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1992 J. Phys.: Condens. Matter 4 2845

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Stability of large bipolarons

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Received 2 August 1991, in final form 21 November 1991

Abstract. The problem of the stability of bipolarons is discussed under the assumption of the Fröhlich electron–phonon interaction. A variational wavefunction for the bipolaron is proposed in a general form, which yields the translationally invariant wavefunction as a special case. A minimization of the expectation value of the Hamiltonian leads to the best estimates if the trial wavefunction is localized. In a broad range of material parameters, the upper bounds obtained for the ground-state energy of the bipolaron are better than those obtained with the help of methods fully exploiting the translational symmetry. A similar property has been observed for the free polarons for which the lowest upper bounds on the ground-state energy in the strong-coupling limit are obtained with the help of localized trial wavefunctions. This suggests that the stability of large bipolarons is connected with their self-trapping. Because of this tendency to localization we do not expect that the large bipolarons contribute to the bipolaronic mechanism of superconductivity in three-dimensional crystals.

1. Introduction

Electrons in crystals interact with lattice vibrations which leads to many interesting phenomena; one of them is the formation of bipolarons [1–9]. In polar crystals, the long-range Fröhlich interaction between the electron and LO phonons dominates all the electron–phonon couplings and leads to the creation of large polarons, which are also called the Fröhlich or optical polarons. The system of two large polarons (a bipolaron) can form a stable bound state if the electron–phonon coupling is sufficiently strong. The criteria for the stability of large bipolarons have been given in [4, 5]. Attempts [6–9] were made to extend the region of the bipolaron stability using translationally invariant computational methods. The theoretical description of the properties of bipolarons became important because of a revival of the concept of bipolaronic superconductivity [10–13]. It has been suggested [10–13] that high-temperature superconductivity can be explained as a result of the Bose–Einstein condensation of large bipolarons. The bipolaronic mechanism of superconductivity can be applied to a description of high- T_c superconductors if the bipolarons are stable and mobile.

This present paper provides a theoretical description of the properties of large bipolarons. In section 2, the problem of the translational symmetry of the bipolaron is discussed and a trial wavefunction is proposed in a general form which yields a translationally invariant wavefunction as a special case. In section 3, the numerical results obtained for both the polaron and the bipolaron with the use of the trial wavefunction with broken translational symmetry are presented. In section 4, the

results obtained by other workers and the bipolaronic mechanism of superconductivity are discussed. Moreover, a physical interpretation of the present results is given.

2. Theory

Electrons in polar crystals are coupled to LO phonons via the Fröhlich interaction. Neglecting other electron-phonon couplings and assuming the effective-mass approximation for the electrons, we can write the Hamiltonian for the system of two electrons (holes) and LO phonon field in the centre-of-mass system in the following form:

$$H = -\frac{\hbar^2}{4m} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{m} \nabla_{\mathbf{r}}^2 + \frac{e^2}{\epsilon_{\infty} r} + \hbar\omega \sum_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \hbar\omega \sum_{\mathbf{k}} \{v_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}) \times [\exp(\frac{1}{2}i\mathbf{k} \cdot \mathbf{r}) + \exp(-\frac{1}{2}i\mathbf{k} \cdot \mathbf{r})] a_{\mathbf{k}} + \text{HC}\}. \quad (1)$$

Here, \mathbf{R} and \mathbf{r} are the centre-of-mass and relative position vectors of the electrons, respectively, m is the effective band mass of the electron (hole), ω is the frequency of the LO phonon, $a_{\mathbf{k}}^{\dagger}$ and $a_{\mathbf{k}}$ are the LO phonon creation and annihilation operators, respectively, $v_{\mathbf{k}}$ is the electron-phonon interaction amplitude given by

