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Properties of the shallow D^- -centers in semiconductors with polar and covalent binding

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Abstract. The theoretical consideration of the energy of the lowest singlet and triplet terms of shallow D^- -centers (two electrons, bound with one-charge Coulomb center) in semiconductors with an ionic and covalent binding has been carried out. The electron-phonon interaction is described by a Fröhlich Hamiltonian. The energy of D^- -center is described with the use of a Buimistrov-Pekar method of canonical transformations for arbitrary electron-phonon coupling. It is shown, that for all area of electron-phonon interaction parameters the Buimistrov-Pekar method yields the lowest values of the ground state energy of D^- -centers and free bipolaron in comparison with the best, for today, numerical calculations of the relevant values which have been carried out within the framework of the direct variation methods. The calculations have shown the lack of the bound metastable triplet states corresponding to the lowest triplet energy term of D^- -center and bipolaron for all the area of electron-phonon interaction parameters, in complete analogy to the Hill theorem about the lack of the bound excited states of H^- ion. It is shown that the account of interaction with acoustic phonons can produce considerable lowering the ground state energy of D^- -center in comparison with the magnitude $1.0555Ry$ (where $Ry^* = m^* e^4 / 2\epsilon_0^2 \hbar^2$, m^* – is the effective mass of an electron, ϵ_0 – is a static permittivity of a crystal).

Keywords: bipolaron, Fröhlich Hamiltonian, electron-phonon interaction.

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1. Introduction

Two-electronic centres in the semiconductors (in Si and Ge [1], in GaAs, InP, InSb [2]) are observed on the study of the frequency dependence of photoconductivity in the field of the far infrared frequencies. Atomic analog of a considered system is the negatively charged atom of hydrogen with an ionization energy $0.0555Ry$. In the neglecting by the chemical shift and the electron-phonon interaction, the centres in a crystal have the same energy, but are measured in effective rydbergs $Ry^* = m^* e^4 / 2\epsilon_0^2 \hbar^2$ (where m^* – is the effective mass of an electron, ϵ_0 – is a static susceptibility of a crystal). The account of interaction with phonons can considerably reduce the binding energy of two-electron system in a crystal in comparison with magnitude $0.0555Ry^*$ [3,4]. In alkali-haloid crystals the analogs of D^- -centres are F^- -centres.

Recently, the subjects bound with the study of the energy structure of two-electron systems has been intensively

spread on the low-dimensional systems, including quantum points. The developments are conducted both in experimental field, and in the field of theoretical study of energy levels of – quasi-two-dimensional systems, analogs of D^- -centres [3] and bipolarons [4] in isotropic crystals. Partly it is connected with the interest to similar systems considerably increased in recent years due to the development of nano-technologies and principal possibility to produce quantum computers using electronic spin resonance and, in particular, in structures Ge-Si [5].

In the first works [6,7] devoted to calculations of energies of similar two-electron formations electron correlations were neglected, which considerably reduced magnitude of D^- -centre binding energy. But nevertheless, the Buimistrov-Pekar method offered in [6] for calculation of an energy of one-electron and two-electron states in crystals for arbitrary coupling of an electron system with phonons is, as we suppose, the one of the most prime and effective method for the calculations of an energy spectrum of electron systems in solids.

This method, in the connection with its simplicity, enough frequently has been utilized for the calculations of an energy of specific systems, both the one-electron, and two-electron once in the crystals with an arbitrary coupling of electrons with the phonon field. Nevertheless, usually it is supposed (see, for example, [8]) that the Buimistrov-Pekar method yields the less exact values of an energy of two-electron systems, in comparison with the method of the optimized canonical transformation offered by Adamowski [4] and up to day giving the lowest values of an energy of two-electron systems (bipolarons and D⁻-centres, or bound bipolarons).

