

BIPOLAR STATES OF CURRENT CARRIERS IN IONIC CRYSTALS

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The system consisting of two conduction electrons in an ionic crystal interacting with the polarization and elastic deformation of the crystal is considered. It is shown that the previous¹ conclusion about the possibility of bipolaron formation does not depend essentially on the approximations applied in reference 1 (variational method, classical treatment of ionic motion) and remains valid in a more rigorous solution.

The effect of elastic deformation, which was not taken into account in reference 1, leads to an improvement in the criterion for the existence of bipolarons and an increase in their binding energy. The motion of bipolarons is considered and the energy of the ground state, effective mass, and moment of inertia are calculated. It is concluded that bipolaron states of the current carriers can exist in ionic crystals at sufficiently low temperatures.

ONE of the approximations usually applied in polaron theory consists in neglecting the exchange degeneracy of the "outer" electrons. In the adiabatic approximation^{2,3} or in the intermediate binding approximation,^{4,5} such a treatment corresponds to choosing a multiplicative form

$$\psi(r_1 \dots r_i \dots r_N) = \prod_{i=1}^N \psi_i(r_i), \quad (1)$$

for the electron part of the wave function of the system; here N is the number of conduction electrons in the crystal.

It is more consistent, however, to choose the corresponding antisymmetrized product as the wave function of the many-electron system under consideration. If the overlap of the single-electron wave functions in the Fock determinant is small, then the multiplicative approximation is a good one. Small overlap of the single-electron functions occurs, obviously, when the Coulomb repulsion of the electrons (proportional to n^{-2} , where n is the index of refraction of the crystal) exceeds the attractive force due to the interaction of each electron with the polarization produced by the remaining electrons (this force is proportional to $c = n^{-2} - \epsilon^{-1}$, where ϵ is the dielectric constant), i.e., for sufficiently small values of the parameters n^2 and c . Then the average distance between conduction electrons is large (in semiconductors, for reasonable values of the concentration of conduction electrons), and the exchange interaction can be neglected.

The exchange forces become essential in the case of significant overlap of the single-electron wave functions. This circumstance can lead to the formation of polaronic quasimolecules in the ionic crystals that have sufficiently high values of n^2 and c . The semiclassical theory constructed by the author and Giterman for two conduction electrons showed that the formation of bipolarons is energetically favorable in crystals with parameters satisfying the condition $n^2 c \geq 0.95$. A bipolaron is a quasiparticle consisting of a self-consistent state of two conduction electrons and the axially symmetric polarization potential well which is produced by them and which binds them.

The treatment in reference 1, like that used in polaron theory,² relies on a straight variational method for calculating the electron part of the wave function of the system. Because of the small value of the calculated energy for bipolaron formation, it might be suspected that this value is due to an insufficiently good choice of the approximate wave function in polaron theory.

Below it will be shown that the previous¹ conclusion about the possible existence of the bipolaron is not based essentially on the variational method. The treatment carried out here differs from that in the previous work in being consistently quantum mechanical. Besides the interaction of the conduction electrons with the polarization deformation, the interaction with the elastic deformation of the crystal is also taken into account. Translation and rotation of bipolarons are also considered.

1. GROUND STATE OF BIPOLARON AT REST

The Hamiltonian of the system consisting of an ionic crystal and two "outer" electrons can be written in the form^{2,3,6,7}

$$\hat{H} = -\frac{\hbar^2}{2\mu} \sum_{i=1}^2 \Delta_i + \sum_{\mathbf{k}, \alpha, i} c_{\mathbf{k}\alpha}^i \chi_{\mathbf{k}\alpha}(\mathbf{r}_i) q_{\mathbf{k}\alpha} + \sum_{\mathbf{k}, \alpha} \frac{\hbar\omega_{\mathbf{k}\alpha}}{2} \left(q_{\mathbf{k}\alpha}^2 - \frac{\partial^2}{\partial q_{\mathbf{k}\alpha}^2} \right) + \frac{e^2}{n^2 |\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2)$$

where the first term is the kinetic energy of the conduction electrons, the second term is their interaction with the polarization and elastic deformations of the crystal, the third is the energy of the ionic oscillations, and the fourth is the energy of electrostatic repulsion of the electrons under consideration; μ is the effective mass of the band electron, $\mathbf{k} = (k_1, k_2, k_3)$ is the index of the normal mode, α is the number of the branch of the mode, $\chi_{\mathbf{k}\alpha}(\mathbf{r}) = (2/V)^{1/2} \sin(\mathbf{k}\alpha \cdot \mathbf{r} + \pi/4)$ are the functions used as a basis for the expansion of the inertial polarization $\mathbf{P}(\mathbf{r})$ and displacement $\mathbf{u}(\mathbf{r})$, $\omega_{\mathbf{k}\alpha}$ and $q_{\mathbf{k}\alpha}$ are the frequency and normal coordinate of the mode.