$$v_{\mathbf{k}} = -(i/k)(2\pi e^2/\epsilon\hbar\omega\Omega)^{1/2} \quad (2)$$

where $k = |\mathbf{k}|$, $1/\epsilon = 1/\epsilon_{\infty} - 1/\epsilon_0$, ϵ_{∞} and ϵ_0 are the optical and static dielectric constants, respectively, and Ω is the quantization volume. Equations (1) and (2) define the Fröhlich Hamiltonian for the bipolaron. The last term in the Hamiltonian (1) describes the interaction of the charge carriers with the polarization field induced by the optical vibrations of the crystal lattice. The interaction amplitude (2) results from a Fourier transform of the electron-dipole interaction potential. The lattice distortion around the electron caused by this long-range interaction has a large spatial extension, i.e. the radius of the Fröhlich polaron is large in comparison with the lattice constant. A system composed of the two large polarons is called a large (Fröhlich) bipolaron.

The symmetry properties of the Hamiltonian (1) can be discussed if we introduce the operator to the translation by the vector t :

$$T(t) = T_{\text{ph}}(t)T_{\text{el}}(t) \quad (3)$$

which is the product of two operators: the translation operator for the phonon field

$$T_{\text{ph}}(t) = \exp\left(-it \cdot \sum_{\mathbf{k}} k a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}\right) \quad (4)$$

and the translation operator for the electrons

$$T_{\text{el}}(t) = \exp(-t \cdot \nabla_{\mathbf{R}}). \quad (5)$$

The transformation properties

$$T_{\text{ph}}^{\dagger}(t)a_{\mathbf{k}}T_{\text{ph}}(t) = a_{\mathbf{k}} \exp(-i\mathbf{k} \cdot t) \quad (6a)$$

and

$$T_{el}^\dagger(t) \mathcal{R} T_{el}(t) = \mathcal{R} + t \quad (6b)$$

lead to

$$T^\dagger(t) H T(t) = H. \quad (7)$$

Therefore, the Hamiltonian of the bipolaron is translationally invariant. The Schrödinger equation for this Hamiltonian can be solved by variational means. The variational trial wavefunction for the bipolaron has been proposed [4,5] in the form

$$|\Psi\rangle = \phi_{el} U |\chi_0\rangle \quad (8)$$

where $\phi_{el} = \phi_{el}(\mathbf{R}, \mathbf{r})$ is the electronic part of the wavefunction, $|\chi_0\rangle$ is the phonon vacuum state having the properties $a_k |\chi_0\rangle = 0$ and $\langle \chi_0 | \chi_0 \rangle = 1$, and U is the operator of unitary transformation, which depends on the electronic coordinates as well as on the phonon creation and annihilation operators. The operator U transforms the phonon operators a_k and a_k^\dagger into new operators; thus, this is the operator of a canonical transformation.

This operator can be written as

$$U = \exp(S - S^\dagger) \quad (9)$$

where the operator S has the form

$$S = \sum_k F_k(\mathbf{R}, \mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{R}) a_k \quad (10)$$

and $F_k(\mathbf{R}, \mathbf{r})$ is an arbitrary function. It should be noted that the translational invariance of the operator U is not necessary. We only have to require that U does not change the expectation values of the Hamiltonian, which is guaranteed by their unitarity.

The unitary transformation in the form given by equations (9) and (10) leads to a great variety of possible trial wavefunctions for the bipolaron, which differ between themselves in the choice of $F_k(\mathbf{R}, \mathbf{r})$. This function can be proposed in the following form:

$$F_k(\mathbf{R}, \mathbf{r}) = f_k(\mathbf{r}) + g_k \exp[-i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}_0)] \quad (11)$$

which is useful in further discussion. The functions f_k and g_k can be determined by minimizing the expectation value of the Hamiltonian (1) calculated with the help of the trial function (8). In [5], according to the method of optimized canonical transformation [14,15], these functions have been proposed in an analytical form dependent on variational parameters. The proposed [5] functions are