We shall show that at enough flexible trial electron wave function (WF), the account of interelectron correlations (WF is directly dependent on the distance between electrons) the Buimistrov-Pekar method yields for all parameters of electron-phonon interaction the lower values, than the Adamowski method. The latter, alongside with tested by us the simple for analytical calculations system of functions, makes possible reliable numerical calculations in the framework of the given method of an energy of two-electron systems (D⁻-centers, bipolarons and exchanged-coupled pairs of paramagnetic centers) in anisotropic crystals, and also in low-dimensional systems for arbitrary coupling of electrons with phonons. In the earlier work [9], the given system of functions was tested for the calculation of an energy bipolaron in crystals with an anisotropic effective mass and inductivity in the requirements of strong electron-phonon interaction.

2. Basic relation

Hereafter we will use the system of units in which $\hbar = 1$, $\omega = 1$ and $2m^* = 1$. It follows that the unit of energy is $\hbar\omega$ and the unit of length is $L_0 = \sqrt{\hbar/2m^*\omega_0}$. In these units a Hamiltonian D⁻ of center in a crystal with an ionic bond (or bound bipolaron in the treatment [4]) is

$$H = \sum_{\mathbf{q}} \mathbf{a}_{\mathbf{q}}^+ \mathbf{a}_{\mathbf{q}} + \frac{\beta}{r_{12}} + \sum_{i=1,2} \left[-\nabla_i^2 - \frac{\gamma}{r_i} + V_{ef}(r_i) \right], \quad (1)$$

For the optical phonons

$$V_{ef}(r_i) = -\sum_{\mathbf{q}} \sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} (\mathbf{a}_{\mathbf{q}} + \mathbf{a}_{-\mathbf{q}}^+) \exp(i\mathbf{q}\mathbf{r}_i) \quad (2)$$

$$\alpha = \frac{e^2}{2\hbar\omega} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \frac{1}{L_0}, \quad \beta = \frac{e^2}{\hbar\omega\epsilon_{\infty}L_0} = \frac{2\alpha}{1-\eta},$$

$$\gamma = \frac{e^2}{\hbar\omega\epsilon_0L_0} = \frac{2\alpha\eta}{1-\eta}, \quad \eta = \frac{\epsilon_{\infty}}{\epsilon_0},$$

where \mathbf{r}_i – is position of i -electron with an effective mass m^* , \mathbf{r}_{12} is a distance between electrons. Let's assume that the Coulomb charge focused at the origin of the coordi-

ates. The influence of polarization of a crystal on a Coulomb field of a static charge is taken into account by introduction static permittivity ϵ_0 . The high-frequency permittivity ϵ_{∞} enters in an operator the electron-electron interaction, $\mathbf{a}_{\mathbf{q}}^+$ ($\mathbf{a}_{\mathbf{q}}$) – is an operator of birth (annihilation) of a longitudinal optical phonon with a wave vector \mathbf{q} . We assume that the frequency of phonons does not depend from \mathbf{q} and is equal to ω , α is the dimensionless Fröhlich constant, V – is a volume of a crystal.

In a covalent crystal the Hamiltonian of electron-phonon interaction can be presented as

$$V_{ef}(r_i) = -\sum_{\mathbf{q}} \sqrt{\frac{4\pi\alpha}{V}} \frac{1}{q} \frac{\hbar^2}{m} (\mathbf{a}_{\mathbf{k}} + \mathbf{a}_{-\mathbf{k}}^+) \exp(i\mathbf{k}\mathbf{r}_i)$$

$$\alpha = \frac{a^2 m^2}{8\pi\rho\hbar^3 c}, \quad (3)$$

where α – is a deformation potential constant, ρ – is a crystal density, c – is a sound velocity (mc^2 serves as the energy unit for acoustic phonons, and the length unit is \hbar/mc).

