ADIABATIC THEORY OF BIPOLARON

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We derive nonlinear differential bipolaron equations, which are asymptotically exact in the adiabatic limit. Particlelike solutions of these equations correspond to the bipolaron bound state. The exact solution yields an ion critical parameter $\eta_c = \varepsilon_\infty / \varepsilon_0 = 0.31$ for which the bipolaron state is stable (ε_∞ and ε_0 are the high-frequency and static dielectric constants).

PACS: 71.10+x, 71.38+i

Intensive study of bipolarons in recent years is not only due to a general theoretical interest but also owing to its important applications, such as interpretation of high-temperature superconductivity [1,2]. The history of bipolaron investigations is rather dramatic, for a long time calculation errors called question the bipolaron existence [3,4].

As distinct from the polaron treatment, where asymptotically exact solutions are known in limits of both the weak and the strong coupling [5,6], the bipolaron theory has no exact solutions by now. Moreover, in the bipolaron case there are no solutions at all for small and intermediate coupling constants a. According to [7] the bound bipolaron state (BBS) is possible only at sufficiently large $\alpha > 7.2$. In the adiabatic limit both the electrons are believed to move in the same potential well induced by their fast oscillations. Therefore, interaction of the electrons of polarization $\phi(r_1, r_2)$ takes the form

$$\phi(r_1, r_2) = F(r_1) + F(r_2). \tag{1}$$

This form is not translation-invariant and corresponds to a phenomenological approach where the potential well is assumed to be localized.

In this paper we develop a translation-invariant bipolaron theory based on the Bogolubov-Tyablikov adiabatic method [8,9]. According to our treatment we can separate the bipolaron motion in the adiabatic limit. The relative electron coordinates describe fast oscillations of electrons in the potential well, such that

$$\phi(r_1, r_2) = \phi(r_1 - r_2). \tag{2}$$

Coordinates of the center of mass describe slow motion of electrons. In this case the polarization potential well is not localized and follows adia-batically the center of mass of electrons. Hence, interaction (2) is translation-invariant.

The results of this approach reveal new properties of bipolarons. In the majority of ionic crystals, where bipolaron states are possible, the electron-phonon coupling is weak or intermediate for a single polaron and strong for the BBS. Critical electron-phonon coupling constants of bipolaron stability are approximately 3 times as small as the corresponding constants given by variational estimates.

Another important result is that the exact solution yields the ion coupling critical parameter $\eta = \varepsilon_\infty / \varepsilon_0 = 0.31$, where ε_∞ and ε_0 are the high-frequency and static dielectric constants of an ionic crystal. According to variational estimates this condition is much more rigid, $\eta = 0.14$ [3,4], and restricts drastically the class of crystals where bipolarons can exist. In the adiabatic limit the best variational estimates of bipolaron energy are also shown to correspond exactly to the phenomenological theory.

The results of three-dimensional bipolaron evaluations are also applied to the two-dimensional bipolaron. We find the energy of 2D-bipolaron and the critical electron-phonon coupling constants of 2D-bipolaron stability.

1. Bipolaron phenomenological theory

In phenomenological model the mean Coulomb field induced by two excess electrons is assumed to

cause the local medium polarization

$$P = D/4\pi\tilde{\varepsilon}\,, \tag{3}$$

where $\tilde{\varepsilon}^{-1} = \varepsilon_\infty^{-1} - \varepsilon_0^{-1}$, D is the electron induction,

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

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

$$E_2[\psi] = \frac{\hbar^2}{2m}\int |\nabla_{r1}\psi|^2 d^3r_1 d^3r_2 + \frac{\hbar^2}{2m}\int |\nabla_{r2}\psi|^2 d^3r_1 d^3r_2 + \frac{e^2}{\varepsilon_\infty}\int \frac{|\psi|^2}{|r_1 - r_2|} d^3r_1 d^3r_2 - \frac{1}{8\pi\tilde{\varepsilon}}\int D^2 d^3r\,, \tag{5}$$

or, invoking (4), it can be rewritten as

$$\begin{aligned} E_2[\psi] = {} & \frac{\hbar^2}{2m}\int |\nabla_{r1}\psi|^2 d^3r_1 d^3r_2 + \frac{\hbar^2}{2m}\int |\nabla_{r2}\psi|^2 d^3r_1 d^3r_2 - \\ & - \frac{2e^2}{\tilde{\varepsilon}}\int \frac{|\psi(r', r_1)|^2 |\psi(r'', r_2)|^2}{|r' - r''|} d^3r' d^3r'' d^3r_1 d^3r_2 + \frac{e^2}{\varepsilon_\infty}\int \frac{|\psi|^2}{|r_1 - r_2|} d^3r_1 d^3r_2\,. \end{aligned} \tag{6}$$