$$f_k(\mathbf{r}) = v_k \left[\lambda_1 / \left(\rho_1^2 a_p^2 k^2 + 1 \right) \right] \left[\exp\left(\frac{1}{2} i\mathbf{k} \cdot \mathbf{r}\right) + \exp\left(-\frac{1}{2} i\mathbf{k} \cdot \mathbf{r}\right) \right] \quad (12a)$$

and

$$g_k = v_k \lambda_2 / \left(\rho_2^2 a_p^2 k^2 + 1 \right)^2 \quad (12b)$$

where a_p is the free-polaron radius equal to $(\hbar/2m\omega)^{1/2}$, and $\lambda_1, \lambda_2, \rho_1$ and ρ_2 are the variational parameters. Comparing equations (11) and (12) with the corresponding formula (equation (9) in [5]), we should remember that the position vectors of the electrons are expressed by the centre-of-mass and relative position vectors as follows: $\mathbf{r}_1 = \mathbf{R} + \frac{1}{2}\mathbf{r}$ and $\mathbf{r}_2 = \mathbf{R} - \frac{1}{2}\mathbf{r}$; moreover, in [5], $\mathbf{R}_0 = 0$.

Substituting (11) into equation (10), we get

$$S = \sum_{\mathbf{k}} [f_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{R}) + g_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}_0)] a_{\mathbf{k}}. \quad (13)$$

The action of the translation operator $T(\mathbf{t})$ on U is reduced to its action on S , which gives no change in the first term on the right-hand side of equation (13), but the second term is multiplied by $\exp(-i\mathbf{k} \cdot \mathbf{t})$. Thus, the presence of the second term in equation (13) breaks the translational symmetry of the bipolaron trial wavefunction. Nevertheless, this wavefunction does not distinguish any position in a crystal. The vector \mathbf{R}_0 in equations (11) and (13) is completely arbitrary; in particular, in [5] it has been chosen as $\mathbf{R}_0 = 0$. The trial wavefunction defined by equations (8), (9), (12) and (13) describes the bipolaron, which is localized around any point in a crystal. This means that the bipolaron becomes self-trapped which is closely connected with the similar self-trapping of the polaron in the strong-coupling limit [1] (see also section 4).

Canonical transformation (9) becomes translationally invariant if we choose $g_{\mathbf{k}} = 0$ in equation (13), which corresponds to the choice $\lambda_2 = 0$ in equation (12b). Then, the operator S takes on the particular form

$$S_1 = \sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{R}) a_{\mathbf{k}}. \quad (14)$$

In this case, the variational wavefunction (8) of the bipolaron is also translationally invariant provided that the electronic wavefunction in equation (8) possesses this symmetry.

When performing the calculations with trial wavefunction (8) it is helpful to construct an effective Hamiltonian for the electrons, which is defined as follows:

$$H_{\text{eff}} = \langle \chi_0 | U^\dagger H U | \chi_0 \rangle. \quad (15)$$

Two equivalent methods for the evaluation of the effective Hamiltonian are discussed in the appendix. The explicit form of the effective Hamiltonian obtained from equation (15) using the transformation U given by equations (9) and (14) is

$$H_{\text{eff}} = -\frac{\hbar^2}{4m} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{m} \nabla_{\mathbf{r}}^2 + \frac{e^2}{\epsilon_{\infty} r} - 2\hbar\omega \sum_{\mathbf{k}} [v_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) \cos(\frac{1}{2}\mathbf{k} \cdot \mathbf{r}) + \text{cc}] \\ + \hbar\omega \sum_{\mathbf{k}} |f_{\mathbf{k}}(\mathbf{r})|^2 + \frac{\hbar^2}{m} \sum_{\mathbf{k}} |\nabla_{\mathbf{r}} f_{\mathbf{k}}(\mathbf{r})|^2 + \frac{\hbar^2}{4m} \sum_{\mathbf{k}} k^2 |f_{\mathbf{k}}(\mathbf{r})|^2. \quad (16)$$

When solving the eigenvalue problem for Hamiltonian (16) one should first separate out the centre-of-mass motion. For this aim, one can propose a variational solution of this problem by assuming that the electronic wavefunction ϕ_{el} is in a form of the product of two functions: a plane wave $\exp(i\mathbf{Q} \cdot \mathbf{R})$ and an arbitrary function of \mathbf{r} . For the ground state the centre-of-mass momentum $\mathbf{P} = \hbar\mathbf{Q}$ should be equal to zero.

