

ADIABATIC THEORY FOR THE BIPOLARON

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A translation-invariant adiabatic theory is constructed for the bipolaron. It is shown that motions in the bipolaron are divided: the relative electron coordinates describe fast electron oscillations in the induced polarization well and the center of mass coordinates represent slow electron movement followed by polarization. Nonlinear differential bipolaron equations are derived which are asymptotically exact in the adiabatic limit. Particlelike solutions of these equations correspond to the bipolaron bound state. The exact solution yields the value of the ion critical parameter $\eta = 0.31$ for which the bipolaron state is stable, where $\eta = \epsilon_\infty / \epsilon_0$ so and $\epsilon_\infty, \epsilon_0$ are high-frequency and static dielectric permittivities. The energy, the total energy, the effective mass, the radius, and the critical values of the electron-phonon coupling constants are calculated for the bipolaron. The results obtained are generalized to the case of two-dimensional bipolarons.

I. INTRODUCTION

Considerable study has been given to bipolarons in recent years not only due to general theoretical interest in the problem but also owing to important applications, such as an interpretation of high-temperature superconductivity.^{1,2}

The history of investigations into the bipolaron theory is rather dramatic: Over a long period of time calculation errors have been calling into question the very possibility of the existence of bipolarons. (For details see Refs. 3,4.)

As distinct from polaron theory, where asymptotically exact solutions are known in both the limit of weak coupling and the limit of strong coupling,^{5,6} bipolaron theory has no exact solutions for now. What is more the bipolaron lacks solutions for small and intermediate values of the coupling constant whatsoever. According to Ref. 7 the bound bipolaron state is possible only at sufficiently large coupling constants $\alpha > 7.2$. It is thought that in the adiabatic limit both electrons move in a common polaron potential well, induced by their oscillations in this well. For this reason the interaction of electrons with polarization $\phi(r_1, r_2)$ is presented as

$$\phi(r_1, r_2) = F(r_1) + F(r_2). \quad (1)$$

This form is not translationally invariant and corresponds to the phenomenological approach where the potential polarization well is assumed to be spatially fixed.

In this paper a consistent adiabatic translationally invariant bipolaron theory is developed, based on Bogolubov-Tyablikov adiabatic theory.^{8,9} According to the approach presented the bipolaron movements are divided in the adiabatic limit. The relative electron coordinates describe fast oscillations of electrons in the potential well, which takes the form of their potential interaction

$$\phi(r_1, r_2) = \phi(r_1 - r_2). \quad (2)$$

The center of mass coordinates describe the slow motion of the electrons. It is suggested that the potential polarization well is not spatially fixed and follows adiabatically the movement of the electron center of mass. Therefore the interaction Eq. (2) is automatically translation invariant.

The results obtained with this approach allow a glance at the nature of bipolarons. In the majority of ionic crystals where bipolaron states are possible and the electron-phonon coupling for one polaron is weak or intermediate, for the bipolaron this coupling is strong. Critical values of electron-phonon coupling at which bipolaron states are stable turn out to be approximately 3 times as small as the corresponding values obtained from variation estimates.

Another important result is in the fact that the exact solution yields the value of the ion coupling critical parameter $\eta = 0.31$, where $\eta = \epsilon_\infty / \epsilon_0$; $\epsilon_\infty, \epsilon_0$ are high-frequency and static dielectric permittivities

of the ionic crystal. According to variation estimates this criterion is much more rigid $\eta = 0.14$ (in Refs. 3,4) and restricts drastically the class of crystals where the bipolarons can exist. It is also shown that the best variation estimates of the bipolaron energy in the adiabatic limit correspond exactly to the phenomenological approach.

The results, obtained for the three-dimensional polaron, are also applied to the two-dimensional (2D) bipolaron. The energy of the 2D bipolaron is found and the critical values of the electron-phonon coupling constants at which the 2D bipolaron is stable are derived.

II. BIPOLARON PHENOMENOLOGICAL THEORY

In phenomenological description of bipolaron states one proceeds from the fact that the mean Coulomb field induced by two excess electrons locally polarizes the medium and polarization P is equal to

$$P = \frac{D}{4\pi\tilde{\epsilon}}, \quad (3)$$

where $\tilde{\epsilon}^{-1} = \epsilon_{\infty}^{-1} - \epsilon_0^{-1}$, D is the electron induction,

$$D = -2e \int |\psi(r', r)|^2 \frac{(r - r')}{|r - r'|^3} d^3 r' d^3 r_1, \quad (4)$$

and $\psi(r_1, r_2)$ is the electron wave function. As a result the bipolaron energy is determined by the functional

