

Polarons, bipolarons, and their interactions in *cis*-polyacetylene

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Explicit solutions for the Brazovskii-Kirova continuum model of *cis*-polyacetylene are presented for the following three configurations: two polarons, two bipolarons, and a polaron and a bipolaron coexisting on a single chain. The results show that two polarons attract each other with a long-range potential reflecting large spatial extension of the polarons and that the attracted polarons form a bipolaron; two bipolarons repel each other; and polarons and bipolarons can freely pass through each other without attractive or repulsive interactions.

I. INTRODUCTION

Polyacetylene (PA), particularly its *trans* isomer, now attracts considerable interest because of its remarkable electric, magnetic, and optical properties. Characteristic twofold degeneracy of *trans*-PA allows domain-wall-like excitations called solitons,^{1,2} and various striking properties of *trans*-PA have been understood in terms of the soliton model.³ The microscopic model due to Su, Schrieffer, and Heeger¹ and its continuum version^{4,5} form a basis of such a soliton model.

In addition to soliton excitations, the possibility of polaron excitations has been suggested theoretically.⁶⁻¹¹ Optical detection of polarons in *trans*-PA has been reported very recently.^{12,13} A polaron is a charge carrier (electron or hole) self-trapped by the lattice distortion which the carrier itself has generated through the electron-lattice interaction. It is ubiquitous in comparison with a soliton, as it does not require twofold degeneracy. In fact, polarons in one-dimensional systems have recently drawn much interest.¹⁴

Brazovskii and Kirova⁷ (BK) proposed a generalization of the *trans*-PA continuum model^{4,5} that is adapted to a general description of polarons in various types of one-dimensional systems. Their model is particularly suited to the *cis* isomer of PA,^{7,15-17} which lacks the twofold degeneracy of *trans*-PA. The BK model further indicates the presence of a bipolaron in *cis*-PA, which is a single lattice deformation containing two charges, or a bound state of two polarons having a lower energy than two free polarons.

In this paper we will investigate the interaction among polaron and bipolaron excitations within the framework of the BK continuum model of *cis*-PA. Since light doping of *cis*-PA will generate polarons and bipolarons, study of their interactions is very interesting. To this end, explicit analytic solutions will be presented for the following three configurations: two polarons, two bipolarons, and a polaron and a bipolaron coexisting on a single *cis*-PA chain. Theoretical treatment of the problem almost parallels our previous work on *trans*-PA, where the reaction of two free polarons into a pair of charged solitons¹⁸ and the free passage of a soliton through a polaron¹⁹ were studied.

In the following section we review the BK model and

its effects on polarons and bipolarons, since the original compact presentation of BK (Ref. 7) is not sufficiently comprehensive to allow further understanding. In Secs. III-V we discuss the three configurations mentioned above. Results of the analysis of these three sections are summarized in Sec. VI, together with its implications in the real *cis*-PA system. Appendixes A and B supplement mathematical details to Secs. III and V.

II. POLARON AND BIPOLARON IN *cis*-PA

In this section we review the Brazovskii-Kirova continuum model⁷ of *cis*-PA and summarize their results on the polaron and bipolaron.

Unlike *trans*-PA, which has two degenerate ground states, *cis*-PA has no such degeneracy. Thus the theoretical model of *cis*-PA requires a modification to the *trans*-PA continuum model⁴ that will remove the degeneracy. Brazovskii and Kirova⁷ ingeniously proposed that the gap parameter $\Delta(x)$ should consist of two contributions,

$$\Delta(x) = \Delta_e + \Delta_i(x). \quad (2.1)$$

The extrinsic term Δ_e is a constant. The intrinsic part $\Delta_i(x)$ arises from the electron-lattice interaction; therefore it is proportional to the displacement field of carbon atoms.

A *cis*-PA chain is then described by the Hamiltonian

$$H = \int dx [\Delta_i(x)]^2 / \pi \lambda v_F + \int dx \Psi^\dagger(x) \left[-i v_F \sigma_2 \frac{\partial}{\partial x} + \Delta(x) \sigma_1 \right] \Psi(x). \quad (2.2)$$

The first term represents the elastic deformation energy of the chain. The parameter λ denotes the dimensionless electron-lattice coupling constant, and v_F is \hbar times the Fermi velocity. The second term consists of electron kinetic energy and electron-lattice-interaction energy. The electron-field operators Ψ^\dagger, Ψ are two-component spinors; the two components correspond to even and odd sites of the dimerized polyene.¹⁸ σ_1 and σ_2 are Pauli matrices. For simplicity, the electron-spin index will be omitted throughout.

