal.

We believe that the search for HTSC in metal–ammonia solutions should be continued and further use of EPR diagnostics may facilitate attempts to repeat Ogg's experiments on HTSC in these materials.

Given the realization of such a possibility in metal–ammonia solutions, the drop in resistance to near zero upon their rapid freezing (when ‘hardening’ of electron and BP concentrations occurs) corresponding to the complete dissociation of alkali metal atoms, e.g., Na, into ions and autolocalized electrons at temperatures relevant to the liquid state [182] can be interpreted as the development of unstable-in-time HTSC. A gradual increase in sample resistance with time from zero (anticipated HTSC at 135 K) to the finite value observed by Dmitrenko and Shchetkin [13] may be due to BP capture by Na^+ ions at low temperatures with the formation of energetically more preferred F- and F' -centers; this accounts for the decrease in the concentration of free BPs and the transition of the solution to the dielectric state. The probability of the formation of F- and F' -centers is higher than that of BPs. Nevertheless, in ionic systems with high static permittivity ($\epsilon_0 \gg \epsilon_\infty$), the bonding of electrons with the positively charged ‘nucleus’ of the F' -center weakens and the singlet electron pair localized at the F' -center can perform translational movements under the action of the external electric field.

The main postulate in one of the first theoretical studies devoted to the anomalous magnetic properties of metal–ammonia solutions [183] was a proposition that complete dissociation of metal atoms into a cation and electron does not occur in such media. It was emphasized that the presence of paramagnetic centers in these solutions (which are analogs of F-centers in alkali–haloid crystals) was confirmed in nuclear magnetic resonance (NMR) experiments. Because

electron correlations were disregarded in the calculation of two-electron systems like F' -centers and bipolarons, the binding energy of these structures was deemed insignificant. Statistical computation of the density of polarons, F-centers, and exchange-coupled pairs for different metal concentrations in a metal–ammonia solution was carried out on the assumption that it contains no other components of interest. The enhanced diamagnetism of the solutions was entirely attributed to the appearance of exchange-coupled pairs or F_2 -centers, i.e., a complete analog of the hydrogen molecule placed in a phonon field and a TCBP prototype. The main proposition of Ref. [183] (the absence of complete electron dissociation in metal–ammonia solutions) has been confirmed in many radio spectroscopy studies [184–186]. The scheme of statistical calculation of the concentration of different constituents in metal–ammonia solutions (polarons, F- and F_2 -centers) at given temperatures and concentrations of dissolved metals, proposed by Deigen [183], may serve as an example for reproducing these findings, taking into account the presence of F' -centers and BPs in the solution. At present, it is the diamagnetic F' -centers that are considered to be responsible for the enhancement of diamagnetism in solutions with a rise in dissolved metal concentration [184–186].

The polaron model of solvated electrons in metal–ammonia solutions, explored in Refs [56, 97, 153, 183, 187], was proposed and developed as an alternative to the cavity model considered, in particular, by Ogg for the explanation of possible autolocalization of one or two electrons in spherically symmetric cavities formed by ammonia molecules. The latter model constituted one of the main lines of research in the physics of solvated electrons [182, 188]. Application of the polaron and BP theory in cluster physics [189–195] made it possible to look at the cavity model in metal–ammonia solutions from the opposite point of view. In either case, a reduction in the system's dimension leads to localization of charged particles virtually at quantum dots [189] simulated by the spherically symmetric cavity or ammonia cluster considered in Refs [190–195]. The polaron theory predicts the minimal cluster size at which an excess electron can be captured. In Refs [190, 191], electronic states in clusters of polar molecules were described in terms of Pekar's polaron model. The approach developed in this work makes it possible not only to estimate the critical cluster size but also to calculate photoionization energy for $(H_2O)_n$ and $(NH_3)_n$ clusters, consistent with its experimental values depending on the number n of molecules in a cluster. The authors of Refs [192, 195] considered BPs and F' -centers localized in clusters. Their data confirm the possibility of the formation of extended one- and two-electron states in water and ammonia clusters. For example, the formation of a polaron and a BP in an ammonia cluster is possible if their radii exceed the critical sizes $R_1 = 36$ Å and $R_2 = 80$ Å, respectively [192]. (For comparison, the effective radius of an ammonia molecule is $R_{\text{eff}} = 2.85$ Å.)

A review of research on metal–ammonia solutions by radio spectroscopy techniques can be found in the work of Edwards [185, 186] and in Ref. [184] concerned with polarons and BPs in these media. The authors not only consider the history of their study and prospects for the search of HTSC in such solutions but also analyze the relationship between the theory of bipolaron superconductivity and BCS theory. Much attention is given to these issues in paper [62], which reviews investigations into large-radius BPs.

The paper by Devreese and Alexandrov [196], focused on the theory of Holstein and Jahn–Teller polarons and small-radius BPs, deals also with Pekar’s polaron and the BP; moreover, studies on large-radius BPs by the trajectory integral method are discussed at length. A separate part of this publication is devoted to polaron excitons.

The present review summarizes an almost 60-year experience in the development of BP theory. The polaron and BP theory being a fundamental one, it has given rise to many new concepts, such as the theory of spin-polarons and BPs in magnetic crystals [197, 198], bipolaron theory of negatively charged clusters [192], and the bipolaron theory of conductivity of polymers [66] and biological molecules [199, 200]. The BP theory may find application in the description of strong interactions between elementary particles [201, 202]; in other words, it has implications for many new issues. As mentioned in the Introduction, elaboration of the bipolaron HTSC theory continues to be relevant and has become highly topical in recent years. The point is that small-radius BPs which were long considered to be the main candidates for Bose particles in HTSC ceramics possess too large a mass and cannot ensure a high critical transition temperature [203]. It was hypothesized that HTSC can be achieved based on the large-radius bipolarons considered in this review, for which the dependence of mass on the electron–phonon coupling constant has a polynomial rather than exponential character. Such an HTSC mechanism appears to be more probable because the data expounded in Section 3.2 suggest that the possibility of BP formation significantly increases in anisotropic polar media, including high-temperature superconductors.

This work was supported by RFBR grants 07-07-00313 and 09-07-12073.

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