Below, the case of an isotropic crystal is considered:

$$\begin{aligned} c_{\mathbf{k}\alpha} &= -e \sqrt{\frac{4\pi\hbar\omega_{\mathbf{k}\alpha}}{c}} c / |\mathbf{k}| && \text{for longitudinal optical modes,} \\ c_{\mathbf{k}\alpha} &= a \sqrt{\hbar\omega_{\mathbf{k}\alpha} / E} && \text{for longitudinal acoustic modes,} \\ c_{\mathbf{k}\alpha} &= 0 && \text{for transverse optical and} \\ &&& \text{acoustic modes.} \end{aligned}$$

Here $E = K + (\frac{4}{3})\mu_0$, where K and μ_0 are the bulk and shear moduli, respectively; a is the constant of the deformation potential.

We seek a solution of the Schrödinger equation with the Hamiltonian (2) in the adiabatic approximation. The main criterion for this approximation is the inequality²

$$\hbar\omega_{\mathbf{k}\alpha} \ll \mu c^2 / m. \quad (3)$$

Thus, large values of c , for which bipolaron states occur (according to reference 1 and the results of the present work), also favor fulfillment of the inequality (3).

According to Pekar,³ solution of the Schrödinger equation in the adiabatic approximation is equivalent to finding the minimum of the corresponding functional with an approximate wave function of the form

$$\Psi(\dots \mathbf{r}_i \dots q_{\mathbf{k}\alpha} \dots) = \psi(\dots \mathbf{r}_i \dots) \Phi(\dots q_{\mathbf{k}\alpha} \dots).$$

Minimization with respect to $\Phi(\dots q_{\mathbf{k}\alpha} \dots)$ leads to the following value for the energy of the system:

$$\begin{aligned} \bar{H} &= \sum_{\mathbf{k}\alpha} \frac{\hbar\omega_{\mathbf{k}\alpha}}{2} (2n_{\mathbf{k}\alpha} + 1) + \min_{\psi} J[\psi], \quad n_{\mathbf{k}\alpha} = 0, 1, 2, \dots; \\ J[\psi] &= \frac{\hbar^2}{\mu} \int |\nabla_1 \psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\tau_{12} \\ &+ \frac{e^2}{n^2} \int \frac{\psi^2(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\tau_{12} - 2 \sum_{\mathbf{k}\alpha} \frac{c_{\mathbf{k}\alpha}^2 K_{-\mathbf{k}\alpha}^2}{\hbar\omega_{\mathbf{k}\alpha}}, \\ K_{-\mathbf{k}\alpha} &= - \int |\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 \chi_{-\mathbf{k}}(\mathbf{r}_1) d\tau_{12}. \end{aligned} \quad (4)$$

As indicated by the remarks above, the electron wave function of the system is sought in the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \text{const} \cdot [\psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1)].$$

The single-electron wave functions $\psi_a(\mathbf{r}_1)$ and $\psi_b(\mathbf{r}_1)$ will be determined later.

Substitution of $\psi(\mathbf{r}_1, \mathbf{r}_2)$ into the functional $J[\psi]$ leads to the expression

$$\begin{aligned} J_{\text{bp}}[\psi] &= \frac{\hbar^2}{\mu} \frac{R_1 + SR_2}{1 + S^2} + \frac{e^2}{n^2} \frac{u_2 + u_4}{1 + S^2} - ce^2 \frac{u_1 + u_2 + 4Su_3 + 2S^2u_4}{(1 + S^2)^2} \\ &- \frac{a^2}{E} \frac{v_1 + (1 + 2S^2)v_2 + 4Sv_3}{(1 + S^2)^2}. \end{aligned} \quad (5)$$

where

$$\begin{aligned} S &= \int \psi_a \psi_b d\tau, \quad R_1 = \int (\nabla \psi_a)^2 d\tau, \quad R_2 = \int \nabla \psi_a \nabla \psi_b d\tau, \\ u_1 &= \int \frac{\psi_a^2(1) \psi_a^2(2)}{r_{12}} d\tau_{12}, \quad u_2 = \int \frac{\psi_a^2(1) \psi_b^2(2)}{r_{12}} d\tau_{12}, \\ u_3 &= \int \frac{\psi_a^2(1) \psi_a(2) \psi_b(2)}{r_{12}} d\tau_{12}, \quad u_4 = \int \frac{\psi_a(1) \psi_b(1) \psi_a(2) \psi_b(2)}{r_{12}} d\tau_{12}, \\ v_1 &= \int \psi_a^4 d\tau, \quad v_2 = \int \psi_a^2 \psi_b^2 d\tau, \quad v_3 = \int \psi_a^3 \psi_b d\tau. \end{aligned} \quad (6)$$