In the adiabatic approximation, the kinetic energy of

the carbon atoms is omitted. We first fix the displacement field $\Delta_i(x)$ [and hence $\Delta(x)$ as well] and solve the one-electron eigenvalue problem,

$$\begin{cases} -v_F \frac{\partial}{\partial x} + \Delta(x) \\ v_F \frac{\partial}{\partial x} + \Delta(x) \end{cases} g_j(x) = \epsilon_j f_j(x), \quad (2.3)$$

where $f_j(x)$ and $g_j(x)$ are one-electron wave functions on even and odd sites normalized such that

$$\int [|f_j(x)|^2 + |g_j(x)|^2] dx = 1. \quad (2.4)$$

This model has electron-hole symmetry: for a positive-energy solution $\{\epsilon_j, f_j(x), g_j(x)\}$, there always exists a corresponding negative-energy solution, $\{-\epsilon_j, f_j(x), -g_j(x)\}$.

The total energy of the system (or adiabatic potential) is then given by

$$E[\Delta(x)] = \int \Delta_i(x)^2 dx / \pi \lambda v_F + \sum_j^{\text{occ}} \epsilon_j [\Delta(x)] \quad (2.5)$$

as a functional of $\Delta(x)$. The summation on the right-hand side is taken over occupied one-electron levels including the valence band. In a stable configuration, the above total energy should be stationary against variation in the gap-parameter function $\Delta(x)$. Such a stability requirement leads to the self-consistency equation,

$$\Delta(x) = \Delta_e - \pi \lambda v_F \sum_j^{\text{occ}} \text{Re}[f_j(x) * g_j(x)]. \quad (2.6)$$

The ground state of the *cis*-PA chain is described by constant gap parameter $\Delta(x) = \Delta_0$. The electron-energy spectrum obtained from Eq. (2.3) is then $\epsilon = \pm E(k)$, where

$$E(k) = (\Delta_0^2 + v_F^2 k^2)^{1/2}. \quad (2.7)$$

A band gap $2\Delta_0$ then occurs at $k=0$. Corresponding wave functions are plane waves. Substituting them into the self-consistency equation (2.6), we obtain

$$\Delta_0 = \Delta_e + \lambda \Delta_0 \ln(W/\Delta_0), \quad (2.8)$$

where W denotes width of the π band. The band gap $2\Delta_0$ is determined as a solution of Eq. (2.8). This model has an important parameter, called the confinement parameter,

$$\gamma = \Delta_e / \lambda \Delta_0, \quad (2.9)$$

which measures relative weight of the extrinsic gap parameter Δ_e . *trans*-PA corresponds to the $\gamma=0$ case. The magnitude of γ in *cis*-PA is not quite known. From their optical measurements, Etemad *et al.*¹⁵ estimate that $\gamma=0.6$.

The characteristic length appearing in this model is

$$\xi_0 = v_F / \Delta_0. \quad (2.10)$$

In *trans*-PA, the magnitude of this length is known to be about seven CH units.¹ Because of the increased band-gap energy in *cis*-PA,²⁰ ξ_0 in *cis*-PA is considered to be about

5 CH units, which still justifies the continuum model, although less favorably than in a *trans* isomer.

When an electron or a hole is placed on a PA chain, it deforms the carbon-atom chain, and the chain, in turn, traps the electron or the hole. Thus, a polaron is formed. Furthermore, two polarons favor a lower-energy configuration, namely the bipolaron, because of strong electron-lattice interaction. Lattice-displacement patterns for the polaron and bipolaron are commonly described by

$$\Delta(x) = \Delta_0 + \kappa_0 v_F \{ \tanh[\kappa_0(x - x_0)] - \tanh[\kappa_0(x + x_0)] \}, \quad (2.11)$$

