

Adiabatic Theory of 2D- and 3D-Bipolarons

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Abstract - Nonlinear differential equations of the bipolaron, asymptotically exact in the adiabatic limit, are obtained. Particle-like solutions to these equations describe the bound bipolaron state. The exact critical value of the ionic binding parameter $\eta = \varepsilon_\infty/\varepsilon_0$ (ε_∞ and ε_0 are the high-frequency and static permittivities), at which the bipolaron state is stable, is found to be $\eta_c = 0.31$.

In recent years, bipolarons have been studied extensively not only because of the general physical interest in these objects, but also in view of their important applications, in particular, to interpreting high-temperature superconductivity [1-4].

Unlike the theory of the polaron, in which solutions asymptotically exact in the limits of weak and strong binding are known [5,6], the bipolaron theory does not describe such solutions. Moreover, for the bipolaron, solutions in the regions of low and intermediate coupling constants α are lacking. According to Adarnowski and Bednarek [7], a bound bipolaron state is only possible at fairly large coupling constants $\alpha > 7.2$. It is believed that, in the adiabatic limit, both electrons move in a common polaron potential well created by their fast oscillations in this well. The interaction potential between electrons and polarization $\phi(r_1, r_2)$ therefore has the form

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

Equation (1) has no translational invariance and corresponds to the phenomenological approach according to which the polarization potential well is fixed in some region of the space.

In this work, a consistent adiabatic translationally invariant theory of the bipolaron is developed. The suggested approach is based on the Bogolyubov-Tyablikov adiabatic theory [8,9]. According to this approach, motions in the bipolaron are separated in the adiabatic limit. The relative coordinates of the electrons describe their fast oscillations in the potential well. This well is determined by the effective electron interaction potential

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

The coordinates of the center of masses of the electrons describe their slow motion. The polarization well is not fixed in the space and adiabatically shifts with the center of masses. Interaction (2) then automatically becomes translationally invariant

The results obtained using this approach shed new light on the nature of bipolarons: in most ionic crystals where bipolaron states are possible and where for monopolarons, electron-phonon coupling is weak, the coupling becomes strong for bipolarons. The critical values of the electron-phonon coupling constant at which bipolaron states are stable are about three times lower than those obtained from variational estimates.

Another important point is that the exact solution leads to the critical ionic coupling parameter $\eta = 0.31$, where $\eta = \varepsilon_\infty/\varepsilon_0$ and ε_∞ and ε_0 are the high-frequency and static permittivities of the ionic crystal. Variational estimates give a far more stringent criterion, $\eta = 0.14$ [3,4], which sharply reduces the number of crystals in which bipolarons can exist. It is also shown that the best variational estimates of the energy of the bipolaron in the adiabatic limit exactly correspond to the phenomenological approach.

The results obtained for the three-dimensional bipolaron are also applicable to bipolarons in the two-dimensional space. The energy of the 2D-bipolaron and the critical electron-phonon coupling constant values at which 2D-bipolaron states are stable are found.

1. PHENOMENOLOGICAL THEORY OF THE BIPOLARON

A phenomenological description of bipolaron states is based on the observation that the mean Coulomb field created by two excessive electrons causes local polarization P of the medium,

$$P = \mathbf{D} / 4\pi\tilde{\epsilon} \quad (3)$$

where $\tilde{\epsilon}^{-1} = \epsilon^{-1}_{\infty} - \epsilon^{-1}_0$; \mathbf{D} is the induction created by the electrons,

$$\mathbf{D} = -2e \int |\Psi(r', r_2)|^2 \frac{(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} d^3r' d^3r_2; \quad (4)$$

and $\psi(r_1, r_2)$ is the wave function of the electrons. The energy of the bipolaron is then given by the functional

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

or, after substituting (4) for \mathbf{D} ,

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

The phenomenological approach therefore yields the expression in which the interparticle interaction potential determined by the polarization field has the form