$$E_2[\psi] = \frac{\hbar^2}{2m} \int |\nabla_{r_1} \psi|^2 d^3 r_1 d^3 r_2 + \frac{\hbar^2}{2m} \int |\nabla_{r_2} \psi|^2 d^3 r_1 d^3 r_2 + \frac{e^2}{\epsilon_{\infty}} \int \frac{|\psi|^2}{|r_1 - r_2|} d^3 r_1 d^3 r_2 - \frac{1}{8\pi\tilde{\epsilon}} \int D^2 d^3 r \quad (5)$$

or, by Eq. (4) it can be rewritten as

$$E_2[\psi] = \frac{\hbar^2}{2m} \int |\nabla_{r_1} \psi|^2 d^3 r_1 d^3 r_2 + \frac{\hbar^2}{2m} \int |\nabla_{r_2} \psi|^2 d^3 r_1 d^3 r_2 - \frac{2e^2}{\tilde{\epsilon}} \int \frac{|\psi(r', r_1)|^2 |\psi(r'', r_2)|^2}{|r' - r''|} d^3 r' d^3 r'' d^3 r_1 d^3 r_2 + \frac{e^2}{\epsilon_{\infty}} \int \frac{|\psi|^2}{|r_1 - r_2|} d^3 r_1 d^3 r_2. \quad (6)$$

So the phenomenological approach yields an expression where the interaction between particles induced by the polarization field takes the form

$$\phi(r_1, r_2) = -\frac{2e^2}{\tilde{\epsilon}} \int \frac{|\psi(r', r_1)|^2 |\psi(r'', r_2)|^2}{|r' - r''|} d^3 r' d^3 r''. \quad (7)$$

The form of Eq. (6) directly suggests an important conclusion. Variation of Eq. (6) over ψ produces a Schrödinger equation, whose efficient potential takes the Coulomb form at sufficiently large $r_1 - r_2$. The bound state exists only if the potential is attractive which is given by the condition

$$\epsilon_{\infty}/\epsilon_0 < 0,5. \quad (8)$$

The stability condition of bipolaron states differs from Eq. (8) and may be written as

$$E_2 - 2E_1 < 0, \quad (9)$$

where

$$E_1 = \frac{\hbar^2}{2m} \int |\nabla \psi|^2 d^3 r - \frac{1}{8\pi\tilde{\epsilon}} \int D_1^2 d^3 r. \quad (10)$$

E_1 is the total energy functional for one polaron; D_1 is obtained from Eq. (4) by replacing $2e$ by e . As

noted above, the best estimates, resulting from Eqs. (6) – (10) suggest the following criterion of stability of bipolaron states.^{3,4}

$$\varepsilon_{\infty}/\varepsilon_0 < 0,14. \quad (11)$$

III. TRANSLATION-INVARIANT ADIABATIC THEORY

The Pekar-Fröhlich Hamiltonian for two electrons in teracting with a phonon field is of the form

$$H = -\frac{\hbar^2}{2m}\Delta_{r_1} - \frac{\hbar^2}{2m}\Delta_{r_2} + \sum_f \hbar\omega_f b_f^* b_f + U(|r_1 - r_2|) + \sum_f \{c_f e^{if(r_1-r_0)} b_f + c_f^* e^{-if(r_1-r_0)} b_f^*\} \\ + \sum_f \{c_f e^{if(r_2-r_0)} b_f + c_f^* e^{-if(r_2-r_0)} b_f^*\}, \quad (12)$$

$$c_f = ef^{-1} \sqrt{2\pi\omega_f / \tilde{\varepsilon}V}, \quad (13)$$

where r_1 and r_2 are the coordinates of the first and the second electron, respectively. ω_f are phonon frequencies and r_0 is the arbitrary reference point. It is generally assumed that $r_0 = 0$ and in this case the Hamiltonian, Eq. (12), is basic in the bipolaron theory.

The degeneracy of the Hamiltonian, Eq. (12), with respect to r_0 has a dominant role in the development of translation-invariant bipolaron theory. Turning to the center of mass coordinates of two electrons r and R by the formulas

$$r = r_1 - r_2, \quad R = (r_1 + r_2)/2, \quad (14)$$

and passing on to complex coordinates of the field q_f using the formulas

$$q_f = \frac{\varepsilon(b_f + b_{-f}^*)}{\sqrt{2}}, \quad -i\frac{\partial}{\partial q_f} = \frac{i(b_f^* - b_{-f})}{\varepsilon\sqrt{2}}, \quad (15)$$

where ε is a small parameter, we can present the Hamiltonian, Eq. (12), in the form

$$H = -\frac{\hbar^2}{4m}\Delta_R - \frac{\hbar^2}{m}\Delta_r + \sum_f A_f \rho_f(r) e^{if(R-r_0)} q_f + U(r) + \frac{1}{2} \sum_f v_f q_f q_{-f} - \frac{\varepsilon^4}{2} \sum_f v_f \frac{\partial}{\partial q_{-f}} \cdot \frac{\partial}{\partial q_f}, \quad (16)$$

