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Bipolaron Formation in the Two-Electron-Plus-Acoustic Phonon System

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Abstract

Using a variational method of the Pekar type, we examine the formation of bipolarons by coupling of two electrons to acoustic phonons, the symmetry property of the system being taken into account. It is found that the bipolaron with an even-parity can exist as a ground state provided that the electron-phonon interaction is strong enough to overcome the Coulomb repulsion. The bipolaron with an odd-parity which is of higher energy and larger in its extension than that with an even-parity is of lower energy than the extended state of polaron or the two noninteracting polaron state for a certain range of the parameters.

1. Introduction

The investigation of the system of two electrons interacting with phonon fields has attracted much attention.[1-7] The two electrons interact with each other through the direct Coulomb repulsion and the indirect attraction mediated by the electron-phonon interactions. When the two electrons are sufficiently far apart from each other, the Coulomb intercation between them can be neglected and the system is reduced to a system of two noninteracting polarons. On the other hand, when the distance between the two electrons is finite, it is possible that the two electrons will be bound together into a bipolaron provided that the attractive force mediated by the electron-phonon interactions overcomes the Coulomb repulsion.

The problem of bipolaron formation in the two electron-plus-acoustic phonon system has been recently investigated with the use of the scaling arguments of Emin and Holstein[8] by Cohen et al..[9] They find that for sufficiently small Coulomb interactions, the bipolaron forms at lower electron-phonon coupling than the polaron and is of lower energy than the two polarons when these become stable. They find also that for larger Coulomb interactions there can be a range of the electron-phonon coupling for which only the polaron is stable and above that a range for which the bipolaron is of lower energy. The bipolaron is a small bipolaron with an even-parity. The orbital part of the two-electron wave function to describe the bipolaron is symmetric with respect to the interchange of the coordinates of the respective particles.

Incidentally a possibility of polaronic superconductivity has been pointed out by Alexandrov and Ranninger[10] based on the speculation that the bipolaronic states in semicon-

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ductors or insulators should behave as the Cooper pairs in superconductors. In such a case the bipolaron states may be not localized as suggested by Cohen et al..[9] The bipolaron state with an odd-parity should be larger in its extension than that with an even-parity, because the wave function to describe the bipolaron with an odd-parity vanishes when the distance between the electrons becomes zero.

In the present paper we investigate the problem of bipolaron formation in the two -electron-plus-acoustic phonon system taking the symmetry property into account. Using a variational method of the Pekar type we calculate the total energy of the system and the mean distance between the two electrons as functions of the electron-phonon coupling constant, the strength of the Coulomb repulsion, the parity of the system and the polaron separation. The bipolaron with an even-parity can exist as a ground state provided that the electron-phonon interaction is strong enough to overcome the Coulomb repulsion. The bipolaron with an odd-parity can also exist as an excited state which is of higher energy than the bipolaron with an even-parity but of lower energy than the extended state of polaron or the two noninteracting polaron state for a certain range of parameters. The mean distance between the electrons in the bipolaron with an odd-parity is larger than that in the bipolaron with an even-parity.

In §2 we obtain analytic expressions for the total energy of the system and for the mean distance between the electrons as functions of the electron-phonon coupling constant, the Coulomb repulsion, the parity of the system and the polaron separation in a variational form. In §3 the energy of the system and the mean distance between the electrons are numerically calculated over a wide range of the parameters and the results are summarized in a phase diagram. The final section is devoted to discussions.

2. Formalism

We consider a system in which two electrons interact with the longitudinal acoustic mode of the phonon field via the deformation potential. The Hamiltonian for the system can be written, in dimensionless units ($\hbar = m = s = 1$, where m is the band electron mass and s is the speed of sound), as

$$H = \frac{1}{2}\sum_{i=1,2} p_i^2 + \sum_q q a_q^+ a_q + \sum_{i=1,2}\sum_q \left(\frac{4\pi\alpha q}{V}\right)^{1/2} \times (a_q + a_{-q}^{\pm}) e^{iq.r_i} + \frac{\beta}{|r_1 - r_2|} \tag{1}$$

where p_i and r_i are the momentum and position operators of the i-th electron. a_q^+ and a_q are the creation and annihilation operators of the acoustic phonon with wave vector q. V is the normalization volume. The dimensionless electron-phonon coupling constant α is given by