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

The form of functional (6) immediately brings us to an important conclusion. Varying (6) with respect to ψ leads to the Schrodinger equation with an effective potential that has the Coulomb form at large $r_1 - r_2$ distances. The bound state only exists if the potential is attractive, that is under the condition

$$\epsilon_{\infty}/\epsilon_0 < 0.5. \quad (8)$$

The stability condition for bipolaron states is different from (8):

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

where

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

E_1 is the total energy functional of a single polaron, and \mathbf{D}_1 differs from (4) by the presence of the coefficient e instead of $2e$. As mentioned, the best estimates obtained from (6) - (10) yield the following criterion for stability of bipolaron states [3,4]:

$$\varepsilon_\infty/\varepsilon_0 < 0.14. \quad (11)$$

2. TRANSLATIONALLY INVARIANT ADIABATIC THEORY

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

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

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

where r_1 and r_2 are the coordinates of the first and second electron, respectively; ω_f are the phonon frequencies; r_0 is an arbitrary value used as the reference point; and f is the wave vector. Usually, r_0 is put to zero, and the resulting Hamiltonian is used as the starting point in studies of bipolarons.

The degeneracy of (12) with respect to r_0 is central to constructing a translationally invariant theory of the bipolaron. In terms of the distance between the electrons r and the coordinates of their center of masses R

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

and the complex field coordinates q_f

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

where ε is a small parameter, Hamiltonian (12) can be written as

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

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

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

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

Following [8, 9], let us write the radius vector of the center of masses of the bipolaron \mathbf{R} as the sum

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

where \mathbf{r}_0 and \mathbf{q} are the fluctuating and translationally invariant parts of the coordinates of the center of masses. We will also replace q_f by new complex field coordinates Q_f related to q_f by

$$q_f = (U_f + \varepsilon Q_f) e^{-i\phi(q)}. \quad (21)$$

Three additional constraints are imposed on the new coordinates,

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

where v_f are the complex numbers satisfying the real-ness relations $v_{-f} = v_f^*$. These numbers are selected to meet the orthogonality conditions

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

where f^α and f^β are the vector \mathbf{f} components.

Relations (20) - (23) are the canonical Bogolyubov-Tyablikov transformations in the theory of the polaron. After the change of variables from R and q_f to r_0 , q , and Q_f satisfying condition (22), Hamiltonian (16) can be rewritten as

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

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

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

which is the total momentum of the whole system (electrons + phonon field). The wave function of the system can therefore be represented as

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

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

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

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

$$H_1 = \sum_f v_f \left(S_f^* - i \frac{v_f}{\hbar} (If) \right) P_f' + \quad (29)$$

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

$$P'_k = P_k - v_k^* \sum_f (kf) U_f P_f,$$

$$P_f = -i \frac{\partial}{\partial Q_f}.$$

In (28) and (29), the total momentum vector \mathbf{P} is replaced by the vector $\mathbf{I} = \varepsilon^2 \mathbf{P}$, and \mathbf{I} is treated as a zero-order quantity to obtain the dependence on the momentum even in the zero approximation.

The (H_1) form linear with respect to Q_f and P'_f should be zero,

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

$$\phi_0 = \varphi_0(r) \theta(r_0, Q_1, \dots, Q_f, \dots, Q_N). \quad (31)$$

It follows that the coefficients of Q_f and P'_f are also zero, yielding the following equations for determining U_f and S_f :

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

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

where vector \mathbf{f} is found from the condition

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

It follows from (28) - (34) that the r_0 and r coordinates separate, and in the zero approximation, the Schrodinger equation takes 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 $c = v/\varepsilon$, and v is the mean translational velocity of the bipolaron. The total energy E_0 is given by

$$E_0 = W_0 + \frac{1}{2} \sum_f |U_f|^2 \left\{ v_f + \frac{(fc)^2}{v_f} \right\}, \quad (37)$$

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

In the limit of low velocities, expanding (37) and (38) in powers of v yields the effective mass of the bipolaron M^* :

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

where

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

Equations (35) - (40) fully determine the problem of motion of a slow bipolaron. Solutions to these equations are considered in the next section.