$$\rho_f(r) = 2 \cos fr / 2, \quad (17)$$

$$A_f = \sqrt{2} c_f, \quad (18)$$

$$\hbar\omega_f = \varepsilon^2 v_f, \quad (19)$$

According to Refs. 8,9 the radius vector of the bipolaron center of mass \mathbf{R} can be written as a sum

$$\mathbf{R} = \mathbf{r}_0 + \mathbf{q}, \quad (20)$$

where r_0 acts as the fluctuating part of the center of mass coordinates and q is the translation-invariant part. We can replace q_f by new complex field coordinates Q_f using the formulas

$$q_f = (U_f + \varepsilon Q_f) e^{-i(fq)}, \quad (21)$$

These new coordinates must be subject to the three additional conditions

$$\sum_f \mathbf{f} v_f^* Q_f = 0, \quad (22)$$

where v_f are the complex numbers, satisfying the relations of reality $v_f = v_f^*$, which are chosen so that the orthogonality conditions might be fulfilled,

$$\sum_f f^\alpha f^\beta v_f^* U_f = \delta_{\alpha\beta}, \quad (23)$$

where f^α, f^β are the components of the vector f .

Relations (20) – (23) present a canonical Bogolubov-Tyablikov transformation in the polaron

theory. Turning in Eq. (16) from the variables R, q_f to the new variables r_0, q, Q_f and observing condition (22) we rewrite the Hamiltonian, Eq. (16), as

$$H = H_0 + \varepsilon H_1 + \varepsilon^2 H_2 + \dots \quad (24)$$

Taking into account that the variable q appears in the transformed Hamiltonian only in the form of canonically conjugate impulse $\hat{P} = -i\hbar\partial/\partial q$,

$$-i\hbar\frac{\partial}{\partial q} = -i\hbar\frac{\partial}{\partial R} + \sum_f \hbar f q_f \frac{\partial}{\partial q_f}, \quad (25)$$

which is the full impulse of the whole system (electrons plus the phonon field), the wave function of the system can be presented as

$$\Psi = e^{ipq} e^{i\sum_f S_f Q_f / \varepsilon} \phi(r, r_0, Q_f), \quad (26)$$

$$\phi = \phi_0 + \varepsilon \phi_1 + \varepsilon^2 \phi_2 + \dots \quad (27)$$

Accordingly the terms of expansion, Eq. (24), do not contain the variable q and take the form

$$H_0 = -\frac{\hbar^2}{4m}\Delta_{r_0} - \frac{\hbar^2}{m}\Delta_r + \sum_f A_f U_f \rho_f(r) + \frac{1}{2} \sum_f v_f |U_f|^2 + \frac{1}{2} \sum_f v_f \left| S_f + i \frac{v_f^*}{\hbar} (If) \right|^2 + U(r), \quad (28)$$

$$H_1 = \sum_f v_f \left(S_f^* - i \frac{v_f}{\hbar} (If) \right) P'_f + \sum_f \left\{ A_f \rho_f(r) + v_f U_f^* - \left(S_f + i \frac{v_f^*}{\hbar} (If) \right) \sum_g v_g \left(S_g^* - i \frac{v_g}{\hbar} (Ig) \right) (gf) v_g^* \right\} Q_f, \quad (29)$$

$$P'_k = P_k - v_k^* \sum_f (kf) U_f P_f, \quad P_f = -i \frac{\partial}{\partial Q_f}.$$

In Eqs. (28) and (29) the vector of the total impulse P is replaced by the vector $\mathbf{I} = \varepsilon^2 \mathbf{P}$. To obtain the impulse dependence in zero approximation, \mathbf{I} is assumed to be of zero order.

Taking into account that the form $\langle H_1 \rangle$, which is linear with respect to Q_f, P'_f turns to zero,

$$\langle H_1 \rangle = \int \phi_0^*(r) H_1 \phi_0(r) d^3r = 0, \quad (30)$$

$$\phi_0 = \phi_0(r) \theta(r_0, Q_1, \dots, Q_f, \dots, Q_N), \quad (31)$$

and taking the coefficients of Q_f, P'_f equal to zero we express U_f and S_f as follows:

$$A_f \int |\phi_0(r)|^2 \rho_f(r) d^3r + v_f U_f^* - \left(S_f + i \frac{v_f^*}{\hbar} (If) \right) \sum_g v_g \left(S_g^* - i \frac{v_g}{\hbar} (Ig) \right) (gf) v_g^* = 0, \quad (32)$$

$$v_f \left(S_f^* - i \frac{v_f}{\hbar} (If) \right) = -i U_f (fc), \quad (33)$$

where the vector c is given by the condition

$$\sum_f \mathbf{f} U_f S_f = 0. \quad (34)$$

It follows from Eqs. (28) – (34) that the coordinates r_0 and r divide and in the zero approximation the Schrödinger equation takes the form