We consider first the case of a crystal in which the interaction between the conduction electrons and the elastic vibrations can be neglected ($a^2/E \rightarrow 0$). We seek $\psi_a(\mathbf{r}_i)$ and $\psi_b(\mathbf{r}_i)$ by a variational method. As a result of this, the calculated bipolaron energy will be raised somewhat. We will represent the approximating functions in the variational method in the form

$$\psi_a(\mathbf{r}_i) = k^{3/2} \psi_a^0(kr_i), \quad \psi_b(\mathbf{r}_i) = k^{3/2} \psi_b^0(kr_i), \quad (7)$$

where $\psi_a^0(\mathbf{r}_i)$ and $\psi_b^0(\mathbf{r}_i)$ are the exact electron wave functions of a polaron and \mathbf{k} is the varied parameter. The functions (7) are normalized to unity for all values of \mathbf{k} .

Substitution of (7) into the functional (5), variation with respect to \mathbf{k} , and use of the expression obtained by Pekar² for the polaron functional J_p lead to

$$\begin{aligned} Q &= \frac{J_{\text{bp}}}{2J_p} = \frac{1}{(n^2 c)^2} \frac{R_1}{(1 + S^2)^3 (R_1 + SR_2) u_1^2} [(u_2 + u_4)(1 + S^2) \\ &- n^2 c (u_1 + u_2 + 4Su_3 + 2S^2u_4)]^2. \end{aligned} \quad (8)$$

The functions $\psi(\mathbf{r})$ in the integrands of S , R_i , and u_i are the exact electron wave functions $\psi_a^0(\mathbf{r})$ and $\psi_b^0(\mathbf{r})$ of the polaron.

The value of the ratio $Q = J_{bp}/2J_p$ depends on R , the distance between the points a and b chosen for the approximate $\psi(\mathbf{r}_1, \mathbf{r}_2)$. To determine the bipolaron energy, Q must be minimized with respect to R . Without solving this problem exactly, we will show that, at least for $n^2c = 1$, there is always a value of R for which $Q > 1$. For this purpose, we expand $Q(R)$ in powers of R . Taking R along the z axis for convenience, it is not difficult to show that

$$Q = 1 + \frac{1}{2} \left(\frac{1}{2} R_1 + \frac{R_3}{6R_1} + \frac{2\pi v_1}{3u_1} + \frac{2u_5}{u_1} \right) R^2 + \dots, \quad (9)$$

where

$$R_3 = \int (\Delta\psi_a)^2 d\tau, \quad u_5 = \int \frac{1}{r_{12}} \psi_a^2(1) \psi_a(2) \frac{\partial^2}{\partial z^2} \psi_a(2) d\tau_{12}.$$

To go further, it is necessary to compute the coefficient of R^2 in the expansion (9). This can be done by choosing the best polaron function found by the variational technique

$$\psi(r) = 0.1229 \alpha^{3/2} (1 + ar + 0.4516 a^2 r^2) e^{-ar}, \quad (10)$$

$$\alpha = 0.6585 \mu e^2 c / \hbar^2$$

in place of the "exact" wave function. The error in the polaron energy calculated with the function (10) is only a fraction of a per cent.² Calculating the integrals R_1 , u_1 , and v_1 we find

$$(\partial^2 Q / \partial R^2)_{R=0} = \alpha^2 (0.4105 - 0.2062) > 0. \quad (11)$$

If, instead of (10), we use the wave function

$$\psi = \frac{\alpha^{3/2}}{\sqrt{7\pi}} (1 + ar) e^{-ar}, \quad \alpha = \frac{\mu e^2 c}{2\hbar^2}, \quad (12)$$

which gives the polaron energy to 1–2 per cent, a value of $\partial^2 Q / \partial R^2$ nearly equal to that in (11) is found. Other approximations used in the polaron theory lead to similar results. Obviously, a small variation of $\psi(\mathbf{r})$ about the exact value $\psi_0(\mathbf{r})$ cannot affect substantially the fulfillment of the criterion (11); the derivative $(\partial^2 Q / \partial R^2)_{R=0}$ is essentially positive.

Thus, if $n^2c = 1$, $Q(R)$ has its minimum at $R = 0$ and is equal to unity at this point. For $R > 0$, this ratio, which is underestimated because of the use of a variational method with just the one approximation parameter k , becomes greater than unity; this assures the energetic stability of the bipolaron.