3. SOLUTION OF EQUATIONS FOR BIPOLARON

In an ionic crystal, $\omega_f = \omega$, where ω is the frequency of longitudinal high-frequency phonons, and the interaction potential $U(r)$ for two electrons corresponds to Coulomb repulsion - screened by high-frequency permittivity,

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

The relation

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

and equations (13) and (18) for A_f will be used to represent integro-differential equations (35) and (36) in the form of the system of two differential equations:

$$\begin{aligned} \frac{\hbar}{m} \Delta \varphi_0 - \frac{e^2}{\varepsilon} \frac{\varphi_0}{r} + e \Pi \varphi_0 - W_0 \varphi_0 &= 0, \\ \Delta \Pi + \frac{32\pi e}{\tilde{\varepsilon}} |\varphi_0|^2 &= 0. \end{aligned} \quad (43)$$

Rewriting (43) in terms of the dimensionless variables

$$\varphi_0(r) = \frac{|W_0|}{e\hbar} \left(\frac{m\tilde{\varepsilon}}{32\pi} \right)^{1/2} Y(x), \quad \Pi(r) = \frac{|W_0|}{e} Z(x), \quad r = \hbar(m|W_0|)^{-1/2} x, \quad (44)$$

we obtain the following system of nonlinear equations for a spherically symmetrical Hamiltonian:

$$Y'' + \frac{2}{x} Y' - \frac{1}{x} Y \kappa \Gamma + ZY - Y = 0, \quad Z'' + \frac{2}{x} Z' + Y^2 = 0. \quad (45)$$

These equations satisfy the boundary conditions

$$Z'(0) = Y(\infty) = Z(\infty) = 0, \quad 2Y'(0) - \kappa \Gamma Y(0) = 0, \quad (46)$$

where

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

$$\kappa = \tilde{\varepsilon} / 8\varepsilon_{\infty}. \quad (48)$$

Solutions of system (43) therefore depend on the sole parameter κ .

The equation for the energy of the bipolaron follows from the normalization condition

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

and has the form

$$W_0 = -\frac{64}{\Gamma^2} \frac{e^4 m}{\hbar^2 \tilde{\varepsilon}^2}. \quad (50)$$

Accordingly, for the total bipolaron energy, we obtain from (37):

$$E_0 = |W_0|(T - \Gamma + \kappa Q \Gamma) / 2\Gamma, \quad (51)$$

where

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

Finally, by definition, bipolaron radius is

$$\langle r \rangle = \int |\varphi_0(r)|^2 r d^3r, \quad (53)$$

and equation (44) yields

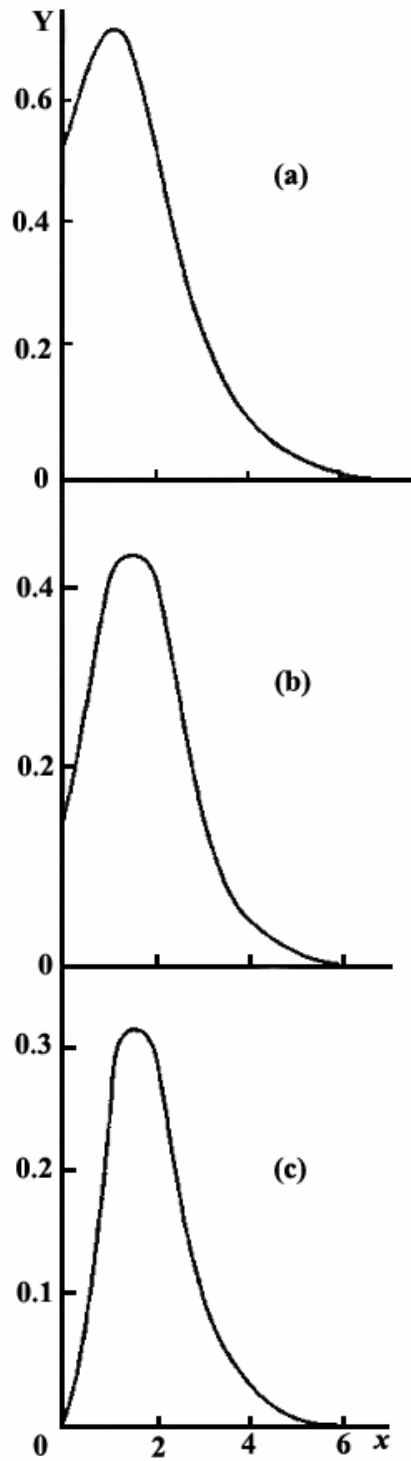
$$\langle r \rangle = \frac{\hbar^2 \tilde{\varepsilon}}{2e^2 m} R, \quad (54)$$