Thus, we get rid of the R -dependence in the eigenvalue problem. The r -dependent part of the wavefunction can be chosen as

$$\phi_{\text{var}}(r) = (\lambda^{3/2}/\pi) \exp(-\lambda r) \quad (17)$$

where λ is the variational parameter and the polaron radius a_p is used as the unit of length. Choosing $f_k(r) = 2v_k \langle \phi_{\text{var}} | \cos(\frac{1}{2}k \cdot r) | \phi_{\text{var}} \rangle$, we get the following simple expression for the expectation value of the effective Hamiltonian:

$$E_{\text{var}} = \langle \phi_{\text{var}} | H_{\text{eff}} | \phi_{\text{var}} \rangle = 2\lambda^2 + \beta\lambda - 5\alpha\lambda + 8\alpha\lambda^3 \quad (18)$$

where energy is expressed in units of $\hbar\omega$, the Fröhlich electron-phonon coupling constant $\alpha = e^2/2\epsilon\hbar\omega a_p$, $\beta = 2\alpha/(1 - \eta)$, and $\eta = \epsilon_\infty/\epsilon_0$ is the ratio of the dielectric constants. A minimization of the right-hand side of equation (18) with respect to λ yields the variational upper bounds E_{var} , which—for all values of α and β —are considerably larger than the ground-state energy of the two polarons calculated by the weak-coupling method [16] (cf equation (22)). The simple approach presented above was a subject of paper [6]. In [6], however, the last term in equation (16) has been omitted, which in turn leads to the lack of the last term in equation (18). The correct form given by equation (18) provides no binding of the bipolaron in the entire range of α and β . Therefore, such a simple approach cannot be helpful in the problem of the bipolaron.

In an early stage of our work on the bipolaron problem, we tried to use a more elaborated trial wavefunction instead of (17). Moreover, the function $f_k(r)$ was determined in the minimization procedure. We obtained slightly better estimates in comparison with those resulting from equation (18). However, no binding had still been obtained. These negative results indicate that the translationally invariant trial wavefunction of the type given by equations (8), (9) and (14) is not flexible enough to provide the stability of the bipolaron.

For this reason in [4, 5] the trial wavefunction has been proposed in a more general form which admits the translationally invariant wavefunction as a special case. The unitary transformation applied in [4, 5] is given by equations (9), (12) and (13). This transformation leads to the effective Hamiltonian (equations (11) and (12) in [5]), which is dependent on the three distances $r_{12} = |r_1 - r_2|$, $r_1 = |r_1|$ and $r_2 = |r_2|$. Therefore, the electronic part of the wavefunction should also be dependent on these distances. A more detailed discussion of the choice of the electronic wavefunction is contained in [5, 17].

3. Results

The first results showing the stability of the bipolaron with the help of the method of optimized canonical transformation have been given in [4, 5]. In this paper, supplementary numerical results are presented.

Two polarons form a stable bipolaron if the ground-state energy E_{bipol} of the bipolaron is lower than the ground-state energy $2E_{\text{pol}}$ of the two polarons, i.e.

$$E_{\text{bipol}} < 2E_{\text{pol}}. \quad (19)$$

This means that the binding energy W defined as

$$W = 2E_{\text{pol}} - E_{\text{bipol}} \quad (20)$$

is positive. Below we first show the very restrictive conditions on the stability of the bipolaron (table 1) and next we shall argue how they can be extended. The values of the material parameters in table 1 have been obtained from inequality (19) by substituting into it the free-polaron energy calculated by the functional-integration method [18]. This method provides the best estimates of the free-polaron energy in the region $3 < \alpha < 30$. The values of α_c and η_c in table 1 are the limits of the bipolaron stability region determined with much caution, which means that the bipolarons are stable at least if $\alpha \geq \alpha_c$ and $\eta \leq \eta_c$, but their stability outside this region is not excluded.