2.1. The application of the Buimistrov-Pekar method for calculating the energy of two-electron systems in polar crystals with arbitrary electron-phonon coupling

In a modern account the Buimistrov-Pekar method is reduced to application to a Hamiltonian (1) canonical transformation $e^{\alpha\mathbf{S}} \mathbf{H} e^{-\alpha\mathbf{S}}$ with a unitary operator $\mathbf{S} =$

$$= \sum_{\mathbf{k}} (F_{\mathbf{k}}^*(\mathbf{r}_1, \mathbf{r}_2) a_{\mathbf{k}} - F_{\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) a_{\mathbf{k}}^+),$$

where $F_{\mathbf{k}}(r_1, r_2)$ – is a certain function of the electron coordinates. Thus, the following expressions are valid: $e^S a_k e^S \Rightarrow a_k + F_k$, $e^S a_k^+ e^S \Rightarrow a_k^+ + F_k^*$.

After the averaging on the phonon variables, we receive the following functional

$$H = \frac{\beta}{r_{12}} + \sum_{k,i} \nabla_i F_k^* \nabla_i F_k +$$

$$+ \sum_{k,i} \left[-\nabla_i^2 - \frac{\gamma}{r_i} + V_k \left(F_k \exp(ikr_i) + F_k^* \exp(ikr_i) \right) \right] +$$

$$+ \sum_k F_k F_k^*. \quad (4)$$

The expression (4) – is the initial one for further operations.

Let's choose the function F_k as

$$F_k = C_k + \gamma_k f(r_1, r_2), \quad (5)$$

where C_k, γ_k – are the variation parameters.

Having substituted (5) in (4), varied on C_k and γ_k (contrary to the Buimistrov-Pekar method in [4], the parameters C_k and γ_k are picked in the given analytical form) we receive the following expression for a functional of the ground state of a two-electronic system:

$$E_{bp} = J_S + J_i, \quad (6)$$

$$J_i = -\sum_k V_k^2 \frac{\tilde{U}_k^2}{2k^2 + U_k \omega_k}, \quad (7)$$

$$\tilde{U}_k = \langle \Psi_{12} | f_k(r_1, r_2) | \Psi_{12} \rangle \langle \Psi_{12} | L_k^*(r_1, r_2) | \Psi_{12} \rangle - \langle \Psi_{12} | f_k(r_1, r_2) L_k^*(r_1, r_2) | \Psi_{12} \rangle, \quad (8)$$

$$L_k^*(r_1, r_2) = \exp(-ikr_1) + \exp(-ikr_2), \quad (9)$$

$$U_k = \langle \Psi_{12} | f_k(r_1, r_2) | \Psi_{12} \rangle \langle \Psi_{12} | f_k^*(r_1, r_2) | \Psi_{12} \rangle - \langle \Psi_{12} | f_k(r_1, r_2) f_k^*(r_1, r_2) | \Psi_{12} \rangle, \quad (10)$$

where J_i is the component which has appeared for an intermediate coupling, and J_S – corresponds to the functional D⁻ – center in the limit of strong electron-phonon interaction

$$J_s = \bar{T}_{12} + \beta \bar{V}_{ee} - \bar{\gamma}_e + \sum_k V_k^2 \left| \langle \exp(-ikr_1) + \exp(-ikr_2) \rangle \right|^2, \quad (11)$$

$$\bar{T}_{12} = \int \Psi_{12} (\Delta_1 + \Delta_2) \Psi_{12} d\tau, \quad \bar{V}_{ee} = \int \frac{|\Psi_{12}|^2}{r_{12}} d\tau,$$

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

The expression (11) is written in the general form and is valid both for optical and acoustic phonons, if we choose for optical or acoustic phonons the corresponding units of length, energies and constants of electron-phonon interaction.