where the parameters κ_0 and x_0 are related by

$$\kappa_0 v_F \coth(2\kappa_0 x_0) = \Delta_0. \quad (2.12)$$

For $\Delta(x)$ of Eq. (2.11), the eigenvalue problem (2.3) admits two discrete levels with energy $\pm\omega_0$,

$$\omega_0 = (\Delta_0^2 - \kappa_0^2 v_F^2)^{1/2}, \quad (2.13)$$

and wave functions

$$\begin{aligned} f_0(x) &= \frac{1}{2} \kappa_0^{1/2} \text{sech}[\kappa_0(x - x_0)], \\ g_0(x) &= \pm \frac{1}{2} \kappa_0^{1/2} \text{sech}[\kappa_0(x + x_0)]. \end{aligned} \quad (2.14)$$

The energy spectrum of the conduction and valence bands remain unchanged, but the wave functions are distorted by the presence of lattice distortion,

$$\begin{aligned} f_k(x) &= A_k e^{ikx} \{ \kappa_0 \tanh[\kappa_0(x - x_0)] - ik \}, \\ g_k(x) &= \pm A_k e^{ikx} \{ \kappa_0 \tanh[\kappa_0(x + x_0)] - ik \} e^{i\phi(k)}, \end{aligned} \quad (2.15)$$

where

$$A_k = \left[2(k^2 + \kappa_0^2) \left(L + \frac{d\delta(k)}{dk} \right) \right]^{-1/2},$$

$$\phi(k) = \tan^{-1}(k v_F / \Delta_0), \quad \delta(k) = 2 \cot^{-1}(k / \kappa_0).$$

The usual periodic boundary condition on electron wave functions leads to

$$kL + \delta(k) = 2\pi n, \quad (2.16)$$

where L is the chain length and n is an integer.

Figure 1 shows the displacement pattern and electron configuration for the polaron and bipolaron. (In an explicit display of various curves, we shall choose $\gamma=0.6$ throughout.) The self-consistency condition, as obtained by substitution of the wave functions (2.14) and (2.15) into (2.6),

$$\frac{\kappa_0 v_F}{\omega_0} \gamma = \sin^{-1} \left[\frac{\omega_0}{\Delta_0} \right] + \frac{\pi}{4} (n_+ - n_-), \quad (2.17)$$

depends on the occupation numbers n_{\pm} of the discrete levels with energy $\pm\omega_0$. For an electron polaron P^- and a hole polaron P^+ , we have, commonly,

$$n_+ - n_- = -1 \quad (\text{polaron}). \quad (2.18)$$

As for the bipolaron, for which

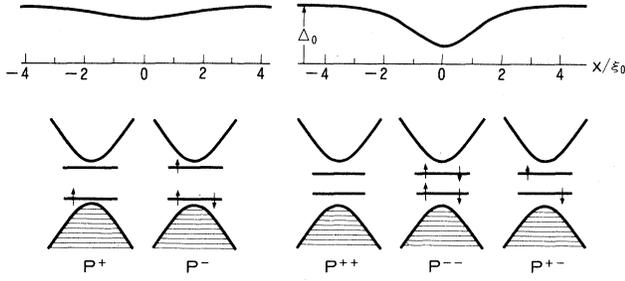


FIG. 1. Pattern of the gap parameter $\Delta(x)$ (top) and electron configurations (bottom) for the polarons, P^+ and P^- , and the bipolarons, P^{++} , P^{--} , and P^{+-} .

$$n_+ - n_- = 0 \quad (\text{bipolaron}), \quad (2.19)$$

we have three kinds of electron configurations, as seen in Fig. 1: electron bipolaron P^{--} , hole bipolaron P^{++} , and exciton polaron P^{+-} .

The formation energy of a polaron (and a bipolaron) is obtained as a result of the calculation of Eq. (2.5),

$$E_p = \frac{4}{\pi} \left[(1-\gamma)\kappa_0 v_F + 2\gamma\Delta_0\kappa_0 x_0 + \omega_0 \sin^{-1} \left[\frac{\omega_0}{\Delta_0} \right] \right] + (n_+ - n_-)\omega_0. \quad (2.20)$$

In fact, a minimization of this energy against ω_0 leads to the self-consistency equation (2.17). In Fig. 2 we plot the energy ω_0 of the localized level and the formation energy for the polaron and bipolaron as functions of γ . (For the bipolaron, half of the formation energy is plotted.) The bipolaron has larger dip in $\Delta(x)$ and stronger electron binding than a polaron on account of the two charges confined in it.