Table 1. Estimated critical values of the electron-phonon coupling constant α_c and the ratio of the optical-to-static dielectric constants η_c .

α_c	7.3	7.5	8	9	11	15	20	30	40	50
η_c	0	0.010	0.029	0.056	0.086	0.115	0.130	0.138	0.139	0.140

Table 2. Upper bounds on the ground-state energy of the free polaron calculated with the help of the optimized canonical transformation (E_{pol}^A), functional-integration [18] ($E_{\text{pol}}^{\text{AGL}}$) and Pekar's strong-coupling method [19, 20] (E_{pol}^P). The energies are expressed in units of $\hbar\omega$ and measured with respect to the bottom of the conduction band.

α	7	9	11	20	30	35	40	50
E_{pol}^A	-7.2500	-10.653	-14.947	-44.997	-98.886	-133.91	-174.33	-271.34
$E_{\text{pol}}^{\text{AGL}}$	-8.1374	-11.538	-15.827	-45.334	-98.524	-133.22	-173.37	-269.70
E_{pol}^P	-5.3171	-8.7896	-13.130	-43.405	-97.662	-132.93	-173.62	-271.28

Determining the criteria of the bipolaron stability we can apply the same computational procedure for both the polaron and the bipolaron. The method of optimized canonical transformation yields the estimates E_{pol}^A of the free-polaron energy, which are quoted in table 2. These values have been obtained from our calculations [15] for the bound polaron by neglecting the Coulomb potential of the centre. If the interelectron separation $r_{12} \rightarrow \infty$ in the electronic wavefunction (cf equation (13) in [5]), then the ground-state energy of the bipolaron calculated by the present approach goes over into the double ground-state energy of the polaron calculated according to [15] in the strong-coupling limit. Thus, both the approaches to the polaron problem are equivalent. In table 2, the upper bounds E_{pol}^A are compared with the results of the functional-integration method [18] ($E_{\text{pol}}^{\text{AGL}}$) and strong-coupling method [1, 19, 20] (E_{pol}^P). The strong-coupling limit for the ground-state energy of the polaron is given by the analytical expression [19, 20]

$$E_{\text{pol}}^P = -0.108513\alpha^2\hbar\omega. \quad (21)$$

The upper bound E_{pol}^A coincides with the result of the Lec-Low-Pines [16] weak-coupling method, i.e.

$$E_{\text{pol}}^{\text{LLP}} = -\alpha\hbar\omega \quad (22)$$

up to $\alpha = 6.34$. For stronger electron-phonon couplings the bound E_{pol}^A lies below $E_{\text{pol}}^{\text{LLP}}$ and becomes comparable with $E_{\text{pol}}^{\text{AGL}}$ [18]. In the region $30 \leq \alpha \leq 50$, the present approach provides the best upper bounds for the ground-state energy of the free polaron. Therefore at least in this region we can use the values E_{pol}^A in calculations of the binding energy of the bipolaron. We shall argue that the application of these upper bounds in the entire region of α can also be justified.