$$\alpha = \frac{D^2 m^2}{8\pi\rho\hbar^3 s} \tag{2}$$

where D is the deformation potential constant and ρ is the density of the material. The Coulomb interaction between the electrons is given with the high frequency dielectric constant ε_∞ of the material,

$$\beta=\frac{e^2}{\varepsilon_\infty \hbar s} \tag{3}$$

where e is the electric charge. We have assumed that the frequency of the acoustic phonon is given by $\omega(q)=sq$. The system is treated with a variational method of the Pekar type in which one assumes that a trial wave function has the following form[6]

$$|T_\varepsilon>=(\psi_1(r_1-R_1)\psi_2(r_2-R_2)+\varepsilon\psi_1(r_2-R_1)\psi_2(r_1-R_2))e^{S_1}e^{S_2}|0>, \tag{4}$$

where $|0>$ is the phonon vacuum,

$$\psi_i(r_j-R_i)=\left(\frac{2}{\pi\gamma^2}\right)^{\frac{3}{4}}e^{-\frac{1}{\gamma^2}|r_j-R_i|^2} \qquad i,j=1,2, \tag{5}$$

and

$$S_i=\sum_q d_i(q)(a_q-a_{-q}^{+})e^{iq.R_i} \qquad i=1,2 \tag{6}$$

The exponential operators S_i produce lattice deformations centered at points R_i and the variational parameters $d_i(q)$ determine the shape of the deformations. $\psi_i(r_j-R_i)$ represents the wave function for the j-th electron in the i-th state. The spatial extension of the polaron γ should be variationally determined. When $\varepsilon=1$ the wave function (4) is symmetric with respect to the interchange of r_1 and r_2, while it is antisymmetric for $\varepsilon=-1$. The expected value of H in the state $|T_\varepsilon>$ is now given with functions of the several parameters,

$$E_\varepsilon(\alpha,\beta,\gamma,d_i(q),q_m,r)=\frac{<T_\varepsilon|H|T_\varepsilon>}{<T_\varepsilon|T_\varepsilon>}, \tag{7}$$

where q_m is the Debye cut-off wave number given by $q_m=\pi/a_o$, a_o is the lattice constant, and $r=|R_1-R_2|$ is the separation between the polarons. After the variation with respect to $d_i(q)$ we obtain the energy of the system to be given by

$$E_\varepsilon(\alpha,\beta,\gamma,q_m,r)=E_K+E_S+E_M+E_C, \tag{8}$$

with

$$E_K=\left\{\frac{3}{\gamma^2}+\frac{\varepsilon}{\gamma^2}\left(3-\frac{r^2}{\gamma^2}\right)e^{-\frac{r^2}{\gamma^2}}\right\}/(1+\varepsilon e^{-\frac{r^2}{\gamma^2}}), \tag{9}$$

$$E_S=-\frac{8\alpha}{\sqrt{\pi}\,\gamma^3}(1+2\varepsilon e^{-\frac{2r^2}{\gamma^2}})\left\{erf\left(\frac{\gamma q_m}{2}\right)-\frac{\gamma q_m}{\sqrt{\pi}}e^{-\frac{\gamma^2 q^2}{4}}\right\}/(1+\varepsilon e^{-\frac{r^2}{\gamma^2}})^2, \tag{10}$$

$$\begin{aligned}E_M=-\Bigg[&\frac{4\alpha}{\sqrt{\pi}\,\gamma^3}e^{-\frac{r^2}{\gamma^2}}\left\{erf\left(\frac{\gamma q_m}{2}+i\frac{r}{\gamma}\right)+erf\left(\frac{\gamma q_m}{2}-i\frac{r}{\gamma}\right)\right\}\\&-\frac{8\alpha}{\pi\gamma^2 r}\sin q_m r\, e^{-\frac{\gamma^2 q_m^2}{4}}+\frac{16\alpha\varepsilon}{\sqrt{\pi}\,\gamma^3}e^{-\frac{5r^2}{4\gamma^2}}\left\{erf\left(\frac{\gamma q_m}{2}+i\frac{r}{2\gamma}\right)\right.\\&\left.+erf\left(\frac{\gamma q_m}{2}-i\frac{r}{2\gamma}\right)\right\}-\frac{64\alpha\varepsilon}{\pi\gamma^2 r}\sin\frac{q_m r}{2}e^{-(\frac{r^2}{\gamma^2}+\frac{r^2 q_m^2}{4})}\Bigg]/(1+\varepsilon e^{-\frac{r^2}{\gamma^2}})^2\end{aligned}, \tag{11}$$

$$E_C=\beta\left\{\frac{1}{r}erf\left(\frac{r}{\gamma}\right)+\frac{2\varepsilon}{\sqrt{\pi}\,\gamma}e^{-\frac{r^2}{\gamma^2}}\right\}/(1+\varepsilon e^{-\frac{r^2}{\gamma^2}}). \tag{12}$$