Thus, the phenomenological model yields an expression, where the interaction between particles, induced by the polarization field, takes on the form

$$\Phi(r_1, r_2) = -\frac{2e^2}{\tilde{\varepsilon}}\int \frac{|\Psi(r', r_1)|^2 |\Psi(r'', r_2)|^2}{|r' - r''|} d^3r' d^3r''. \tag{7}$$

Functional (6) suggests an important conclusion. Variation of it over ψ gives a Schrodinger equation whose efficient potential is of the Coulomb form at sufficiently large r_1-r_2. The BBS exists only if the potential is attractive or

$$\frac{\varepsilon_\infty}{\varepsilon_0} < 0.5\,. \tag{8}$$

The stability condition for BBS differs from (8) and may be written as

$$E_2 - 2E_1 < 0\,, \tag{9}$$

where

$$E_1 = \frac{\hbar^2}{2m}\int |\nabla\Psi|^2 d^3r - \frac{1}{8\pi\tilde{\varepsilon}}\int D_1^2 d^3r \tag{10}$$

is the total energy functional for a single polaron and D_1 is taken from (4) at substitution of $2e$ for e. As noted above, the best estimates resulting from (6)-(10) yield the condition of bipolaron stability [3,4] as

$$\frac{\varepsilon_\infty}{\varepsilon_0} < 0.14\,. \tag{11}$$

2. Translation-invariant adiabatic theory

The Pekar-Frohlich Hamiltonian for two electrons interacting with a phonon field has the form

$$H = -\frac{\hbar^2}{2m}\Delta_{r1} - \frac{\hbar^2}{2m}\Delta_{r2} + \sum_f \hbar\omega_f b_f^+ b_f + U\left(|r_1 - r_2|\right) + \\ + \sum_f \left\{c_f\, e^{if\left(r_1 - r_0\right)} b_f + c_f^*\, e^{-if\left(r_1 - r_0\right)}\right\} + \sum_f \left\{c_f e^{if\left(r_2 - r_0\right)} b_f + c_f^* e^{-if\left(r_2 - r_0\right)} b_f^+\right\}, \tag{12}$$

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

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

Degeneracy of (12) with respect to r_c plays a dominant role in the translation-invariant theory. We introduce coordinates

$$r = r_1 - r_2, \qquad R = \frac{r_1 + r_2}{2}, \tag{14}$$

and complex coordinates of the field g/ by

$$q_f = \frac{b_f + b_{-f}^+}{\varepsilon\sqrt{2}}, \qquad -i\frac{\partial}{\partial q_f} = \frac{\varepsilon i\left(b_f^+ - b_{-f}\right)}{\sqrt{2}}, \tag{15}$$

where ε is a small parameter. As a result we present Hamiltonian (12) as

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

$$\rho_f(r) = 2\cos\frac{fr}{2}, \tag{17}$$

$$A_f = \sqrt{2c_f}\,, \tag{18}$$

$$\hbar\omega_f = \varepsilon^2 \nu_f\,. \tag{19}$$

According to [8,9] the radius-vector R of the bipolaron center of mass can be written as a sum

$$R = r_0 + q, \tag{20}$$

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

$$q_f = (U_f + \varepsilon Q_f) e^{-i(\mathrm{fq})}. \tag{21}$$

These new coordinates must meet three additional conditions

$$\sum_f f\upsilon_f^* Q_f = 0\,, \tag{22}$$

where υ_f are the complex numbers satisfying the relations of reality $\upsilon_{-f} = \upsilon_f$, which are chosen so that the orthogonality conditions might be fulfilled

$$\sum_f f^\alpha f^\beta \upsilon_f^* U_f = \delta_{\alpha\beta} , \tag{23}$$

where f^α and f^β are the components of vector f. Relations (20)-(23) are a canonical Bogolubov-Tyablikov transform in the polaron theory. Replacing in (16) variables R and q_f by new variables r_0, q, and Q_f and using (22), we rewrite Hamiltonian (16) as

$$H = H_0 + \varepsilon H_1 + \varepsilon^2 H_2 + \ldots, \tag{24}$$

The variable q appears in the transformed Hamiltonian only via the canonically conjugate momentum $\hat{P} = -i\hbar\partial/\partial q$,