Let us consider equation (20) defining the binding energy of the bipolaron. When calculating both the energies E_{pol} and E_{bipol} with the help of the same variational procedure, one can expect that the upper bound for the polaron energy is closer to the exact value than that for the bipolaron because of a greater complexity of the eigenvalue problem for the bipolaron. We can express this property quantitatively by introducing the error ΔE defined as a difference between the variational and exact energy. Then, we have the following inequalities: $\Delta E_{\text{pol}} \geq 0$, $\Delta E_{\text{bipol}} \geq 0$ and $\Delta(2E_{\text{pol}}) \leq \Delta E_{\text{bipol}}$. It follows from these inequalities that, if $W_{\text{var}} > 0$ for the variational binding energy obtained by substituting into equation (20) the variational upper bounds on E_{pol} and E_{bipol} , then $W_{\text{exact}} > 0$, too. Therefore, if the condition for stability is fulfilled for the variational estimates of E_{pol} and E_{bipol} , it should also be fulfilled for the exact values of both the energies. In particular, the results of calculations of the binding energy (table 3) obtained with the use of the estimates E_{pol}^A allow us to draw conclusions about the stability of the bipolaron. A similar procedure was applied by Bassani *et al* [7], who use the estimates $E_{\text{pol}}^{\text{LLP}}$ [16], which for large α are worse than the present estimates E_{pol}^A .

Table 3. Binding energy of the bipolaron in units of $\hbar\omega$ calculated with the use of the estimates E_{pol}^A of the free-polaron energy.

η	Binding energy for the following values of α							
	5.5	6	7	8	9	10	15	20
0	0.086	0.601	1.567	2.410	3.346	4.376	11.12	20.51
0.01	0.002	0.487	1.410	2.198	3.048	4.037	10.32	19.07
0.1	0	0	0	0.232	0.450	0.777	2.782	5.341

Such a procedure allows us to extend the region of values of material parameters for which the stability of the bipolaron is expected. This region is much broader than that determined with the help of table 1. The smallest value of the electron-phonon coupling constant at which the bipolaron is stable is estimated as $\alpha_c \simeq 5.4$ for the optical-to-static dielectric constant ratio $\eta = 0$. The critical value α_c increases with increasing η . For example, $\alpha_c \simeq 7.2$ for $\eta = 0.1$.

4. Discussion

The binding energy and the stability region of the bipolaron obtained by the present method are larger than those given by Bassani *et al* [7] and Verbist *et al* [8, 9]. The values of the bipolaron binding energy calculated by Bassani *et al* [7] are one order of magnitude smaller than the present results and $\alpha_c \simeq 6$ for $\eta = 0$. Because of the use of the functional-integration approach [8, 9], which overestimates the contribution of the Coulomb potential, the critical values of the strength β of this potential are

smaller than those obtained by the present method, e.g. for $\alpha = 9$ Verbist *et al* [9] obtained $\beta_c = 18.68$ in comparison with the present value $\beta_c = 19.07$. The estimated [8, 9] value of α_c (for $\eta = 0$) is $\alpha_c \simeq 6.8$.

The bipolaron energy can be evaluated with the help of the strong-coupling method which is based on Pekar's [1] approach to the polaron problem. This approach leads to formula (21) for the ground-state energy of the polaron [19, 20]. Table 2 shows that this estimate becomes useful for very large α . Pekar's method applied to the bipolaron problem provides estimates [21–23] of the bipolaron ground-state energy which are also proportional to α^2 with coefficients of proportionality dependent on η . It has been shown [5] that the bipolaron energy varies as α^2 only for very strong electron–phonon coupling, i.e. in this case the ratio W/E_{pol} is independent of α . However, for $\alpha < 30$ the dependence of the bipolaron energy on α becomes more complicated and cannot be approximated by any simple analytical formula. The best estimates of the binding energy W and the critical value η_c below which the bipolaron is stable obtained [23] with the use of the strong-coupling method of Pekar are $W^P/|E_{\text{pol}}^P| = 0.42$ (for $\eta = 0$) and $\eta_c^P = 0.125$. The corresponding values obtained with the help of the present approach are $W^A/|E_{\text{pol}}^A| = 0.49$ (for $\alpha = 50$ and $\eta = 0$) and $\eta_c^A = 0.140$ (for $\alpha = 50$). Therefore, in the strong-coupling regime the present method provides a larger binding energy and a broader region of the bipolaron stability than those obtained in [21–23].