E_K is the kinetic energy of the electrons, E_S denotes the self-interaction energy of the electrons with the lattice deformations created by themselves. The term E_M is interpreted as the mutual interaction energy which vanishes as $r \to \infty$. The last term E_C decribes the electrostatic interaction energy between the electrons which also vanishes as $r \to \infty$. At large polaron separation ($r \to \infty$) the problem breaks down to the case of two noninteracting polarons. E_ε is then given by

$$E_\varepsilon(\alpha, \gamma, q_m) = \frac{3}{\gamma^2} - \frac{8\alpha}{\sqrt{\pi}\,\gamma^3}\left\{erf\left(\frac{\gamma q_m}{2}\right) - \frac{\gamma q_m}{\sqrt{\pi}} e^{-\frac{r^2 q_m^2}{4}}\right\}, \tag{13}$$

which is twice as large as the energy of one polaron.[11] It is well known that the equation (13) expresses the ground state energies corresponding to the two different states of polaron according to the values of the electron-phonon coupling constant α and of the extension of polaron γ. When the electron-phonon interaction is weak, $\alpha < \alpha_c$, the extended state of polaron is the ground state where γ is infinite. On the other hand when α is larger than α_c the small polaron state with finite γ is the ground state. The critical coupling constant α_c varies with the Debye cut-off wave number q_m.[12] The mean distance between the two electrons can be calculated as follows,

$$d_\varepsilon(\alpha, \beta, \gamma, q_m, r) = \{< T_\varepsilon || r_1 - r_2|^2 | T_\varepsilon > / < T_\varepsilon | T_\varepsilon >\}^{1/2}$$

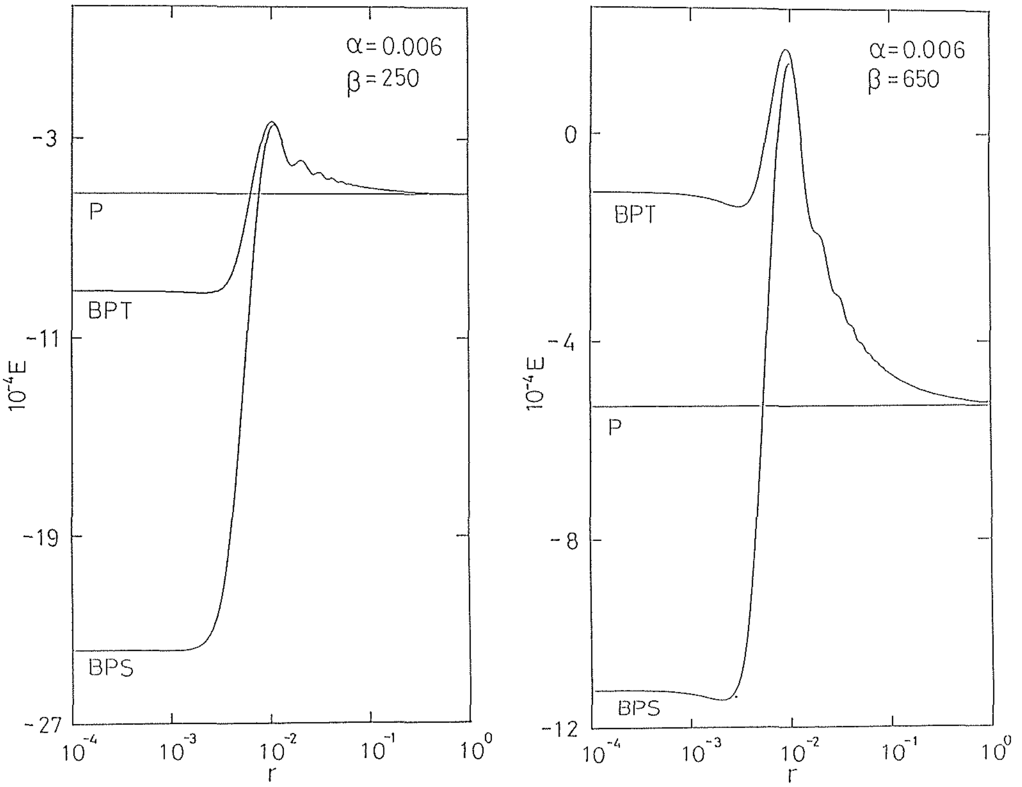
$$= \left(\frac{3}{2}\gamma^2 + \frac{r^2}{1+\varepsilon e^{-\frac{r^2}{\gamma^2}}}\right)^{1/2}, \tag{14}$$