In the case of mixed ion-covalent binding a good approximation, can be obtained by summing the contribution of optical and acoustic phonons, which is valid assuming that the optical and acoustic branches of phonon operators commute among themselves. Thus, passing in (11) from the summation to the integration on the wave vector, the phonon contribution to the complete functional valid for ion - covalent crystals can be expressed as

$$J_f = -2e^2 \left(\frac{1}{\varepsilon_0} - \frac{1}{\varepsilon_\infty} \right) \int \frac{\Psi_{12}^2 \Psi_{23}^2}{r_{23}} d\tau - 2 \frac{a^2}{\rho c^2} \int \Psi_{12}^2 \Psi_{23}^2 d\tau \quad (12)$$

Choosing $f_k(r_1, r_2) = L_k^*(r_1, r_2)$, and, hence, $\tilde{U}_k = U_k$, we receive

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$$J_i = -\sum_k V_k^2 \frac{U_k^2}{2k^2 + U_k \omega_k}. \quad (13)$$

3. Numerical calculations

Let's choose the two-electron VF as a linear combination of Gaussian orbitals

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{N_{12}}} \times \sum_{i=1}^N C_i (1 + (-1)^S P_{12}) \exp(-a_{1i} r_1^2 - 2a_{2i} \mathbf{r}_1 \mathbf{r}_2 - a_{3i} r_2^2), \quad (14)$$

where P_{12} – is the electron coordinate permutation operator, $S = 0$ and $S = 1$ for the singlet and triplet states, correspondingly.

WFs of the polaron and F center are chosen as

$$\Psi_p(\mathbf{r}) = \frac{1}{N_1} \sum_{i=1}^n C_i \exp(-a_i r^2), \quad (15)$$

where $C_i, \alpha_i, \alpha_{1i}, \alpha_{2i}, \alpha_{3i}$ – are variation parameters, \mathbf{r} is the coordinate of an electron in the polaron, $\mathbf{r}_1, \mathbf{r}_2$ – are, accordingly, the coordinates of the first and second electrons in bipolaron, N_{12}, N_1 – are normalization multipliers.

In the limit $\eta \rightarrow 0$ ($\eta = \varepsilon_\infty / \varepsilon_0$, where ε_∞ and ε_0 – are high-frequency and static permittivity correspondingly) the connection of electrons with the Coulomb kernel weakens and D⁻ centre becomes equivalent to the one-centre bipolaron or Pekar bipolaron.

The one-center bipolaron configuration can be considered as the elementary two-electron system in a crystal. At the same time, the functional of the given system includes the most complex part describing nonlocal interaction of the two-electron system with a phonon field. From this point of view the adding of interaction with a field of a static charge just slightly complicates numerical calculations of an energy spectrum of the bound bipolaron or D⁻center.

The Table 1 lists the values of the free bipolaron energy E_{Bp} obtained using the Gaussian functions (14) ($S = 0$).

For all the area of bipolaron existence, the Buimistrov-Pekar method yields the lowest values for the energy of the ground state and the widest field of existence of the free bipolaron in comparison with the best numerical calculations of the given values carried out within the scope of direct variation methods [10]. In Table 1, also for comparison, given are the best for today numerical calculations of the energy E_{Bp}^A , carried out in [10]. An amount of items in WF (14) for calculation of the bipolaron energy are $N = 5$.

Table 1. The values of the bipolaron energy in units $\hbar\omega$ calculated by the Buimistrov-Pekar method (E_{Bp}) and that of optimized canonical transformation (E_{Bp}^A) [10] for various parameters of the electron-phonon interaction. An amount of items in WF (14) for calculation of the bipolaron energy are $N = 5$.

The energy of the free bipolaron ground state for various α values								
α	6		7		9		20	
η	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A	E_{Bp}	E_{Bp}^A
0	-12.703	-12.601	-16.234	-16.067	-24.927	-24.652	-111.928	-110.504
0.01	-12.595	-12.487	-16.053	-15.91	-24.650	-24.354	-110.497	-109.064
0.1			-14.598	-14.500	-22.068	-21.756	-96.878	-95.335

Fig. 1 shows the dependencies of the free bipolaron (1) and double polaron (2) energy, respectively, from parameters of electron-phonon coupling constant α calculated by the Buimistrov-Pekar method for $\eta = 0$ in $\hbar\omega$ units). Fig. 2 shows the phase diagram of the range of a bipolaron existence in the plane of parameters $\{\eta, \alpha\}$.