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

Particle-like solutions to boundary-value problem (45), (46) for several parameter κ values are shown in the figure. According to the figure, the probability of the occurrence of the electrons at the same point of space decreases with increasing κ . Simultaneously, the maximum of the electron density distribution shifts to the right and goes to infinity at the critical value $\kappa_c = 0.5$. Indeed, at fairly large r , the asymptotic behavior of the potential in (4) is described by

$$r \left\{ e\Pi(r) - \frac{e^2}{\varepsilon_{\infty} r} \right\}_{r \rightarrow \infty} \approx \frac{4}{\tilde{\varepsilon}} - \frac{1}{\varepsilon_{\infty}}.$$

Localized solution (43) exists only if the right-hand side of (56) is positive, that is, if $\kappa < 0.5$.



Particle-like solutions of (45) for κ = (a) 0.18, (b) 0.30, and (c) 0.36.

Accordingly, for the ionic coupling parameter $\eta = \varepsilon_{\infty}/\varepsilon_0$ related to κ by

$$\eta = (8\kappa - 1)/8\kappa, \quad (57)$$

we obtain $\kappa_c = 0.75$, which substantially exceeds ionic coupling parameter (8) of the phenomenological theory.

4. CALCULATION OF BIPOLARON CHARACTERISTICS FOR REAL CRYSTALS

The numerical values of the T , Γ , R , Q , and also M

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

parameters are given in Table 1. These values are used to calculate energies (50), total energies (51), and bipolaron radii (54) for various parameter η values satisfying the condition $\eta < \eta_c$. The critical η_c value, at which the bipolaron state is stable, is determined from the condition that the bipolaron state should be energetically favored with respect to the decomposition into two separate polaron states:

$$E_0 \leq 2E_{pol}. \quad (59)$$

Here E_{pol} is the energy of a separate polaron. In the limit of strong coupling, this energy is determined by the relation [5]

$$E_{pol} = -\frac{2}{\Gamma_0^2} \frac{e^4 m}{\hbar^2 \tilde{\epsilon}^2}, \quad \Gamma_0 = 3.5052. \quad (60)$$

Equations (51) and (60) and the data given in Table 1 show that inequality (59) is satisfied if $\eta < \eta_c$, where $\eta_c = 0.31$.

Table 2 contains parameter values for crystals satisfying the condition $\eta < \eta_c$ and the calculated radii and effective masses of bipolarons. In the absence of experimental effective electron masses m , the results that only depend on the $\mu = m/m_0$ ratio, where m_0 is the free electron mass in the vacuum, are given.

5. CRITICAL COUPLING CONSTANTS FOR BIPOLARONS

The condition of adiabatically strong coupling can be written as $|W_0| \hbar \gg \omega$, that is, the frequency of electron oscillations in the polaron well should far exceed the frequency of lattice vibrations. It follows from Table 2 that, for bipolarons, this condition is met only for reasonable electron effective masses. We therefore arrive at the conclusion that, whereas for a separate polaron the condition of weak or intermediate coupling is met, for bipolarons, the condition of strong coupling is met in the crystals under consideration. This enables us to estimate the critical electron-phonon coupling constants α_c at which bipolarons can occur in the bound state. For this purpose, bipolaron energy (51) is represented in the form

$$E_0 = 64 \frac{|T - \Gamma + \kappa Q \Gamma|}{\Gamma^3} \alpha^2 \hbar \omega, \quad (61)$$

$$\alpha = \frac{e^2}{\hbar \tilde{\epsilon}} \left(\frac{m}{2\hbar \omega} \right)^{1/2}. \quad (62)$$