where r and γ are determined so as to give the minimum value of E for given values of α, β and q_m. In the next section we evaluate E_ε and d_ε numerically.

3. Numerical calculations and results

In order to find the ground state of the system for arbitrary values of the electron -phonon coupling constant α and of the strength of the Coulomb repulsion β, we calculate numerically the energy E given in eq. (8) as a function of the polaron separation by minimizing the expression with respect to the variational parameter γ. For simlicity we choose $q_m = 584$ determined from the physical parameters appropriate for germanium. We take $s = 5 \times 10^5$ cm/sec, $m = 0.22\ m_e$ with the bare electron mass m_e and $a_o = 5.66$ Å.

In Figs. 1 (a)~1 (c) we show the energies of the system as a function of r for three sets of parameters : (a) $\alpha = 0.006$, $\beta = 250$, (b) $\alpha = 0.006$, $\beta = 650$, (c) $\alpha = 0.006$, $\beta = 950$. BPS, BPT and P express respectively the energies for the bipolaron state with an even-parity, for the bipolaron state with an odd-parity and for the two noninteracting polaron state. When the Coulomb repulsion is small, the minima of the energies for both of the bipolaron states are realized at finite r and they are lower than the energy for the two noninteracting polaron state (Fig. 1 (a)). In this case both of the bipolaron states are stable compared with the two noninteracting polaron state. As the Coulomb repulsion increases the bipolaron state with an odd-parity becomes unstable compared with the polaron (Fig. 1 (b)). For a larger Coulomb repulsion both of the bipolaron states are of higher energy than the polaron (Fig. 1 (c)). To see the variation of the energies in detail, we plot the energies E_ε as a function of



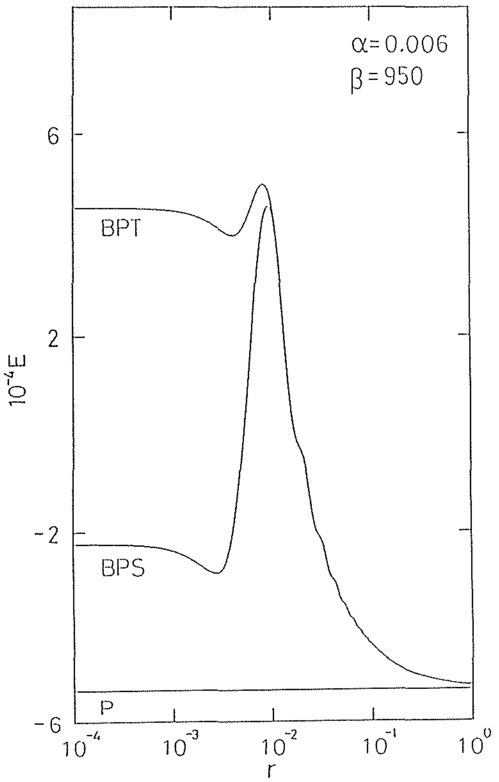


Figure 1 Energies for the bipolaron state with an even-parity (BPS), the bipolaron state with an odd-parity (BPT) and the two noninteracting polaron state (P) versus the separation between the polarons r for three different sets of the electron -phonon coupling constant α and the strength of the Coulomb repulsion β, (a) $\alpha=0.006$, $\beta=250$, (b) $\alpha=0.006$, $\beta=650$ and (c) $\alpha=0.006$, $\beta=950$.