If n^2c decreases from unity, the ratio $Q(R)$ decreases, as is clear from Eq. (8); obviously, however, if n^2c is large enough it can stay greater than unity.

Substitution of (12) into Eq. (8) for $Q(R)$ and maximization with respect to R allow the values of Q and R at the maximum of $Q(R)$ to be de-

termined for arbitrary n^2c . The results obtained coincide with the results of the semiclassical treatment.¹ Bipolaron formation is energetically favored for

$$n^2c \gtrsim 0.95 \quad (13)$$

($Q_{\max} = 1.08$ for $n^2c = 1$). More exact results can be obtained if the following are taken into account:

a) correlation in the motion of the electrons, which introduces into the expression for the approximate function a factor that depends on the separation $|\mathbf{r}_1 - \mathbf{r}_2|$ of the electrons;

b) polar states which correspond to an approximating function of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = N \{ \psi_a(1) \psi_b(2) + \psi_a(2) \psi_b(1) + \gamma_a \psi_a(1) \psi_a(2) + \gamma_b \psi_b(1) \psi_b(2) \},$$

where γ_a and γ_b are variational parameters and N is the normalization factor;

c) mutual deformation of the ψ -clouds of the electrons, as a result of which the polaron function which is originally spherically symmetric becomes axially symmetric.

We have estimated ΔJ , the reduction in the bipolaron energy, due to these causes,* using the numerical results obtained in solving the analogous problem in the theory of F-centers.⁷⁻¹⁰ The radius of the electron ψ -cloud is larger in the bipolaron than in color centers, and therefore the values for the additional binding energy of the bipolaron are underestimated. Even this underestimate is rather significant and amounts to 3–5 per cent of the total bipolaron energy.

We turn now to the consideration of the interaction with elastic deformation. In order to find the minimum of $J_{bp}(R)$ and decide whether or not the bipolaron occurs, it is necessary to repeat with the functional (5) the calculation performed in reference 1. Owing to computational difficulties the calculation has not been accomplished for arbitrary values of n^2 , c , a , and E ; it can be performed for a particular crystal with given values of these parameters. To obtain an estimate of the role of the interaction between the conduction electrons and the elastic deformation of the crystal, we will again consider the special case $n^2c = 1$, $R = 0$. Using (5) and the results of references 6 and 11, we obtain

$$J_{bp}/2J_p > Q(0) = 1 + B,$$

where B , which has been calculated by the author,¹¹ is the ratio of the interaction energy of the polaron

*The results of this calculation will be published separately.

with the elastic deformation of the lattice to the total polaron energy:

$$B = \frac{(1 - \sqrt{1 - \gamma})^3}{\gamma - 2(1 - \gamma)(1 - \sqrt{1 - \gamma})}, \quad \gamma = \frac{437}{2^8 \cdot 7\pi} \frac{e^2 \mu^2 a^2 c}{\hbar^4 E}.$$

According to the estimate made by the author,¹¹ in a real crystal B can have values up to several tenths. B increases with increasing γ . Thus, the elastic interaction can play a significant role in bipolaron formation if, besides a large value of c , the crystal also has large values of the parameters a and μ and small elastic moduli.

2. BIPOLARON MOTION

Up to this point in our treatment, we have not considered the possibility of bipolaron motion, which can occur because of the translational and rotational symmetry of the isotropic crystal. In the solution of this problem, the mathematical apparatus developed by Pekar^{12,13} for treating a nucleon moving in a meson field and generalized to the case where the normal modes have branches with different dispersion laws can be used.

The minimum value of the potential energy, $J[\psi(\mathbf{r}_1, \mathbf{r}_2)]$, of the system will be realized in every case when the function

$$\tilde{\psi} = Y_{\vartheta, \varphi} T_{\xi} \psi(\mathbf{r}_1, \mathbf{r}_2)$$

with arbitrary values of ξ , ϑ , and φ is used for $\psi(\mathbf{r}_1, \mathbf{r}_2)$; here T_{ξ} is the bipolaron translation operator for displacement ξ , $Y_{\vartheta, \varphi}$ is the bipolaron rotation operator, and the angles ϑ and φ give the position of the bipolaron symmetry axis in an arbitrarily chosen Cartesian coordinate system. The order of operation of $Y_{\vartheta, \varphi}$ and T_{ξ} on $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is not essential, but since these operators do not commute, we specifically consider translation first and then rotation. Under these conditions, the coordinate transformation is

$$x'_{\mu} = \sum_{\nu=1}^3 a_{\mu\nu} (x_{\nu} - \xi_{\nu}), \quad (14)$$

where the matrix $\|a\|$ has the form:

$$\|a\| = \begin{vmatrix} \cos \vartheta \cos \varphi & \sin \varphi & -\sin \vartheta \cos \varphi \\ -\cos \vartheta \sin \varphi & \cos \varphi & \sin \vartheta \sin \varphi \\ \sin \vartheta & 0 & \cos \vartheta \end{vmatrix}. \quad (15)$$