Considering the bound bipolaron, there appears the additional parameter describing electron interaction with the field of a static charge. Let's express the energy of

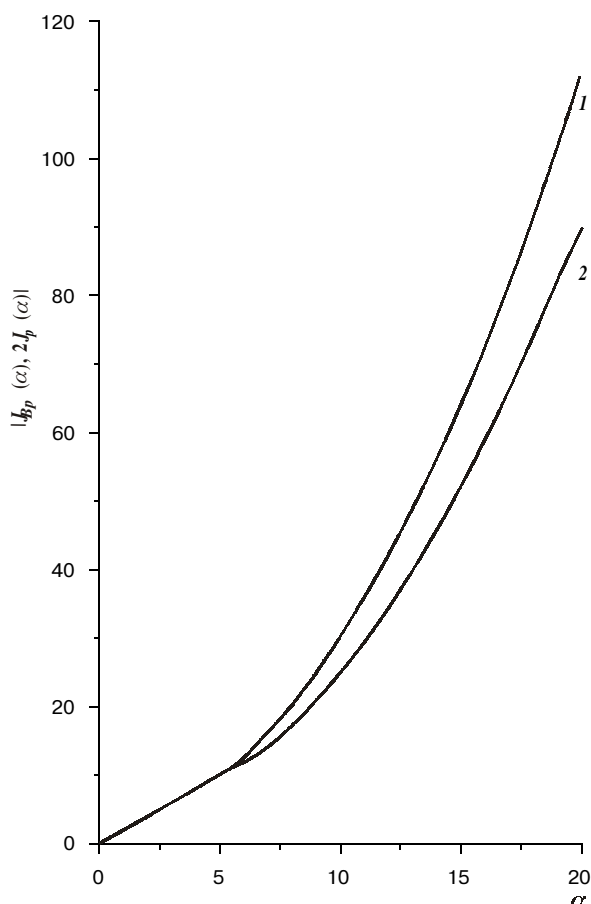


Fig. 1. The dependencies of the bipolaron (1) and double polaron (2) energy respectively from parameters of electron-phonon coupling constant α calculated by Buimistrov-Pekar method for $\eta = 0$ in units $\hbar\omega$.

D⁻-center as a function of two dimensionless parameters, constant of electron-phonon interaction Fröhlich $\alpha = \alpha = e^2 / (2r_0 \hbar \omega) \tilde{\epsilon}$, (where $1/\tilde{\epsilon} = 1/\epsilon_\infty - 1/\epsilon_0$, $r_0 = \sqrt{\hbar / 2m^* \omega}$, $\hbar\omega$ is a frequency of long wavelength longitudinal optical phonons, m^* – is an effective electronic mass) and the ratio of an effective Rydberg to $\hbar\omega - R = m^* e^4 / 2\epsilon_0^2 \hbar^3 \omega = (e^2 / 2r_0 \hbar \omega \epsilon_0)^2$.

The Table 2 lists the energies of the ground state of D⁻ ($S = 0$) and D⁰ centers, E^- and E^0 correspondingly for a number of the crystals. The binding energy is designated as E_B . All energies are expressed in terms of $\hbar\omega$. The superscripts L and A designate values obtained in [3] and [4] correspondingly. The number of terms in WF (14) and (15), at the calculations of the energy D⁻- and D⁰-centers were $N = 12$ and $n = 12$, correspondingly.

To estimate the acoustic phonons contribution to the energy of D⁻-centers in a covalent crystal, we shall choose the typical for similar crystals parameters. So in silicon the value $2a^2 / (\rho c^2 a_0^{*3} Ry^*) \approx 0.065$ (where a_0^* is the effective Bohr radius) and the account of the condensation effect reduces in the lowering the energy of the ground state of D⁻ centres up to $1.064 Ry^*$. In crystals with smaller effective Bohr radius, the contribution of acoustical phonons can play more considerable role.