Table 1. $\Gamma(47)$, Q , $T(52)$, $R(55)$, and $M(58)$ integrals at various parameter η values

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

Condition (59) that the bipolaron state should be energetically favorable now takes the form

$$|E_0| > 2\alpha\hbar\omega. \quad (63)$$

This results in the following condition for the existence of the bipolaron state:

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

Substituting the T , Γ and Q values given in Table 1 into (63) yields critical coupling constant values listed in Table 3. Note that the critical coupling constants obtained from the exact solution to the bipolaron equations are substantially lower than those determined using trial variational functions. For instance, according to Adamowski and Bednarek [7], the critical value is $\alpha_c = 5.4$ for $\eta = 0$ and $\alpha_c = 7.2$ for $\eta = 0.1$, which is more than three times larger than the values obtained from the exact solution to the bipolaron problem.

Table 2. Electronic energies (W_0), total energies (E_0), radii ($\langle r \rangle$), and effective masses (M^*) of bipolarons

Crystal	ϵ_∞	ϵ_0	$\hbar\omega$, eV	mlm_0	α	W_0 , eV	E_0 , eV	$\langle r \rangle$, Å	M^*/m
LiF	1.93	9.04	0.082	0.78	4.63	8.37	1.66	2.93	52
LiCl	2.79	11.86	0.052		$4.43 \mu^{1/2}$	4.6μ	0.93μ	3.7μ	$40.3 \mu^2$
LiBr	3.22	13.23	0.079		$5.25 \mu^{1/2}$	3.2μ	0.62μ	4.5μ	$71.7 \mu^2$
LiH	3.6	12.9	0.14		$1.98 \mu^{1/2}$	2.2μ	0.42μ	5.5μ	$1.3 \mu^2$
TlBr	5.34	30.4	0.014	0.315	2.55	0.49	0.1	20	4.78
TlCl	4.76	23.6	0.02	0.33	2.56	0.71	0.15	16.2	5.62
TlI	6.8	21.6	0.012		$3.4 \mu^{1/2}$	0.54μ	0.1μ	11.3μ	$0.6 \mu^2$
CsF	2.17	8.08	0.03		$7.13 \mu^{1/2}$	6.3μ	1.2μ	3.3μ	$222 \mu^2$
RbF	1.94	6.48	0.036		$7.03 \mu^{1/2}$	7μ	1.25μ	3μ	$186 \mu^2$
SrTiO ₃	5	320	0.0153		$1.84 \mu^{1/2}$	2.9μ	0.67μ	4.4μ	$1.98 \mu^2$

Note: The experimental parameters values are taken from Kartheuser [10] and the effective mass for LiF from Iadonisi *et al.* [11], $\mu = m/m_0$.

6. RESULTS FOR 2D-BIPOLARONS

Some of the results obtained above can easily be extended to two-dimensional bipolarons. Interest in the problem of bipolarons in the two-dimensional space was generated by the discovery of high-temperature superconductivity. The simplest model used to describe polarons in the D -dimensional space is obtained by substituting $c_{f,D}$ for c_f in (12) [12,13]:

$$c_{f,D} = \hbar\omega \left(\frac{\alpha_D}{Vf^{D-1}} \left(\frac{\hbar}{2m\omega} \right)^{1/2} \times (2\pi^{1/2})^{D-1} \Gamma\left(\frac{D-1}{2}\right) \right)^{1/2}. \quad (65)$$

It is assumed that the physical parameters (frequencies, dielectric constants, and effective masses) in the two-dimensional layer are the same as in the bulk, and the dependence of $c_{f,D}$ on the wave vector is determined from the condition that the interaction potential between electrons and polarization in D -dimensional systems has the Coulomb form ($\sim 1/r$). The numerical coefficient in (65) is selected from the condition that at $D = 3$, $C_{f,D}$ should coincide with c_f :

$$\alpha_{3D} = \alpha = \frac{e}{\hbar\omega\tilde{\epsilon}} \left(\frac{m\omega}{2\hbar} \right)^{1/2}. \quad (66)$$