We consider the states of the system in which the potential energy differs little from its minimum value. The polarization $\mathbf{P}(\mathbf{r})$ and the elastic displacement $\mathbf{u}(\mathbf{r})$ can be written in the form:

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}_0(\mathbf{r}, \xi, \vartheta, \varphi) + \mathbf{P}'(\mathbf{r}),$$

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}, \xi, \vartheta, \varphi) + \mathbf{u}'(\mathbf{r}), \quad (16)$$

where \mathbf{P}_0 and \mathbf{U}_0 belong to the family of solutions

corresponding to the equilibrium state of the system and are chosen such that \mathbf{P}' and \mathbf{u}' can be considered as small perturbations in the region of space where the wave function of the electrons differs from zero.

In accordance with the above, the parameters ξ , ϑ , and φ which appear in \mathbf{P}_0 and \mathbf{u}_0 are determined by minimizing the energy of the system, H_1 , as calculated by perturbation theory, for states near the equilibrium state. This energy is

$$H_1 = J[\psi_0] + \frac{1}{2} \sum_{\alpha, \mathbf{k}} \hbar \omega_{\mathbf{k}\alpha} [(q_{\mathbf{k}\alpha} - q_{\mathbf{k}\alpha}^0)^2 - \partial^2 / \partial q_{\mathbf{k}\alpha}^2], \quad (17)$$

where $q_{\mathbf{k}\alpha}^0$ are the new equilibrium positions of the harmonically oscillating ions; they depend on the parameters ξ , ϑ , φ :

$$q_{\mathbf{k}\alpha}^0 = \frac{2c_{\mathbf{k}\alpha}}{\hbar \omega_{\mathbf{k}\alpha}} \int \tilde{\psi}^2 \chi_{-\mathbf{k}}(\mathbf{r}_1) d\tau_{12}.$$

In place of the condition for finding the values of ξ , ϑ , and φ which lead to the best description of the states of the system in which the configuration is nearly the equilibrium configuration with the approximation (16), one can use, according to Pekar,¹² the relation

$$\sum_{\alpha} \int \frac{\partial q_{\alpha}^0}{\partial v_i} \hat{\omega}_{\alpha} \varphi_{\alpha} d\tau = 0; \quad (18)$$

where $v_i = \xi_i$ ($i = 1, 2, 3$), $v_4 = \varphi$, $v_5 = \vartheta$;

$$\varphi_{\alpha}(\mathbf{r}) = \sum_{\mathbf{k}} \Phi_{\mathbf{k}\alpha} \chi_{\mathbf{k}}(\mathbf{r}), \quad \Phi_{\mathbf{k}\alpha} = \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}\alpha}}} q_{\mathbf{k}\alpha},$$

$$\varphi_{\mathbf{k}\alpha}^0 = \sqrt{\frac{\hbar}{2\omega_{\mathbf{k}\alpha}}} q_{\mathbf{k}\alpha}^0;$$

The operator $\hat{\omega}_{\alpha}$ is equal to ω_0 for the optical modes ($\alpha = 1$); for the acoustic modes ($\alpha = 2$), it acts according to $\hat{\omega}_{\mathbf{k}\alpha} \chi_{\mathbf{k}}(\mathbf{r}) = (\mathbf{E}/\rho)^{1/2} \mathbf{k} \chi_{\mathbf{k}}(\mathbf{r})$.

In terms of the coordinates $q_{\mathbf{k}}$ and $q_{\mathbf{k}}^0$, (18) takes the form

$$\sum_{\mathbf{k}, \alpha} q_{\mathbf{k}\alpha} \partial q_{\mathbf{k}\alpha}^0 (\dots v_i \dots) / \partial v_i = 0. \quad (19)$$

We seek the solution of the Schrödinger equation with the Hamiltonian (17) (with the supplementary condition (19)) in the form

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2) \Phi(\dots q_{\mathbf{k}\alpha} \dots),$$

$$\Phi(\dots q_{\mathbf{k}\alpha} \dots) = V(\dots v_i \dots) \exp \left\{ -\frac{1}{2} \sum_{\alpha, \mathbf{k}} (q_{\mathbf{k}\alpha} - q_{\mathbf{k}\alpha}^0)^2 \right\}. \quad (20)$$