$$\left\{ -\frac{\hbar^2}{m} \Delta_r + \mathbf{\Pi}(r) + U(r) - W_0 \right\} \phi_0(r) = 0, \quad (35)$$

$$\mathbf{\Pi}(r) = \sum_f \frac{v_f |A_f|^2 \int \rho_f^*(r) \phi_0(r) d^3r}{v_f^* - (cf)^2} \rho_f(r), \quad (36)$$

where $c = v/\varepsilon$ and v is the mean velocity of the bipolaron forward movement. The total energy E is

$$E = W_0 + \frac{1}{2} \sum_f |U_f|^2 \left\{ v_f + \frac{(fc)^2}{v_f} \right\}, \quad (37)$$

$$U_f = -\frac{A_f^* v_f}{v_f^2 - (cf)^2} \int \rho_f^*(r) |\varphi_0(r)|^2 d^3r. \quad (38)$$

Using the expansions in v from these equations we can express the bipolaron effective mass M^* in the limit of small velocities,

$$E = E_0 + M^* v^2/2 + \dots, \quad (39)$$

where

$$M^* = \frac{1}{3} \cdot \frac{\hbar^2}{\epsilon^4} \sum_f \frac{A_f^2 f^2}{v_f^3} \left| \int \varphi_0^*(r) \rho_f(r) \varphi_0(r) d^3r \right|^2. \quad (40)$$

Equations (35) – (40) completely determine the problem of the slow bipolaron motion. They will be solved in the next section.

IV. SOLUTIONS TO BIPOLARON EQUATIONS

We consider the ion crystal $\omega_f = \omega$, where ω is the frequency of longitudinal optical phonons, and the interaction between two electrons $U(r)$ corresponds to the Coulomb repulsion, screened by high-frequency dielectric permittivity,

$$U(r_1 - r_2) = \frac{e^2}{\epsilon_\infty |r_1 - r_2|}. \quad (41)$$

Using the relation

$$\frac{1}{r} = \frac{1}{2\pi^2} \int \frac{e^{-ifr}}{f^2} d^3f \quad (42)$$

and expressions (13) and (18) for A_f we can present integro-differential equations (35) and (36) as a system of two differential equations,

$$\frac{\hbar^2}{m} \Delta \varphi_0 - \frac{e^2}{\epsilon_\infty} \cdot \frac{\varphi_0}{r} + e \mathbf{\Pi} \varphi_0 - W \varphi_0 = 0, \quad \Delta \mathbf{\Pi} + \frac{32\pi e}{\tilde{\epsilon}} |\varphi_0|^2 = 0. \quad (43)$$

Turning in Eq. (43) to dimensionless variables

$$\varphi_0(r) = \frac{|W|}{e\hbar} \sqrt{\frac{m\tilde{\epsilon}}{32\pi}} Y(x), \quad \mathbf{\Pi}(r) = \frac{|W|}{e} Z(x), \quad r = \frac{\hbar}{\sqrt{m|W|}} x, \quad (44)$$

we get in the spherically symmetric case the following system of nonlinear equations:

$$Y'' + \frac{2}{x} Y' - \mathfrak{a} \Gamma \frac{Y}{x} + ZY - Y = 0, \quad Z'' + \frac{2}{x} Z' + Y^2 = 0, \quad (45)$$

which satisfies the boundary conditions

$$Z'(0) = Y(\infty) = Z(\infty) = 0, \quad 2Y'(0) - \mathfrak{a} \Gamma Y(0) = 0, \quad (46)$$

where

$$\Gamma = \int_0^\infty Y^2 x^2 dx, \quad (47)$$

$$\mathfrak{a} = \frac{\tilde{\epsilon}}{8\epsilon_\infty}. \quad (48)$$

It follows that the solutions of Eq. (43) depend on a single parameter \mathfrak{a} .