The present approach is based on the variational trial wavefunction which admits translational symmetry. However, the lowest upper bounds for the bipolaron ground-state energy have been obtained for $g_k \neq 0$, i.e. for the trial wavefunction with the broken translational symmetry, which describes a localized system. Despite the lack of this symmetry, in a broad range of material parameters, the present upper bounds for the energy of the bipolaron are better than those obtained with the help of translationally invariant methods.

It is interesting that for the free polaron a similar property of the upper bounds on the ground-state energy can be observed. The translationally invariant method [18], which is a generalization of Feynman's [24] theory, yields the best estimates of the polaron ground-state energy only for $\alpha < 30$ (cf table 2). For larger values of the electron–phonon coupling constant the better estimates are provided by the methods [1, 15] which apply the localized trial wavefunctions. In particular, for $\alpha > 50$ the best upper bounds for the polaron ground-state energy are given by formula (21).

These results can be regarded as a strong suggestion of the tendency to localization of both the polaron and the bipolaron. This means that in the strong-coupling limit the polaron as well as the bipolaron can be treated as self-trapped systems. An additional problem arises for the bipolaron which is that the two-electron system is unstable for weak electron–phonon coupling. The self-trapping of the bipolaron can be connected with its transition into the stable (bound) state which, therefore, appears for smaller values of the electron–phonon coupling constant than the self-trapping of the polaron.

However, we have to stress that the above conclusions are based on the results of variational calculations. We cannot therefore exclude that the stability of the bipolaron which has been obtained with the help of the localized trial wavefunction is the result of an extremely large effective mass of the bipolaron. The first estimates [9] indicate that this mass takes on large values.

In the framework of the present method, a physical interpretation [5] can be provided of our main outcome stating that the two electrons form a bound state for a

sufficiently strong coupling with phonons. The formation of this state is the result of two competing effects. On the one hand, the electron–electron coulombic repulsion counteracts the binding of the pair. This interaction has a two-body character. On the other hand, the electrons interact with the lattice polarization field, which induces a potential well acting on the electrons as an attractive potential. The LO phonons are the quanta of this field; therefore, this interaction has a many-body character. The polarization field screens the electron–electron interaction and considerably weakens it. However, the effective polaron–polaron interaction remains repulsive and provides a positive contribution to the energy of the system. The negative contribution is due to a lowering of the self-energy of the two polarons in the bound state with respect to that of the two separate polarons. This can be explained as follows. The double electronic charge of the bipolaron induces a more extended and deeper potential well than that for the single polaron. The interaction with this potential well is stronger for the bipolaron than for the two separate polarons and leads to instantaneous self-trapping which should, therefore, appear for the weaker electron–phonon coupling in the case of the bipolaron than in the case of the polaron. According to the present approach, this effect is most important for the binding of the polarons into the bipolaron.

Let us consider the role of large bipolarons in a possible explanation of superconductivity [10–12]. According to the bipolaronic mechanism of high-temperature superconductivity discussed by Emin [12], a necessary condition for the material to become a bipolaronic supraconductor is that the bipolarons be stable and mobile. The results of the present paper suggest that the stability of the bipolarons is achieved if they are localized (or almost localized); thus, their effective mass should be extremely large and their mobility negligibly small. The superconducting transition temperature is the temperature of the Bose–Einstein condensation of bipolarons [12], which is inversely proportional to the bipolaron effective mass and is predicted to be very small. Therefore, we do not expect that the large bipolarons formed in three-dimensional isotropic crystals play a role in the bipolaronic mechanism of high-temperature superconductivity [12]. However, it is not excluded that the bipolarons created by the combined interaction of the electrons with both the optical and the acoustic phonons [12] or soft vibrational modes [13] contribute to the conductivity of crystals. Moreover, bipolaronic superconductivity can appear in two-dimensional structures [9] and strongly anisotropic crystals.