The variables $q_{\mathbf{k}\alpha}$ enter Φ directly and are also contained in the $v_i (\dots q_{\mathbf{k}\alpha} \dots)$. We will use $\partial / \partial^* q_{\mathbf{k}\alpha}$ to designate differentiation with respect to only the $q_{\mathbf{k}\alpha}$ which do not occur as variables in the v_i . Then

$$\frac{\partial^2}{\partial q_{\mathbf{k}\alpha}^2} = \frac{\partial^2}{\partial^* q_{\mathbf{k}\alpha}^2} + \sum_{i,j} \frac{\partial v_i}{\partial q_{\mathbf{k}\alpha}} \frac{\partial v_j}{\partial q_{\mathbf{k}\alpha}} \frac{\partial^2}{\partial v_i \partial v_j} + \sum_{i,j} \frac{\partial v_i}{\partial q_{\mathbf{k}\alpha}} \left(\frac{\partial}{\partial v_j} \frac{\partial v_i}{\partial q_{\mathbf{k}\alpha}} \right) \frac{\partial}{\partial v_j}$$

$$+ \sum_i \frac{\partial v_i}{\partial q_{\mathbf{k}\alpha}} \left(\frac{\partial^2}{\partial v_i \partial^* q_{\mathbf{k}\alpha}} + \frac{\partial^2}{\partial^* q_{\mathbf{k}\alpha} \partial v_i} \right). \quad (21)$$

The derivatives $\partial v_i / \partial q_{k\alpha}$ occurring in (21) can be calculated from the conditions (18) and (19). By varying $q_{k\alpha}$ arbitrarily, i.e., by arbitrary variation of $\varphi_\alpha(\mathbf{r})$, we obtain

$$-\sum_j dv_j \int_\alpha \int \frac{\partial^2 \varphi_\alpha^0}{\partial v_i \partial v_j} \hat{\omega} \varphi_\alpha d\tau = \sum_\alpha \int \frac{\partial \hat{\omega}_\alpha^0}{\partial v_i} \hat{\omega} \varphi_\alpha d\tau = \frac{\hbar}{2} \sum_{\alpha, k} \frac{\partial q_{k\alpha}}{\partial v_i} dq_{k\alpha}. \quad (22)$$

By using the fact that, due to the choice of ξ , ϑ , and φ , φ_α differs little from φ_α^0 , replacing φ_α by φ_α^0 in (22), and introducing the notation

$$R_{ij}^{(n)} = \sum_\alpha \int \frac{\partial \varphi_\alpha^0}{\partial v_i} \frac{\partial \hat{\omega}_\alpha^n \varphi_\alpha^0}{\partial v_j} d\tau,$$

we represent Eq. (22) in the form

$$\sum_j R_{ij}^{(1)} \partial v_j / \partial q_{k\alpha} = \frac{1}{2} \hbar \partial q_{k\alpha}^0 / \partial v_i.$$

The solution of this system of linear equations gives the desired values of the derivatives $\partial v_i / \partial q_{k\alpha}$.

Substitution of the above relations into the Hamiltonian (17) leads to

$$\begin{aligned} H_1 \Phi &= \left\{ J [\psi_0] + \sum_{\alpha, k} \frac{1}{2} \hbar \omega_{\alpha k} - \frac{\hbar}{2} \frac{O^{(2)} + P^{(2)}}{O^{(1)} + P^{(1)}} \right. \\ &\quad \left. - \hbar \frac{O^{(2)}}{O^{(1)}} - \hbar \frac{R^{(2)}}{R^{(1)}} + \mathcal{H}(\vartheta, \varphi) \right\} \Phi, \\ \mathcal{H}(\vartheta, \varphi) &= -\frac{1}{2} \left\{ A \Delta_\xi + \sum_{i, j=1}^3 A_{ij} \frac{\partial^2}{\partial \xi_i \partial \xi_j} \right. \\ &\quad \left. + A_5 \left(\frac{\partial^2}{\partial \vartheta^2} + \text{ctg } \vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right) \right\}, \end{aligned} \quad (23)^*$$

where

$$A = \frac{\hbar^2}{2} \frac{O^{(2)}}{O^{(1)2}}, \quad A_{ij} = \frac{\hbar^2}{2} \left[\frac{O^{(2)} + P^{(2)}}{(O^{(1)} + P^{(1)})^2} - \frac{O^{(2)}}{O^{(1)2}} \right] a_{i3} a_{j3},$$

a_{i3} , a_{j3} are components of the matrix (15)

$$\begin{aligned} O^{(n)} &= -\sum_\alpha \int \frac{\partial^2 \varphi_\alpha^0(\mathbf{r})}{\partial x^2} \hat{\omega}_\alpha^n \varphi_\alpha^0(\mathbf{r}) d\tau, \\ O^{(n)} + P^{(n)} &= -\sum_\alpha \int \frac{\partial^2 \varphi_\alpha^0(\mathbf{r})}{\partial z^2} \hat{\omega}_\alpha^n \varphi_\alpha^0(\mathbf{r}) d\tau, \\ R^{(n)} &= R_{55}^{(n)}, \quad A_5 = \hbar^2 R^{(2)} / 2R^{(1)2} \end{aligned}$$