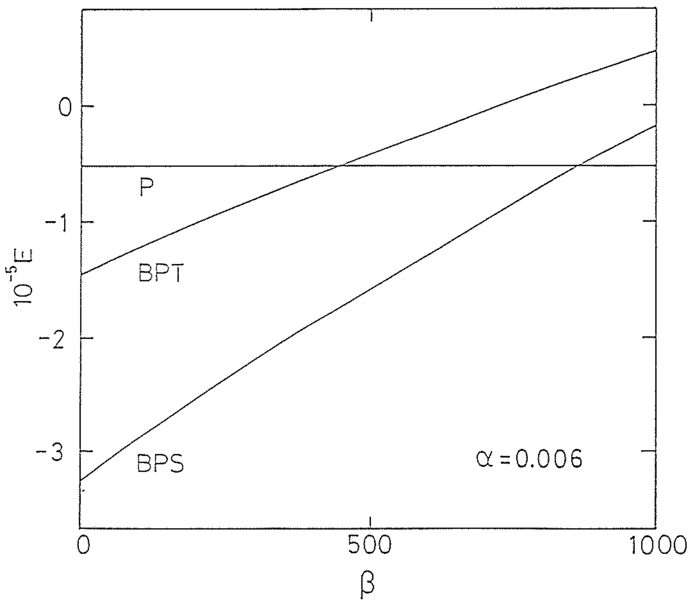


Figure 2 Energies for the bipolaron state with an even-parity (BPS), the bipolaron state with an odd-parity (BPT) and the two noninteracting polaron state (P) versus the strength of the Coulomb repulsion β for the electron-phonon coupling constant $\alpha=0.006$.

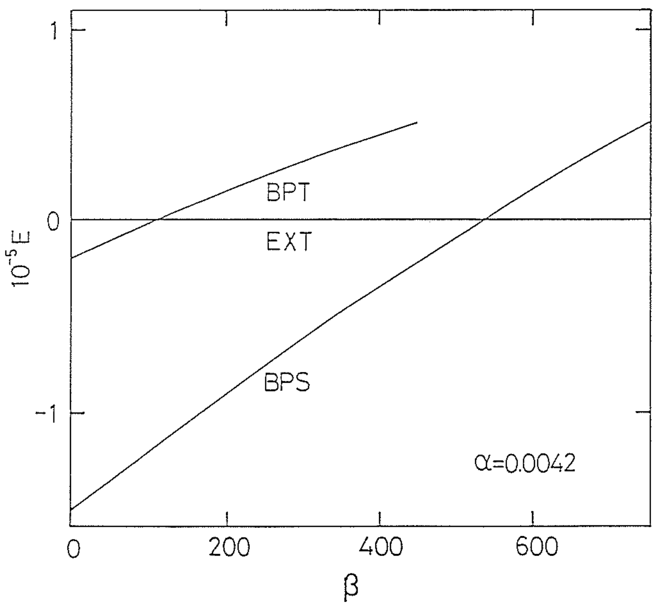


Figure 3 Energies for the bipolaron state with an even-parity (BPS), the bipolaron state with an odd-parity (BPT) and the extended state of polaron (EXT) versus the strength of the Coulomb repulsion β for the electron-phonon coupling constant $\alpha=0.0042$.

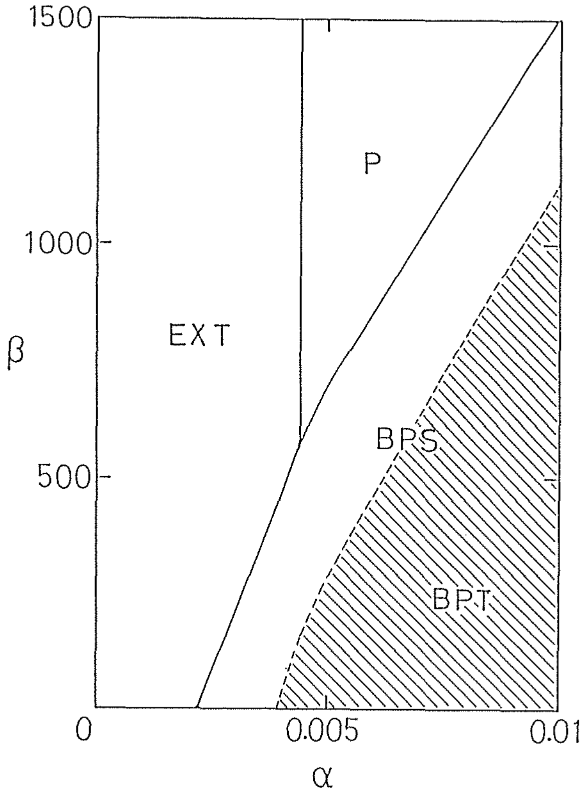


Figure 4 Phase diagram for the ground state in the (α, β) plane indicating the regions of the extended state of polaron (EXT), the two noninteracting polaron state (P) and the bipolaron state with an even-parity (BPS). The shaded region (BPT) shows the region where the bipolaron state with an odd-parity which is an excited state of the system is of lower energy than the extended state of polaron or the two nonintracting polaron state. α is the electron-phonon coupling constant and β is the strength of the Coulomb repulsion.