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

which is the total momentum of the system (electrons plus the phonon field). Then, wave function of the system can be presented by

$$\psi = \exp(ipq)\exp\left(i\sum_f S_f Q_f/\varepsilon \right)\phi\left(r, r_{0,} Q_f\right), \tag{26}$$

$$\phi = \phi_0 + \varepsilon\phi_1 + \varepsilon^2\phi_2 + \cdots. \tag{27}$$

Accordingly, the terms of expansion (24) do not contain variable 9 and are given by

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

$$\begin{aligned} H_1 &= \sum_f v_f \left(S_f^* - i\frac{\upsilon_f}{\hbar}(If) \right) P_f' + \\ &+ \sum_f \left\{ A_f \rho_f(r) + v_f U_f^* - \left(S_f + i\frac{\upsilon_f^*}{\hbar}(If) \right) \sum_g v_g \left(S_g^* - i\frac{\upsilon_g}{\hbar}(I_g) \right)(gf)\upsilon_g^* \right\} Q_f \end{aligned} \tag{29}$$

$$P_\kappa' = P_\kappa - \upsilon_\kappa^* \sum_f (\kappa f) U_f P_f , \qquad P_f = -i\frac{\partial}{\partial Q_f} .$$

In (28) and (29) vector P of the total momentum is replaced by the vector $I = \varepsilon^2 P$. To consider the momentum dependence in zero approximation, I is assumed to be of the zero order. The form $\langle H_1 \rangle$, linear with respect to Q_f, P_f', should be equal to zero

$$\langle H_1 \rangle = \int \varphi_0^*(r) H_1 \varphi_0(r) d^3 r = 0 , \tag{30}$$

$$\phi_0 = \varphi_0(r)\theta\left(r_0, Q_1, \ldots, Q_f, \ldots, Q_N\right), \tag{31}$$

and taking the coefficients at Q_f, P_f' equal to zero, we express U_f and S_f as

$$A_f \int |\varphi_0(r)|^2 \rho_f(r) d^3 r + v_f U_f^* - \left(S_f + i \frac{\upsilon_f^*}{\hbar} (If) \right) \sum_g v_g \left(S_g^* - i \frac{\upsilon_g}{\hbar} (Ig) \right) (gf) \upsilon_g^* = 0 , \quad (32)$$

where the vector e is given by the condition

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

It follows from (28)-(34) that coordinates r_0 and r are separated in the zero approximation, and the Schrodinger equation takes on the form

$$\left\{ -\frac{\hbar^2}{m} \Delta_r + \Pi(r) + U(r) - W_0 \right\} \varphi_0(r) = 0 , \quad (35)$$

$$\Pi(r) = \sum_f \frac{v_f |A_f|^2 \int \rho_f^*(r) |\varphi_0(r)|^2 d^3 r}{v_f^2 - (cf)^2} \rho_f(r) , \quad (36)$$

where $c = \upsilon/\varepsilon$, υ s the mean velocity of bipolaron rectilinear motion. Total energy E is

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

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

Using the expansion of these equations over υ, we can express bipolaron effective mass M^* in the slow-velocity limit

$$E = E_0 + \frac{M^* \upsilon^2}{2} + \cdots , \quad (39)$$

where

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

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

3. Solutions to bipolaron equations

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

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

Using the relation

$$\frac{1}{r} = \frac{1}{2\pi^2}\int \frac{e^{-i f r}}{f^2} d^3 f \tag{42}$$

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

$$\begin{gathered} \frac{\hbar^2}{m}\Delta\varphi_0 - \frac{e^2}{\varepsilon_\infty} + e\Pi\varphi_0 - W\varphi_0 = 0, \\ \Delta\Pi + \frac{32\pi e}{\widetilde{\varepsilon}}\left|\varphi_0\right|^2 = 0. \end{gathered} \tag{43}$$

Then, using in (43) dimensionless variables

$$\varphi_0(r) = \frac{|W|}{e\hbar}\sqrt{\frac{m\widetilde{\varepsilon}}{32\pi}}\,\mathrm{Y}(x), \qquad \Pi(r) = \frac{|W|}{e} Z(x), \qquad r = \frac{\hbar}{\sqrt{m|W|}} x, \tag{44}$$