By setting $V(\dots v_i \dots) = \exp(i\mathbf{f} \cdot \boldsymbol{\xi}) F(\vartheta, \varphi)$, we obtain the equation for F :

$$\begin{aligned} \left\{ -\frac{1}{2} A_5 \left[\frac{\partial^2}{\partial \vartheta^2} + \text{ctg } \vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \right] \right. \\ \left. + \frac{1}{2} A f^2 + \frac{1}{2} \sum_{i, j=1}^3 A_{ij} f_i f_j \right\} F = W F. \end{aligned} \quad (24)$$

For sufficiently small \mathbf{f} , the last term in (24) can be treated as a perturbation. Then, in the zeroth approximation

$$F(\vartheta, \varphi) = e^{im\varphi} P_l^{|m|}(\cos \vartheta), \quad W^0 = \frac{1}{2} A_5 l(l+1) + \frac{1}{2} A f^2, \\ m = 0, \pm 1, \pm 2, \dots; \quad l = 0, 1, 2, \dots, \quad (25)$$

*ctg = cot.

$P_l^{|m|}$ is the associated Legendre function. The matrix element of the perturbation is

$$W' = \frac{1}{2} B f^2 \langle \cos^2 \delta \rangle, \quad B = \frac{\hbar^2}{2} \left\{ \frac{O^{(2)} + P^{(2)}}{[O^{(1)} + P^{(1)}]^2} - \frac{O^{(2)}}{O^{(1)2}} \right\}, \\ \langle \cos^2 \delta \rangle = \int \cos^2 \delta |F(\vartheta, \varphi)|^2 d\tau_{\vartheta, \varphi}; \quad (26)$$

where δ is the angle between the direction of the translational motion of the bipolaron and its symmetry axis.

The quantity $W_1 = \frac{1}{2} (A + B \langle \cos^2 \delta \rangle) f^2$ is the translational kinetic energy of the bipolaron, and $M = \hbar^2 / (A + B \langle \cos^2 \delta \rangle)$ is its effective phonon-field mass; the latter, as is evident from formulas (25) and (26), depends on the rotational quantum numbers, l and m . For example, for a non-rotating bipolaron ($l, m = 0$) we have $M_{0,0} = \hbar^2 / (A + \frac{1}{3} B)$; for $l = 1, m = 0$, we have $M_{1,0} = \hbar^2 / (A + \frac{3}{5} B)$, etc.

The quantity $W_2 = \frac{1}{2} A_5 l(l+1)$ is the rotational energy of the bipolaron; $I = \hbar^2 / A_5$ is the phonon-field moment of inertia. The total energy of the moving (translating and rotating) bipolaron is

$$\begin{aligned} H_1 &= J [\psi_0] - \frac{\hbar}{2} \frac{O^{(2)} + P^{(2)}}{O^{(1)} + P^{(1)}} - \hbar \frac{O^{(2)}}{O^{(1)}} - \hbar \frac{R^{(2)}}{R^{(1)}} \\ &\quad + \frac{\hbar^2 f^2}{2M_{l,m}} + \frac{\hbar^2 l(l+1)}{2I}. \end{aligned}$$

The criterion for the existence of bipolarons takes the form

$$\begin{aligned} Q &= \bar{H}_1(\mathbf{f}, l, m = 0) / 2\bar{H}_p \\ &= \frac{J_{\min} [\psi(\mathbf{r}_1, \mathbf{r}_2)] - \hbar O^{(2)} / O^{(1)} - \hbar(O^{(2)} + P^{(2)}) / 2(O^{(1)} + P^{(1)}) - \hbar R^{(2)} / R^{(1)}}{2 \{ (J_{\min} [\psi])_p - 3\hbar O^{(2)} / 2O^{(1)} \}_p} > 1. \end{aligned} \quad (27)$$

The subscript "p" indicates that the corresponding quantity refers to polarons, not bipolarons.

The remainder of the calculation amounts to just the computation of the integrals $O^{(n)}$, $P^{(n)}$, and $R^{(n)}$ which appear in the expressions for the bipolaron energy, effective mass, and moment of inertia.