The expression for the bipolaron energy is given by the normalizing condition

$$\int |\varphi_0(r)|^2 d^3r = 1 \quad (49)$$

and takes the form

$$W = -\frac{64e^4m}{\Gamma^2\hbar^2\tilde{\epsilon}^2}. \quad (50)$$

Accordingly the total energy is, by Eq. (37), written as

$$E = |W| \frac{T - \Gamma - \mathfrak{a}Q\Gamma}{2\Gamma}, \quad (51)$$

where

$$T = \int_0^\infty Y'^2 x^2 dx, \quad Q = \int_0^\infty Y^2 x dx. \quad (52)$$

Finally, using the formula

$$\langle r \rangle = \int |\varphi(r)|^2 r d^3r \quad (53)$$

and relations Eq. (44) we present the bipolaron radius $\langle r \rangle$ as

$$\langle r \rangle = \frac{\hbar^2 \tilde{\epsilon}}{2e^2 m} R, \quad (54)$$

$$R = \int_0^\infty Y^2 x^3 dx. \quad (55)$$

Figure 1 shows particlelike solutions of the boundary problem, Eqs. (45) and (46), for several values of the parameter \mathfrak{a} . It is evident from the figure that the occurrence of the electrons in one and the same spatial point decreases as the parameter \mathfrak{a} grows. With growing parameter \mathfrak{a} the maximum in the electron density distribution shifts to the right and at the critical value $\mathfrak{a}_{kr} = 0.5$ goes to infinity. It follows from the fact that at sufficiently large r the asymptotic of the potential appearing in Eq. (43) is of the form

$$r \left\{ e\Pi(r) - \frac{e^2}{\epsilon_\infty r} \right\}_i r \xrightarrow{\infty} \frac{4}{\tilde{\epsilon}} - \frac{1}{\epsilon_\infty}. \quad (56)$$

A localized solution, Eq. (43), exists only on condition that the right-hand side of Eq. (56) is positive, i.e., $\mathfrak{a} < 0.5$. Accordingly for the ion coupling parameter $\eta = \epsilon_\infty/\epsilon_0$, which relates to \mathfrak{a} as

$$\eta = \frac{8\mathfrak{a} - 1}{8\mathfrak{a}}, \quad (57)$$

we get $\eta_{kp} = 0.75$, which is considerably greater than the corresponding value, Eq. (8), resulting from the phenomenological theory.

V. CALCULATION OF BIPOLARON CHARACTERISTICS FOR SOME PARTICULAR CRYSTALS

Table I lists numerical values for the quantities T , Γ , R , Q , and M ,

$$M = \int_0^\infty Y^4 x^2 dx, \quad (58)$$

which can be used to calculate the energies, Eq. (50), total energies, Eq. (51), and the bipolaron radius, Eq. (54), for various values of the parameter η , such that $\eta < \eta_c$. The critical value of the parameter η_c at which the bipolaron state is stable, is determined from the condition of energetic advantage of the bipolaron state relative to its dissociation into two separate polaron states,

$$E \leq 2E_{pol}, \quad (59)$$

where E_{pol} is the energy of a single-polaron state, which in the limit of strong coupling is given by⁵

$$E_{pol} = -\frac{2e^4 m}{\Gamma_0^2 \hbar^2 \tilde{\epsilon}^2}, \Gamma_0 = 3,5052, \quad (60)$$

It follows from Eqs. (51) and (60) and Table I that inequality (59) is fulfilled for $\eta < \eta_c$, where $\eta_c = 0.31$.

Table II lists the parameter values for crystals, which satisfy the condition $\eta < \eta_c$, and presents the calculated values of radius energies and effective masses of bipolarons. When the experimental value of the electron effective mass m is lacking, we show the results which depend only on the relation m/m_0 , where m_0 is the mass of a free electron in vacuum.

TABLE I. The values of integrals

$$T = \int_0^\infty Y'^2 x^2 dx, \quad \Gamma = \int_0^\infty Y^2 x^2 dx, \quad Q = \int_0^\infty Y^2 x dx, \quad R = \int_0^\infty Y^2 x^3 dx, \quad M = \int_0^\infty Y^4 x^2 dx,$$

for different values of the parameter η .

| η | Γ | T | R | Q | M |
|--------|----------|------|-------|------|------|
| 0 | 4.79 | 1.22 | 13.14 | 2.21 | 1.31 |
| 0.053 | 4.88 | 1.23 | 13.50 | 2.22 | 1.31 |
| 0.094 | 4.97 | 1.23 | 13.87 | 2.24 | 1.32 |
| 0.132 | 5.06 | 1.23 | 14.30 | 2.25 | 1.32 |
| 0.166 | 5.16 | 1.23 | 14.73 | 2.26 | 1.33 |
| 0.199 | 5.26 | 1.23 | 15.18 | 2.27 | 1.33 |
| 0.228 | 5.37 | 1.23 | 15.67 | 2.28 | 1.33 |
| 0.256 | 5.48 | 1.23 | 16.19 | 2.30 | 1.34 |
| 0.282 | 5.60 | 1.23 | 16.74 | 2.30 | 1.34 |
| 0.305 | 5.71 | 1.24 | 17.33 | 2.32 | 1.34 |
| 0.317 | 5.78 | 1.24 | 17.64 | 2.32 | 1.34 |