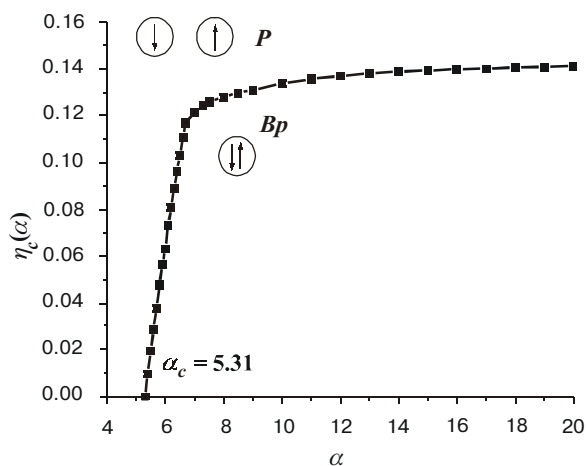


Fig. 2. The phase diagram of the range of a bipolaron existence in the plane of parameters $\{\eta, \alpha\}$.

Table 2. The energy of the ground state of D⁻ center (the bound bipolaron). The superscripts L and A designate values obtained in [3] and [4], correspondingly. The number of terms in WF (14) and (15), at the calculations of the energy D⁻- and D⁰-centers were $N = 12$ and $n = 12$ correspondingly.

The energy of the ground state of D ⁻ center (the bound bipolaron)								
	α	R	$\hbar\omega$, meV	E^-	E_0	E_B^-	E_B^0	E_B^-/E_B^0
CdTe	0.272	0.657	21.08	-1.266	-0.965	0.029	0.693	0.042
CdS	0.529	0.783	38.0	-1.931	-1.363	0.039	0.834	0.047
ZnSe	0.45	0.924	31.4	-1.926	-1.428	0.048	0.978	0.049
AgBr	1.64	1.68	15.4	-5.656 -5.637 ^L	-3.818 -3.817 ^L	0.198 0.180 ^L 0.132 ^A	2.178 2.177 ^L 2.166 ^A	0.091 0.083 ^L 0.061 ^A
AgCl	1.9	1.9	24.4	-6.668 -6.643 ^L -6.662 ^A	-4.483 -4.482 ^L	0.285 0.261 ^L 0.202 ^A	2.583 2.582 ^L 2.560 ^A	0.110 0.101 ^L 0.078 ^A
CdF ₂	2.53	1.274	50.0	-7.357	-4.510	0.317	1.98	0.016

To determine of the flexibility of the considered functions, we calculated the ground state energy of a negatively charged atom of hydrogen H^- . The relevant energy has made -1.055470 ($n = 28$ in (14)) in comparison with the exact value -1.055502 [11].

The problem deserves a separate considerations is deserved of the possibility of the metastable triplet states of D⁻-centres existence. The special importance of the given problem gains owing to the lack of the bound triplet states of D⁻-centers (that is similar to lack of the bound excited states of the ion H^- [12]) is the one of the key requirements for the realization of a method of detection of a two-electron system spin state in the quantum computers based on electron spin resonance [5]. The proposed in [5] process can be briefly described in the following way: the application of an electric field along the line connecting the exchange coupled pair of shallow paramagnetic centers, that are in a singlet state, can result in the transition of the charges on the one of Coulomb centers and formation of D⁻-center. In the triplet state, the similar transition is impossible. The donors remain neutral, and the charge transport from center to center is absent. Just the latter makes observable a spin state of the system.

The variation calculations using the functions (14) for $S = 1$ have shown that for all the area of electron-phonon interaction parameters, including the limiting case of strong coupling ($\alpha > 20$) the relation $E_p + E_D \leq E_{Dt}$ (where E_p , E_D , E_{Dt} – is energy of a polaron, neutral donor and D⁻-center in the triplet state correspondingly) is fulfilled. I.e. in the continual approximation the electron-phonon interaction does not reduce to formation of the metastable triplet state of D⁻-center, in complete analogy to the theorem of lack of bound excited states of a negatively charged atom of hydrogen H^- [12].

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