This problem does not involve any difficulties of principle, but in many cases involves cumbersome computations. If only the optical modes ($\alpha = 1$) are considered and the frequency dispersion is neglected, then the criterion for bipolaron existence (27) can be written

$$Q = \frac{J_{\min} [\psi(\mathbf{r}_1, \mathbf{r}_2)] - 5\hbar\omega_0 / 2}{2 (J_{\min} [\psi(\mathbf{r}))]_p - 6\hbar\omega_0} > 1,$$

where ω_0 is the limiting frequency.

This criterion is somewhat stricter than that given above in Eq. (13). The reason for the difference is that the equivalence mentioned in Sec. 1 of this paper between the adiabatic approximation and the variational method with multiplicative

wave functions holds for systems which do not have translational symmetry. If the latter is present, then the treatment of the present section is more rigorous and does not give complete equivalence.

However, for the values of the frequency ω_0 usually encountered in ionic crystals, the difference of $\frac{1}{2}\hbar\omega_0$ between the bipolaron energies of this section and of Sec. 1 is not very significant. The bipolaron energy decrement, ΔJ , mentioned in the remarks following Eq. (13), is related to $\frac{1}{2}\hbar\omega_0$ by (according to the estimate)

$$|\Delta J| \gtrsim \frac{1}{2}\hbar\omega_0.$$

Such a quantitative change in the bipolaron existence criterion does not change in principle the conclusion that bipolarons can exist.

The values of the bipolaron effective mass and moment of inertia can be calculated in the same approximation with the aid of the integrals

$$\begin{aligned} O^{(n)} &= -2e^2c\omega_0^{n-2} \int \frac{1}{r_{13}} \psi^2(r_1, r_2) \frac{\partial^2}{\partial x_3^2} \psi^2(r_3, r_4) d\tau_{1234} \\ &= -e^2c\omega_0^{n-2} (1+S^2)^{-2} [\langle aaaa \rangle + \langle aabb \rangle \\ &\quad + 2S(\langle aaab \rangle + \langle abaa \rangle) + 2S^2 \langle abab \rangle], \end{aligned}$$

$$\begin{aligned} 3O^{(n)} + P^{(n)} &= 8\pi ce^2\omega_0^{n-2} \int \psi^2(r_1, r_2) \psi^2(r_1, r_3) d\tau_{123} \\ &= 4\pi ce^2\omega_0^{n-2} (1+S^2)^{-2} [v_1 + (1+2S^2)v_2 + 4Sv_3], \end{aligned}$$

where

$$\langle klmn \rangle = \int \psi_k(r_1) \psi_l(r_1) \frac{1}{r_{12}} \frac{\partial^2}{\partial x_2^2} \psi_m(r_2) \psi_n(r_2) d\tau_{12}.$$

The two-point integrals $\langle klmn \rangle$, v_2 , v_3 and S can be reduced to linear combinations of the overlap integrals tabulated by Kopineck.¹⁵

By using the limiting values of the integrals $O^{(n)}$ and $P^{(n)}$, it is easy to find, in particular, the limiting value of the ratio of the effective masses of the bipolaron and polaron:

$$M_{0,0}/M_P \rightarrow 4 \quad (R \rightarrow 0), \quad M_{0,0}/M_P \rightarrow 2 \quad (R \rightarrow \infty).$$

3. CONCLUSION

The results obtained above show that the current carriers can be bipolarons in ionic crystals with sufficiently high values of the parameters n^2 , c , μ , a , E^{-1} , and $(\hbar\omega_0)^{-1}$.

The conclusion does not contradict the assertion that bipolarons cannot exist which is contained in Pekar's monograph,² since only the special case $R = 0$, $a = 0$ is considered there.

The case $c = 0$, $a = 0$ corresponds to the "doublon" state considered by Vol'kenshtein and Bonch-Bruevich.¹⁴ The doublon energy level, however, is located above the bottom of the conduction band. Due to the presence of lattice polarization and elastic deformation, the paired states of the

current carriers are appropriate to the ground state of the system. This circumstance can lead to a large number of experimentally verifiable effects, for example, superconductivity, and also sharp changes in magnetic, optical, and other properties of the crystal around the temperature at which the ratio of the equilibrium concentrations of bipolarons and polarons — which are excited states of the current carriers — goes through unity.

It is possible that taking into account exchange forces due to interaction of the quasiparticles with the phonon field could lead to the appearance of quasimolecules in other cases (for example, biexcitons). This problem may also be of interest in many-body theory other than that used in solid state problems, for example, in the treatment of nucleons interacting with the meson field.

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