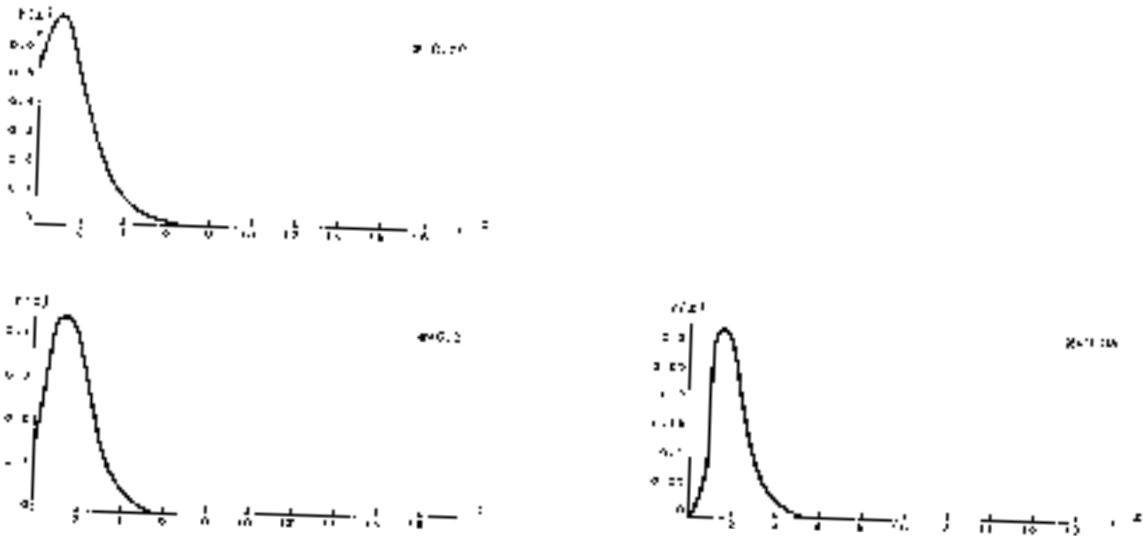


FIG. 1. Particlelike solutions of Eq. (45) for different values of the parameter α .

VI. CRITICAL COUPLING CONSTANTS FOR THE BIPOLARON

The condition of adiabatically strong coupling consists in the requirement that $|W|/\hbar \gg \omega$; i.e., the frequency of electron oscillations in a polaron well significantly exceeds the frequency of lattice oscillations. Table II suggests that in the case of bipolarons this condition is fulfilled for reasonable values of the electron effective mass. Therefore while for a single polaron the condition of weak or intermediate coupling is fulfilled, the bipolaron comply with the condition of strong coupling. This allows one to estimate the critical values of electron density constants α_c at which the bipolaron state is possible. For this purpose we present the bipolaron energy, Eq. (51), in the form

$$E = 64 \frac{T - \Gamma + \alpha Q \Gamma}{\Gamma^3} \alpha^2 \hbar \omega, \quad (61)$$

$$\alpha = \frac{e^2}{\hbar \tilde{\epsilon}} \sqrt{\frac{m}{2\hbar\omega}}. \quad (62)$$

From the above consideration the condition of advantage of the bipolaron state takes the form

$$|E| > 2\alpha \hbar \omega, \quad (63)$$

which leads to the following condition of the existence of the bipolaron state:

$$\alpha > \alpha_c = \frac{\Gamma^3}{32|T - \Gamma + \alpha Q \Gamma|}. \quad (64)$$

Using the values of T , Γ , Q , listed in Table I and inequality (63) we can get the values of the critical coupling constants, presented in Table III.

Note that the values of the critical coupling constants, obtained on the basis of the exact solution to the bipolaron equations, are much less than the values obtained with the help of probe variation functions. Thus, according to Ref. 11 the critical value for $\eta = 0$ is $\alpha_c \cong 5.4$ and for $\eta = 0.1$ it is $\alpha_c \cong 7.2$, which are more than 3 times as great as the values obtained on the basis of the exact solution of the bipolaron problem.

TABLE II. Summary of the data to energy (W), total energy (E), radius (r), and effective bipolaron mass (M^*).