Among the three kinds of bipolaron configurations, P^{++} and P^{--} will be formed by acceptor and donor

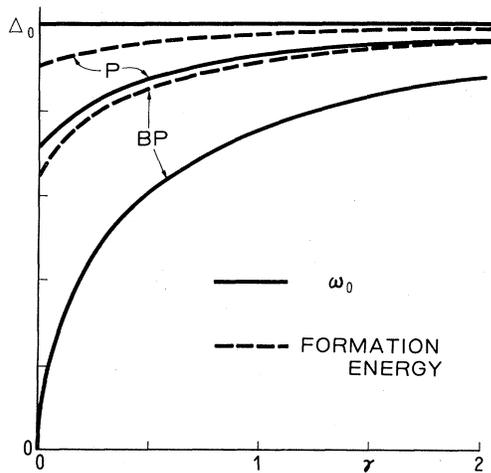


FIG. 2. Energy ω_0 of the discrete level (solid curves) and formation energy (dashed curves) of the polaron, P , and the bipolaron, BP . For the bipolaron, half of the formation energy is plotted.

doping. In contrast to this, the exciton polaron P^{+-} is an excited state; it can be generated by photoexcitation. As seen from the extreme right panel of Fig. 1, the exciton polaron admits both light emission and absorption at photon energy $E=2\omega_0$. Optical measurements can therefore determine the magnitude of ω_0 in the bipolaron. According to Lauchlan *et al.*,²¹ luminescence spectra of *cis*-PA peak at 1.9 eV, tailing down to 1.3 eV. They interpret the luminescence as hot luminescence (transient luminescence before quasiequilibrium at the minimum-energy configuration is reached) and choose¹⁵ $2\omega_0=1.3$ eV, which, when combined with the band-gap energy $2\Delta_0=2.05$ eV, gives $\gamma=0.6$.

In addition, transient optical absorption due to the exciton polaron P^{+-} has been observed by Orenstein and Baker.²² The absorption spectra peak at 1.55 eV, tailing down to ~ 1.3 eV. This tail energy may be taken as $2\omega_0$ if we again understand that the quasiequilibrium is not yet reached in the main absorption peak.

At present we are obliged to rely on an uncertain estimate disturbed by the hot process. Optical detection of the polaron and bipolaron generated by doping would determine γ more directly. In Sec. VI comments will be given on experimental detection of polarons and bipolarons in doped *cis*-PA, which has not yet been attained, as far as I am aware.

III. REACTION OF TWO POLARONS INTO A BIPOLARON

Having finished describing the polaron and bipolaron, we now consider their interaction. In this section we study how two polarons attract each other and form a bipolaron. Because of the electron-hole symmetry of the system, only the positively charged species will be considered.

When *cis*-PA is dilutely doped (with acceptors), polarons (P^+) are formed because the polaron-formation energy given by Eq. (2.20) is smaller than the energy Δ_0 of a free carrier. Thus the elementary process of doping is polaron formation. When the doping level is raised, two polarons can appear close on a single chain. These two polarons will tend to form a complex, a bipolaron, which has a lower energy than two separated polarons.

The mechanism of such a reaction process,



may be viewed in a similar way as in *trans*-PA,¹⁸ where two polarons decay into two charged solitons. When two polarons approach each other, the energy levels $\pm\omega_0$ are each split into two levels (bonding and antibonding states) owing to the overlap of electron wave functions trapped in the two polaron dips in $\Delta(x)$. The system can lower its energy by accommodating the two electrons in the lower level, $-\omega_2$, as shown in Fig. 3. Consequently, an attractive force operates between the two polarons. The system further lowers its energy by lowering the level $-\omega_2$ down until it is absorbed into the valence band. The end product of such a reaction process is a bipolaron, where two charges are confined in a single dip.