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

$$\begin{gathered} \mathrm{Y}'' + \frac{2}{x}\mathrm{Y}' - \kappa\Gamma\frac{\mathrm{Y}}{x} + Z\mathrm{Y} - \mathrm{Y} = 0, \\ Z'' + \frac{2}{x}Z' + \mathrm{Y}^2 = 0, \end{gathered} \tag{45}$$

subject to the boundary conditions where

$$\begin{gathered} Z'(0) = \mathrm{Y}(\infty) = Z(\infty) = 0, \\ 2\mathrm{Y}'(0) - \kappa\Gamma\,\mathrm{Y}(0) = 0, \end{gathered} \tag{46}$$

where

$$\Gamma = \int_0^\infty \mathrm{Y}^2 x^2 d x, \tag{47}$$

$$\kappa = \frac{\widetilde{\varepsilon}}{8\varepsilon_\infty}. \tag{48}$$

It follows that the solutions to (43) depend on a single parameter κ. Expression for the bipolaron energy is given by the normalizing condition

$$\int \left|\varphi_0(r)\right|^2 d^3 r = 1, \tag{49}$$

and takes on the form

$$W = -\frac{64}{\Gamma^2}\frac{e^4 m}{\hbar^2\widetilde{\varepsilon}^2}. \tag{50}$$

Accordingly, the total energy (37) is

$$E = |W|\frac{T - \Gamma + \kappa Q\Gamma}{2\Gamma}. \tag{51}$$

where

$$T = \int_0^\infty \mathrm{Y}'^2 x^2 d\,x\,, \qquad Q = \int_0^\infty \mathrm{Y}^2 x d\,x\,. \tag{52}$$

Finally, using the definition of bipolaron radius

$$\langle r \rangle = \int \left|\varphi_0(r)\right|^2 r\, d^3 r\,, \tag{53}$$

and relations (44), we present it as

$$\langle r \rangle = \frac{\hbar^2 \widetilde{\varepsilon}}{2 e^2 m} R\,, \tag{54}$$

$$R = \int_0^\infty \mathrm{Y}^2 x^3 d\,x\,. \tag{55}$$

Figure 1 shows particlelike solutions of boundary problem (45)-(46) for various parameters κ. It is evident that the probability of the two electrons occurring at the same spatial point decreases as parameter κ grows. With growing κ the maximum in electron density distribution shifts to the right and at critical value $\kappa_c = 0.5$ goes to infinity. It follows from the asymptotic of potential (43) at sufficiently large r that

$$r\left\{ e\,\Pi(r) - \frac{e^2}{\varepsilon_\infty r} \right\}_{r\to\infty} \approx \frac{4}{\widetilde{\varepsilon}} - \frac{1}{\varepsilon_\infty}\,. \tag{56}$$

Localized solution to (43) exists only if the right-hand side of (56) is positive, i.e., $\kappa < 0.5$. Accordingly for ion coupling parameter $\eta = \varepsilon_\infty/\varepsilon_0$ which relates to κ as

$$\eta = \frac{8\kappa - 1}{8\kappa}\,, \tag{57}$$

we get $\eta_c = 0.75$, which is considerably greater than that resulting from the phenomenological theory by (8).

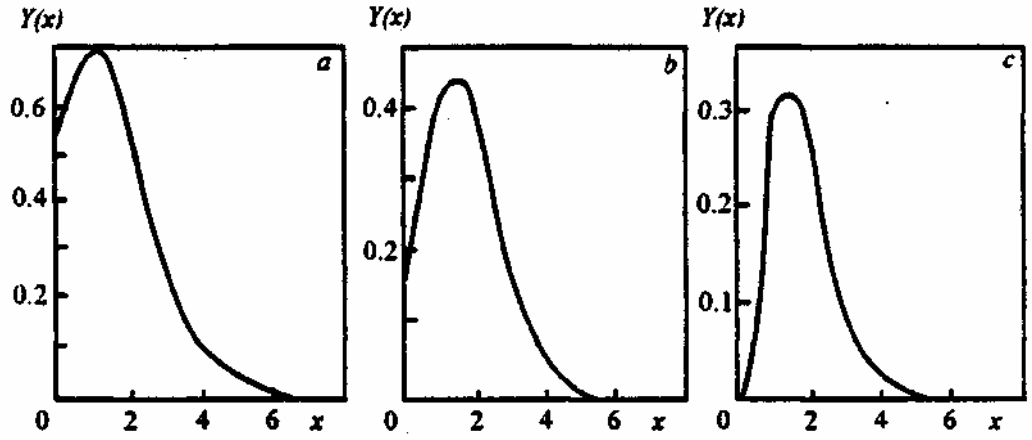

Figure 1. Particlelike solutions of equation (45) for different parameter κ: $\kappa = 0.18$ (a), 0.3 (6), and 0.36 (c).