Direct experimental evidence for the existence of large (Fröhlich) bipolarons should be possible in strongly polar crystals with the electron–LO coupling constant $\alpha \simeq 5.4$ or larger. Looking for materials which fulfil the conditions of the bipolaron stability we can notice that ionic crystals [25] possess large enough values of the electron–phonon coupling constant α ; nevertheless, for these materials the ratio of dielectric constants η is larger than 0.2, which exceeds the estimated interval $\eta \leq \eta_c \simeq 0.1$ in which the bipolarons are expected to be stable.

The bipolaron ground-state energy level should lie in the band gap and should be shifted downwards by an amount W with respect to the bottom of the polaronic conduction band. Because the LO phonon energy takes on values [25] from 10 to 100 meV, this shift is estimated to be of the order of 1–10 meV. It is an open question whether the excited states of the bipolaron are also bound like those of the exciton.

If the system of polarons is subjected to any confinement potential, we expect the conditions of bipolaron stability to be more easily fulfilled. Such conditions can be achieved in quantum well structures and low-dimensional crystals [7, 9, 26, 27]. The

anisotropy of the crystal is also favourable for the stability of bipolarons.

5. Conclusions

The results of the present work show that large bipolarons are stable in a broad region of material parameters characterizing the polar crystals. The method of optimized canonical transformation provides estimates of the binding energy of the bipolaron which—in most cases—are better than those obtained by other methods. We have estimated the values of material parameters indicating for which materials a possible experimental observation of the large bipolarons is expected. In particular, we have found that the conditions of bipolaron stability are fulfilled if the electron-phonon coupling constant is about 5.4.

It results from the present calculations that the optimum trial wavefunction for the bipolaron is localized. It allows us to make a suggestion that the large bipolarons are self-trapped (similarly to the free polarons in the strong-coupling limit). Therefore, the large bipolarons should possess a very large effective mass and a negligibly small mobility. We do not expect the large bipolarons to play an essential role in the bipolaronic mechanism of superconductivity in three-dimensional crystals.

Appendix

Let us consider two methods of constructing the effective Hamiltonian (equation (15)). The unitary transformation U in equation (15) can be chosen as either the single transformation $U = U_1$, similar to [5, 15], or the product of two transformations $U = U_2 = T_{\text{ph}}(\mathbf{R})U_0$, similar to [7, 14]. The relevant transformations can be expressed in the form

$$U_j = \exp(S_j - S_j^\dagger) \quad (j = 0, 1) \quad (\text{A1})$$

where

$$S_0 = \sum_k f_k(r) a_k \quad (\text{A2})$$

and S_1 is given by equation (14).

The transformations U_1 and U_2 are equivalent because they provide the same effective Hamiltonian, i.e.

$$H_{\text{eff}} = \langle \chi_0 | U_1^\dagger H U_1 | \chi_0 \rangle = \langle \chi_0 | U_2^\dagger H U_2 | \chi_0 \rangle. \quad (\text{A3})$$

The validity of equation (A3) results from the following calculation:

$$\begin{aligned} U_2 | \chi_0 \rangle &= T_{\text{ph}} U_0 | \chi_0 \rangle = T_{\text{ph}} U_0 T_{\text{ph}}^{-1} T_{\text{ph}} | \chi_0 \rangle = T_{\text{ph}} U_0 T_{\text{ph}}^{-1} | \chi_0 \rangle \\ &= \exp(T_{\text{ph}} S_0 T_{\text{ph}}^{-1} - T_{\text{ph}} S_0^\dagger T_{\text{ph}}^{-1}) | \chi_0 \rangle = \exp(S_1 - S_1^\dagger) | \chi_0 \rangle = U_1 | \chi_0 \rangle \end{aligned} \quad (\text{A4})$$

where we make use of the following properties of the translation operator: $T_{\text{ph}}^{-1}(\mathbf{R}) = T_{\text{ph}}^\dagger(\mathbf{R})$ and $T_{\text{ph}} | \chi_0 \rangle = | \chi_0 \rangle$. The effective Hamiltonian of the system can be determined by either of the expectation values in equation (A3).

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