The above observation greatly aids in the construction

of an explicit expression of the gap parameter $\Delta(x)$ for a two-polaron system. We impose a requirement on $\Delta(x)$ —it should admit four discrete levels as shown in Fig. 3. Then $\Delta(x)$ can be constructed as a solution to the inverse problem of Eq. (2.3), as detailed in Appendix A. The gap parameter $\Delta(x)$ describing two polarons is

$$\Delta(x) = \Delta_0 + \frac{(\kappa_1^2 - \kappa_2^2)v_F}{\kappa_1 \coth(\kappa_1 x - \beta_1) - \kappa_2 \tanh(\kappa_2 x - \beta_2)} - \frac{(\kappa_1^2 - \kappa_2^2)v_F}{\kappa_1 \coth(\kappa_1 x + \beta_1) - \kappa_2 \tanh(\kappa_2 x + \beta_2)}, \quad (3.2)$$

where

$$\tanh 2\beta_j = \kappa_j v_F / \Delta_0 \quad (j=1,2). \quad (3.3)$$

We have two independent parameters, κ_1 and κ_2 , related to the energies ω_1 and ω_2 of the discrete levels by

$$(\kappa_j v_F)^2 + \omega_j^2 = \Delta_0^2 \quad (j=1,2). \quad (3.4)$$

The above expression for $\Delta(x)$ is the same as that for two polarons in *trans*-PA.¹⁸

Despite the appearance of Eq. (3.2), it is not the parameters β_j that determine the separation between two polarons. Instead, the difference $\kappa_1 - \kappa_2$ determines the separation. The configuration of two infinitely separated polarons corresponds to $\kappa_1 = \kappa_2 = \kappa_0$. When they approach, the difference $\kappa_1 - \kappa_2$ appears, giving rise to bonding-antibonding splitting of the discrete levels. According to the analysis of Appendix B, the polaron separation d is asymptotically given by

$$d = \frac{1}{\kappa_0} \ln \frac{4\kappa_0}{\kappa_1 - \kappa_2} \quad (3.5)$$

at large distances. (This expression holds for *trans*-PA as well.)

For $\Delta(x)$ given by Eq. (3.2), the eigenvalue problem (2.3) admits four discrete levels with energies $\pm\omega_1$ and $\pm\omega_2$. The dispersion relations of the conduction and valence bands remain the same. The corresponding wave functions are given in Appendix A. One point to be noted here is that the phase shift $\delta(k)$ to be used in the boundary condition (2.16) now becomes

$$\delta(k) = 2 \cot^{-1}(k/\kappa_1) + 2 \cot^{-1}(k/\kappa_2). \quad (3.6)$$

The physical quantity of immediate interest is the total energy (2.5) of such a system. The elastic deformation en-

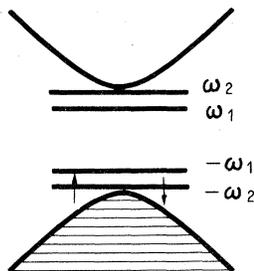


FIG. 3. Electron configuration of two-polaron system.

ergy is readily integrated using Eqs. (A7) and (A8) given in Appendix A. Energy shift of the electrons in the valence band is given by^{23,4}

$$E_{\text{val}} = 2 \left[\int_{-k_F}^{k_F} \frac{dE(k)}{dk} \delta(k) \frac{dk}{2\pi} + 2\Delta_0 \right], \quad (3.7)$$

where $k_F = W/2v_F$. The first factor 2 takes account of twofold spin degeneracy, and $2\Delta_0$ is the correction term that arises from the two bound levels branched off from the top of the valence band. Adding both contributions, we obtain the total energy,

$$E = \frac{4}{\pi} \sum_{j=1}^2 \left[(1-\gamma)\kappa_j v_F + \gamma \Delta_0 \tanh^{-1}(\kappa_j \xi_0) + \omega_j \sin^{-1} \left[\frac{\omega_j}{\Delta_0} \right] \right] + \sum_{j=1}^2 N_j \omega_j, \quad (3.8)$$

relative to the ground state. The energy E depends on the electron configuration through

$$N_j = n_{+j} - n_{-j} \quad (j=1,2), \quad (3.9)$$

where $n_{\pm j}$ denotes the occupation number of the discrete level with energy $\pm\omega_j$. In the two-polaron system with which we are concerned,

$$N_1 = 0 \quad \text{and} \quad N_2 = -2, \quad (3.10)$$

as seen from Fig. 3.