4. Bipolaron characteristics for some particular crystals

Table 1 lists data on quantities T, Γ, R, Q, and

$$M = \int_0^\infty \mathrm{Y}^4 x^2 d\,x\,, \tag{58}$$

which can be used to calculate energies (50), total energies (51), and bipolaron radii (54) for parameter $\eta < \eta_c$. Critical parameter η_c of the

Table 1. Integrals $T = \int_0^\infty \mathrm{Y}'^2\, x^2 d\,x;\ \Gamma = \int_0^\infty \mathrm{Y}^2 x^2 d\,x;\ Q = \int_0^\infty \mathrm{Y}^2 x\, d\,x;\ R = \int_0^\infty \mathrm{Y}^2 x^3 d\,x;\ M = \int_0^\infty \mathrm{Y}^4 x^2 d\,x$ for various parameters 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

BBS stability is determined from the energetic advantage of the bipolaron state with respect to its decay into two independent polaron states.

$$E \le 2\,E_{pol}\,, \tag{59}$$

where E_{pol} is the energy of a single polaron state [5] in the strong-coupling limit

$$E_{pol} = -\frac{2}{\Gamma_0^2}\frac{e^4 m}{\hbar^2 \widetilde{e}^{\,2}}\,, \qquad \Gamma_0 = 3.5052\,. \tag{60}$$

It follows from (51), (60), and Table 1 that inequality (59) is valid for $\eta < \eta_c$ where $\eta_C = 0.31$.

Table 2 lists data on crystals satisfying the condition $\eta < \eta_c$, and the calculated radius. en-ergies, and effective masses of bipolarons. When no experimental data on the electron effective mass m are available, we present results depending only on the ratio m/m_0, where m_0 is the free electron mass.

5. Critical coupling constants for bipolaron

Condition of the adiabatically-strong coupling is $|W|/\hbar >> \omega$, i.e., the frequency of electron oscillations in the polaron well should be much greater than the frequency of lattice vibrations. It follows from Table 2 that this condition is met for reasonable electron effective mass. Thus, while a single polaron meets the condition of

Table 2. 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[6]	1.93	9.04	0.082	0.780	4.63	8.37	1.66	2.93	52
LiCl	2.79	11.86	0.052		$4.43\sqrt{\frac{m}{m_0}}$	$4.60\frac{m}{m_0}$	$0.93\frac{m}{m_0}$	$3.7\frac{m_0}{m}$	$40.3\left(\frac{m}{m_0}\right)^2$
LiBr	3.22	13.23	0.079		$5.25\sqrt{\frac{m}{m_0}}$	$3.20\frac{m}{m_0}$	$0.62\frac{m}{m_0}$	$4.5\frac{m_0}{m}$	$71.7\left(\frac{m}{m_0}\right)^2$
LiH	3.60	12.90	0.140		$1.98\sqrt{\frac{m}{m_0}}$	$2.20\frac{m}{m_0}$	$0.42\frac{m}{m_0}$	$5.5\frac{m_0}{m}$	$1.3\left(\frac{m}{m_0}\right)^2$
TlBr	5.34	30.40	0.014	0.315	2.55	0.49	0.10	20	4.78
TlCl	4.76	23.60	0.020	0.330	2.56	0.71	0.15	16.2	5.62
TlI	6.80	21.60	0.012		$3.40\sqrt{\frac{m}{m_0}}$	$0.54\frac{m}{m_0}$	$0.10\frac{m}{m_0}$	$11.3\frac{m_0}{m}$	$0.6\left(\frac{m}{m_0}\right)^2$
CsF	2.17	8.08	0.030		$7.13\sqrt{\frac{m}{m_0}}$	$6.30\frac{m}{m_0}$	$1.20\frac{m}{m_0}$	$3.3\frac{m_0}{m}$	$222\left(\frac{m}{m_0}\right)^2$
RbF	1.94	6.48	0.036		$7.03\sqrt{\frac{m}{m_0}}$	$7\frac{m}{m_0}$	$1.25\frac{m}{m_0}$	$3\frac{m_0}{m}$	$186\left(\frac{m}{m_0}\right)^2$
$SrTiO_3$	5	320	0.0153		$1.84\sqrt{\frac{m}{m_0}}$	$2.9\frac{m}{m_0}$	$0.67\frac{m}{m_0}$	$4.4\frac{m_0}{m}$	$1.98\left(\frac{m}{m_0}\right)^2$

[a] Experimental parameters are taken from [1O].
[b] Effective mass for LiF is taken from [11].