β for $\alpha=0.006$ in Fig. 2 and $\alpha=0.0042$ in Fig. 3. For $\alpha=0.006$ as β increases the ground state starts from the bipolaron state with an even-parity and then switches at $\beta=860$ to the two noninteracting polaron state. The bipolaron state with an odd-parity which starts as an excited state becomes at $\beta=447$ unstable compared with the polaron state. On the other hand for $\alpha=0.0042$, as β increases the ground state starts from the bipolaron state with an even-parity and switches at $\beta=525$ to the extended state of polaron. The bipolaron state with an odd-parity which starts as an excited state becomes at $\beta=100$ unstable compared with the extended state of polaron and ceases to exist at $\beta=445$. For α which is smaller than $\alpha_c=0.0044$ the extended state of polaron is of lower energy than the small polaron. In Fig. 4 we summarize our findings in a phase diagram. EXT, P and BPS indicate respectively the regions where the extended state of polaron, the two noninteracting polaron states and the bipolaron state with an even-parity are the ground states for the respective values of α and β. The shaded region BPT shows the region where the bipolaron state with an odd-parity is an excited state but of lower energy than the extended state of polaron or the two noninteracting polaron state.

The mean distance between the two electrons d_ε for arbitrary values of α and β can be calculated using the expression (14). The variational parameters γ and r are determined so as to give the minima of E_ε for given values of α and β. For the given pairs of α and β which correspond to the regions EXT and P in Fig. 4, d_ε becomes infinity because γ and r are infinite respectively for the extended state of polaron and for the two noninteracting polaron state. For the pairs of α and β corresponding to the BPS and BPT regions d_ε are finite. We show in table 1 the consequence of our calculations for some pairs of α and β corresponding to the shaded region in Fig. 4. The mean distance between the electrons d in the bipolaron state with an odd-parity is larger than that in the bipolaron state with an even-parity.

Table 1 The mean distance between the electrons d with the variational parameters: the separation between the polarons r and the extension of polaron γ for some pairs of the electron-phonon coupling constant α, the strength of the Coulomb repulsion β and the parity of the system ε.

α	β	ε	$r(\times10^{-3})$	$\gamma(\times10^{-3})$	$d(\times10^{-3})$
0.01	0	1	0	2.71	3.32
0.01	0	−1	0.91	2.83	4.52
0.01	100	1	0.48	2.74	3.37
0.01	100	−1	1.13	2.85	4.57
0.01	500	1	1.20	2.89	3.64
0.01	500	−1	1.63	2.90	4.80

4. Discussions

Taking into account the symmetry property of the system we have examined the formation of bipolarons by coupling of two electrons to acoustic phonons by using a variational method of the Pekar type. We find that the bipolaron state with an even-parity can exist as a ground state provided that the electron-phonon interaction is strong enough to overcome the Coulomb repulsion. The phase diagram for the ground state is essentially the same as those obtained before.[9,13] The energy of the bipolaron with an even-parity is always lower than that of the bipolaron with an odd-parity for the given values of the electron-phonon coupling constant α and the strength of the Coulomb repulsion β. The situation is the same as in the case of the hydrogen molecule in which the ground state is described with the symmetric wave function[14,15] but is different from the case of the two-dimensional ripplonic bipolaron in which the ground state is described with the symmetric or anti-symmetric wave functions according to the values of the parameters.[16] The bipolaron state with an odd-parity which is an excited state of the system is of lower energy than the extended state of polaron or the two noninteracting polaron state for a certain range of the parameters shown in Fig. 4. The mean distance between the electrons in the bipolaron with an odd-parity is larger than that in the bipolaron with an even-parity as expected. However the order of the distance is of an order of a lattice constant and it may be insufficient for the mechanism of bipolaronic superconductors. The large bipolaron would be created if we include the electron-optical phonon interaction in addition to the electron-acoustic phonon interaction.[4,5,7]

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