| Crystal ^a | ϵ_∞ | ϵ_0 | $\hbar\omega$ (eV) | m/m_0 | α | $ W $ (eV) | $ E $ (eV) | $\langle r \rangle$ (Å) | M^*/m |
|----------------------|-------------------|--------------|--------------------|---------|--------------------|-------------|-------------|-------------------------|-----------------|
| LiF ^b | 1,93 | 9,04 | 0,082 | 0,78 | 4,63 | 8,37 | 1,66 | 2,93 | 52 |
| Li-Cl | 2,79 | 11,86 | 0,052 | | $4,43\sqrt{m/m_0}$ | $4,6m/m_0$ | $0,93m/m_0$ | $3,7m_0/m$ | $40,3(m/m_0)^2$ |
| Li-Br | 3,22 | 13,23 | 0,079 | | $5,25\sqrt{m/m_0}$ | $3,2m/m_0$ | $0,62m/m_0$ | $4,5m_0/m$ | $71,7(m/m_0)^2$ |
| Li-H | 3,6 | 12,9 | 0,14 | | $1,98\sqrt{m/m_0}$ | $2,2m/m_0$ | $0,42m/m_0$ | $5,5m_0/m$ | $1,3(m/m_0)^2$ |
| Tl-Br | 5,34 | 30,4 | 0,014 | 0,315 | 2,55 | 0,49 | 0,1 | 20 | 4,78 |
| Tl-C1 | 4,76 | 23,6 | 0,02 | 0,33 | 2,56 | 0,71 | 0,15 | 16,2 | 5,62 |
| Tl-I | 6,8 | 21,6 | 0,012 | | $3,4\sqrt{m/m_0}$ | $0,54m/m_0$ | $0,1m/m_0$ | $11,3m_0/m$ | $0,6(m/m_0)^2$ |
| Cs-F | 2,17 | 8,08 | 0,03 | | $7,13\sqrt{m/m_0}$ | $6,3m/m_0$ | $1,2m/m_0$ | $3,3m_0/m$ | $222(m/m_0)^2$ |
| Rb-F | 1,94 | 6,48 | 0,036 | | $7,03\sqrt{m/m_0}$ | $7m/m_0$ | $1,25m/m_0$ | $3m_0/m$ | $186(m/m_0)^2$ |
| SrTiO ₃ | 5 | 320 | 0,0153 | | $1,84\sqrt{m/m_0}$ | $2,9m/m_0$ | $0,67m/m_0$ | $4,4m_0/m$ | $1,98(m/m_0)^2$ |

^a The experimental data of the parameters have been taken from Ref. 10.

^b The value of the effective mass for Li-F has been taken from Ref. 11.

TABLE III. Critical values of electron-phonon coupling constant α_c for different values of the parameter q .

| | | | | | | | | | | | |
|------------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| η | 0 | 0,053 | 0,094 | 0,132 | 0,166 | 0,199 | 0,228 | 0,256 | 0,282 | 0,305 | 0,307 |
| α_c | 1,54 | 1,64 | 1,74 | 1,85 | 1,97 | 2,10 | 2,25 | 2,40 | 2,58 | 2,77 | 2,90 |

VII. COMPARISON WITH VARIATION ESTIMATES

Variation calculations of the bipolaron coupling energy are based on minimization of the full energy, which is obtained by averaging of the Hamiltonian, Eq. (12), using the probe wave functions^d

$$|\psi\rangle = \Psi(r_1, r_2) \hat{S}|0\rangle$$

$$\hat{S} = \prod_f \exp(c_f^* b_f - c_f b_f^*) . \quad (65)$$

Varying the obtained free energy functional over $\Psi(r_1, r_2)$ we have a Schrödinger equation of the form

$$\left[\frac{\hat{P}_1^2}{2m} + \frac{\hat{P}_2^2}{2m} + U(|r_1 - r_2|) + \phi(r_1, r_2) \right] \Psi(r_1, r_2) = W \Psi(r_1, r_2) , \quad (66)$$

where the potential of interaction of two electrons, caused by the induced polarization, is

$$\phi(r_1, r_2) = -2 \sum_f \frac{|c_f|^2}{\hbar\omega_f} [\rho_f^* (e^{ifr_1} + e^{ifr_2}) + c.c.] , \quad (67)$$

$$\rho_f = \frac{1}{2} \int d^3r_1 d^3r_2 (e^{ifr_1} + e^{ifr_2}) |\Psi(r_1, r_2)|^2 . \quad (68)$$

It follows from Eq. (67) that $\phi(r_1, r_2)$ is written as $\phi(r_1, r_2) = F(r_1) + F(r_2)$ and, as was noted in the Introduction, cannot be presented in the form $\phi(r_1 - r_2)$. Substitution of Eq. (68) into Eq. (67) leads to Schrodinger equation (66) which is obtained by variation of the functional (6) over $\Psi(r_1, r_2)$. So variation estimates with the probe wave function of Eq. (65) yield the same results as that within the phenomenological approach (Sec. II).