The binding energy of the 2D-bipolaron can be estimated using the equation relating the results obtained for the two- and three-dimensional problems [12]:

$$E_{2D,\text{bip}}(\alpha_{2D}, U_{2D}) = \frac{2}{3} E_{3D,\text{bip}} \left(\frac{3\pi}{4} \alpha_{2D}, \frac{3\pi}{4} U_{2D} \right). \quad (67)$$

Table 3. Critical electron-phonon coupling constants α_c at various parameter η values

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

Using (67) yields the following binding energy for the 2D-bipolaron:

$$E_{2D,\text{bip}} = \frac{2}{3} \left(\frac{3\pi}{4} \right)^2 E_{3D,\text{bip}}, \quad (68)$$

where $E_{3D,\text{bip}}$ is the energy of the 3D-bipolaron given by (51). Accordingly, $\kappa_{2D} = \kappa_{3D}$, and $\eta_{2D} = \eta_{3D}$. The critical electron-phonon coupling constant in two-dimensional systems is obtained from (67):

$$\alpha_{c,2D} = \frac{3}{4\pi} \alpha_{c,3D}.$$

The α_c values are given in Table 3. Note that equation (67) is not exact, and was obtained in the Gaussian approximation [12, 13]. We should therefore treat (68) and (69) as qualitative estimates for 2D-bipolarons.

7. DISCUSSION

The translationally invariant theory of the bipolaron developed in this work leads to results that are qualitatively different from those obtained following the usual adiabatic approach. In general, the situation is as follows. On the formation of the bipolaron state, the electrons are localized within a deep potential well and their excitation energy $|W_0|$ is about 1 eV. This energy remains approximately constant up to the critical η_c parameter value of 0.31, at which the bipolaron state dissociates into separate polaron states. It follows that, up to the critical value $\eta = \eta_c$, the bipolaron state should be described using the adiabatic approximation, which is valid if the $|W_0|/\hbar \gg \omega$ condition is satisfied. In other words, up to critical parameter η values, the frequency of oscillations of the electrons in the bipolaron potential well far exceeds the frequency of oscillations of ions in the lattice. The adiabaticity criterion is not only met for crystals with very low electron-phonon coupling constants such as PbSe ($\alpha = 0.215$) and PbS ($\alpha=0.317$) where $\eta < \eta_c$ and where bipolaron states are possible in principle.

The clearest idea about the characteristics of bipolarons can be formed through considering TlBr and TlCl crystals. For these crystals, continual approximations hold well, and the radii of the states are 20 and 16 Å, respectively. The adiabaticity condition is also satisfied even at a very conservative estimate, in spite of a comparatively small coupling constant $\alpha \sim 2.5$. It is important that, in these crystals, not only the stability criterion given by (59) and (60) but also the $E < -2\alpha\hbar\omega$ criterion [equation (63)] is satisfied, because the dissociation of the bipolaron yields weakly or intermediately bound polarons. The condition of stability of the bipolaron states is met in such crystals even for refined polaron energies obtained using the theory of intermediate coupling: in the region of $\alpha - 3 - 5$, the polaron energies obtained in Feynman [14] are lower than $-\alpha\hbar\omega$ by about 10%.

Note that all systems included in Table 2 are characterized by large differences between bipolaron electronic energies W_0 and the total energies E . The bipolaron electronic energy is about five times as high as the total energy, whereas for a separate strongly bound polaron, three times. This feature has many interesting consequences, one of which is a large difference between bipolaron photo- and thermodissociation energies.

Some crystals are characterized by near critical conditions for the formation of stable bipolaron states. For instance, bipolarons are stable in RbF at room temperature ($\epsilon_0 = 6.48$ and $\eta = 0.3$, i.e., $\eta < \eta_c$) and unstable at helium temperature ($\epsilon_0 = 5.99$ and $\eta = 0.32$, i.e., $\eta > \eta_c$). It follows that cooling RbF from room to helium temperatures results in the dissociation of bipolarons. This effect should manifest itself in absorption spectra, mobility and cyclotron frequency variations, etc.

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