Table 3. Critical electron-phonon coupling constants α_c for different parameters η.

η	0	0.053	0.094	0.132	0.166	0.199	0.228	0.256	0.282	0.305	0.317
α_c	1.54	1.64	1.74	1.85	1.97	2.10	2.25	2.40	2.58	2.77	2.90

weak or intermediate coupling, a bipolaron follows the strong coupling condition. This enables us to evaluate critical electron-phonon coupling constants a_c when the BBS is possible. For this purpose we present bipolaron energy (51) as

$$|E| = 64\frac{|T-\Gamma+\kappa Q\Gamma|}{\Gamma^3}\alpha^2\hbar\omega, \tag{61}$$

$$\alpha = \frac{e^2}{\hbar\tilde{\varepsilon}}\sqrt{\frac{m}{2\hbar\omega}}. \tag{62}$$

The condition of energetic advantage of the BBS has the form

$$|E| > 2\alpha\hbar\omega, \tag{63}$$

which leads to the following requirement of the bipolaron formation,

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

Using T, Γ, and Q listed in Table 1 and inequality (63), we can get the critical coupling constants presented in Table 3.

Note that critical coupling constants given by the exact solution to bipolaron equations are much smaller than those evaluated by trial variational functions. Thus, according to [11], the critical constants are $\alpha_c \approx 5.4$ for $\eta = 0$ and $\alpha_c \approx 7.2$ for $\eta = 0.1$, i.e., they appear to be three times as large as those given by exact solution to the bipolaron problem.

6. Discussion

Our translation-invariant bipolaron theory yields results qualitatively different from those given by the standard adiabatic method. On the whole the situation looks as follows. In the bipolaron formation the electrons localize in a deep potential well with the electron excitation energy $W \sim 1$ eV. This energy remains the same up to the critical parameter $\eta_c = 0.31$ when the BBS decays into independent polaron states. Up to critical values $\eta = \eta_C$ the frequency of electron oscillations in the bipolaron potential well greatly exceeds the frequency of lattice vibrations, and we can use the adiabatic approximation. The criterion of adiabaticity fails only for crystals with very small electron-phonon coupling constants, such as PbSe ($\alpha = 0.215$) and PbS ($\alpha = 0.317$), where $\eta < \eta_c$, and bipolaron states are conceptually possible.

Bipolaron characteristics are best presented in crystals TiBr and TlCl, where continual approximations are fulfilled well, the radii of states are 20 Å and 16 Å respectively. The adiabaticity condition is also met with a great safety, despite a relatively small constant $\alpha \approx 2.5$.

We emphasize that these crystals satisfy not only the stability criterion given by (59) and (60), but also condition (63) $E < -2\alpha\hbar\omega$, since the bipolaron decays into weakly or intermediately coupled polarons. The stability criterion also remains valid in these crystals, if we use data on polaron energy improved by intermediate coupling results. In the range α = 3-5 the polaron energy [12] is approximately 10% lower than $-\alpha\hbar\omega$.

It is significant that in all the cases listed in Table 2 there is a great difference between electron energy W and total energy E of bipolaron. Absolute electron energy is approximately 5 times as great as the total energy, while for a single strongly coupled polaron this ratio is 3. This distinction can lead, particularly, to a great difference between the energies of photo-and thennodissociation.

In some crystals the criterion of stable bipolaron is at a bound of accuracy. Thus, in RbF the bipolaron is stable at room temperature ($\varepsilon_0 = 6.48$; $\eta = 0.3 < \eta_c$), and unstable at helium temperature ($\varepsilon_0 = 5.99$; $\eta = 0.32 > \eta_c$). Therefore, in Rbf the cooling from room temperature to helium one leads to the bipolaron dissociation. This phenomenon could be observed in absorption spectra, changes in mobility and cyclotron frequency, etc.

In conclusion the author wishes to thank R. Gabdullin for numerical calculation of equations (45) and (46).

This work was supported by the Russian Foundation for Basic Research (Project Code 95-0"-11432a).

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