VIII. RESULTS FOR THE 2D BIPOLARONS

Some of the results obtained can be easily extended to the two-dimensional case. The bipolaron problem in the two-dimensional formulation has come into importance in the context of the discovery of high-temperature superconductivity. The simplest model used for a description of polarons in D-dimensional space is given by Eq. (12) with c_f replaced by $c_{f,D}$,¹²

$$c_{f,D} = \hbar\omega \left[\frac{\alpha_D}{Vf^{D-1}} \sqrt{\frac{\hbar}{2m\omega}} (2\sqrt{\pi})^{D-1} \Gamma\left(\frac{D-1}{2}\right) \right]^{1/2} . \quad (69)$$

It is assumed that in the two-dimensional layer the physical parameters (frequencies, dielectric constants, effective masses) are the same as in space, and the wave-vector dependence of $c_{f,D}$ is chosen from the condition that the electron-polarization interaction be of the Coulomb form $1/r$. The numerical factor in Eq. (69) is chosen from the condition that $c_{f,D}$ correspond to c_f for $D = 3$:

$$\alpha_{3D} = \alpha = \frac{e^2}{\hbar\omega\epsilon} \sqrt{\frac{m\omega}{2\hbar}} . \quad (70)$$

To estimate the bipolaron coupling energy in the two-dimensional case we can use the expres-

sion relating the results of the two- to the three-dimensional case,¹²

$$E_{2D\ bip}(\alpha_{2D}, U_{2D}) = \frac{2}{3} E_{3D\ bip} \left(\frac{3\pi}{4} \alpha_{2D}, \frac{3\pi}{4} U_{2D} \right). \quad (71)$$

The bipolaron coupling energy will be

$$E_{2D\ bip} = \frac{2}{3} \left(\frac{3\pi}{4} \right)^2 E_{3D\ bip}, \quad (72)$$

where $E_{3D, bip}$ is the bipolaron energy in the three-dimensional case, Eq. (51). Accordingly, $\mathfrak{a}_{2D} = \mathfrak{a}_{3D}$, $\eta_{2D} = \eta_{3D}$. By Eq. (71) in the two-dimensional case the critical value of the electron-phonon coupling constant is written as

$$\alpha_{c, 2D} = \frac{3}{4\pi} \alpha_{c, 3D}, \quad (73)$$

where $\alpha_{c, 3D}$ are listed in Table III.

Note that relation (71) is not exact and in Ref. 12 was obtained in Gaussian approximation. So the results, Eqs. (72) and (73), can be considered as quantitative estimates for the bipolaron in the two-dimensional case.

IX. DISCUSSION OF RESULTS

The translation-invariant bipolaron theory developed in this paper leads to qualitative dissimilarity from the results obtained within the general adiabatic scheme. On the whole the picture is as follows. In formation of the bipolaron state the electrons are localized in a deep potential well with the electron excitation energy $|W|$ of the order of 1 eV. This energy remains almost unchanged up to $\eta_c = 0,31$, where the bipolaron state breaks into separate polaron states. So, until the critical value becomes $\eta = \eta_c$ the bipolaron state can be described within the adiabatic approximation which holds true for $|W|/\hbar \gg \omega$. In other words, up to the critical values of the parameter η the frequency of electron oscillations in a bipolaron potential well significantly exceeds the frequency of the lattice oscillations. Only for crystals with very small electron-phonon coupling constants Pb-Se ($\alpha = 0,215$) and Pb-S ($\alpha = 0,317$), in which $\eta < \eta_c$ — i.e., the bipolaron states are principally possible — is the adiabatic criterion not fulfilled.

The best idea of bipolaron characteristics is given by the crystals Tl-Br and Tl-Cl, where the continuum approximations are fulfilled well and the radiuses are 20 and 16 Å, respectively. The adiabatic condition is also met with good allowance despite the considerably small coupling constant $\alpha \sim 2,5$.

It is important to stress that these crystals obey not only the stability criterion, given by Eqs. (59) and (60), but also the criterion $E < -2\alpha\hbar\omega$, Eq. (63), since as the bipolaron dissociates into single states weak and intermediate coupling polarons are formed. The stability condition of the bipolaron state is also fulfilled in these crystals for improved values of the polaron energy by using the intermediate coupling results: In the region (3–5) α the polaron energy values obtained in Ref. 13 are approximately 10% lower than — $\alpha\hbar\omega$.

It is important to stress that in all cases of Table II there is a great difference between the bipolaron electron energy W and the total energy E . The absolute value of the bipolaron electron energy is approximately 5 times as great as the bipolaron total energy, while in the case of a single strong coupling polaron this ratio is equal to 3. This fact leads to a number of interesting consequences, such as a great difference between the photo- and ther-modissociation energies of the bipolaron.

In some crystals the criterion of stability of bipolaron states is on the limit of validity. Thus, in the crystal Rb-F the bipolaron is stable at room temperature ($\epsilon_0 = 6,48$, $\eta = 0,3$; i.e., $\eta < \eta_c$) and unstable at helium temperature ($\epsilon_0 = 5,99$, $\eta = 0,32$; i.e., $\eta > \eta_c$). So, as Rb-F is being cooled from room temperature to helium temperature, the bipolaron dissociates. This effect could be observed over

the absorption spectrum, the change in the mobility, cyclotron frequency, etc.

The obtained results show that the bipolarons are more stable than was considered before. They can testify to the polaron nature of high-temperature superconductivity and possibility to its description with large radius bipolarons.^{14, 15}

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