The energy E is a function of two parameters, ω_1 and ω_2 . Figure 4 shows the constant-energy curves for the confinement parameter $\gamma=0.6$. The configuration of two

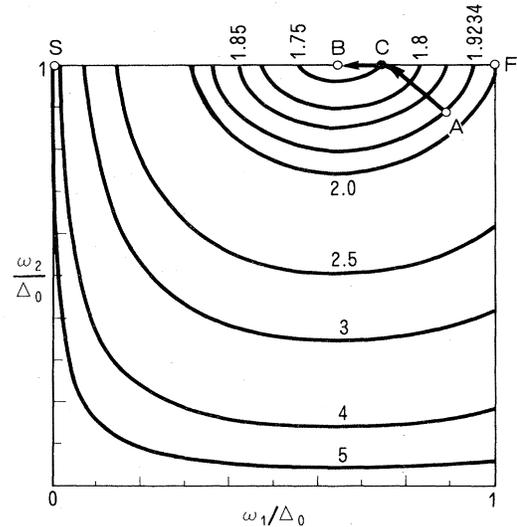


FIG. 4. Constant-energy contour of Eq. (3.8) for two polarons ($N_1=0$ and $N_2=-2$). Confinement parameter γ is taken to be 0.6. The numbers labeling the lines indicate the energy E in units of Δ_0 . Point A represents two infinitely separated polarons with twice the polaron-formation energy. The two-polaron configuration, starting from point A, relaxes along the steepest descent path, touches the $\omega_2 = \Delta_0$ line at point C, and finally descends to the bipolaron, B. Point F represents a configuration of two free carriers with the lattice undistorted.

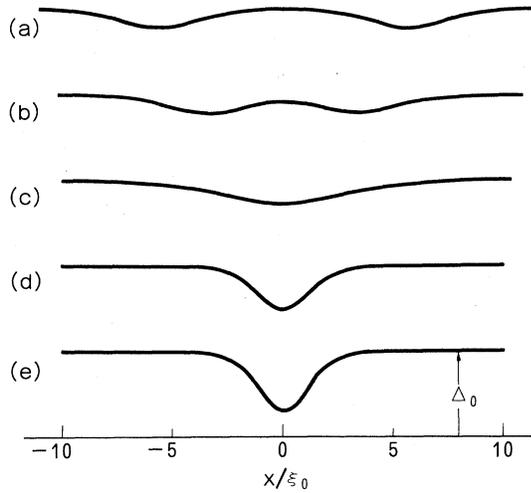


FIG. 5. Behavior of the gap parameter $\Delta(x)$ for five points on the steepest descent path of Fig. 4. Here, (d) corresponds to point *C* in Fig. 4 and (e) to the bipolaron, *B*. The figure, from top to bottom, shows the reaction process (3.1).

infinitely separated polarons takes place at the point *A*. The system, starting from point *A*, will descend along the steepest path, the thick solid lines in Fig. 4. It finally reaches the stable configuration *B*, which is simply the bipolaron.

It is interesting to compare this reaction process with that in *trans*-PA. In *trans*-PA the confinement parameter γ vanishes, and the stable point occurs at *S* in Fig. 4, which represents two charged solitons infinitely separated. Thus two polarons decay into a soliton pair by way of the bipolaron.¹⁸ In *cis*-PA, breakdown of the degeneracy (or the nonvanishing confinement parameter) confines the two solitons to form a single complex, a bipolaron. The term "confinement" refers to this situation.

To visualize this reaction process, in Fig. 5 we show the displacement pattern on five representative points on the steepest descent path. Values of ω_1 , ω_2 , and energy E for the five cases are given in Table I. The figure clearly shows how two separated polarons attract each other and form a bipolaron.

Finally, in Fig. 6 we show the energy E as a function of the separation d between two polarons. Two polarons attract each other with a long-range potential caused by large spatial extension of the polarons. The range is on the order of $10\xi_0$.

Asymptotic expression of the attractive potential can be obtained using Eq. (3.5). The leading term of the attraction comes from the occupation of the two electrons in

TABLE I. Values of ω_1 and ω_2 for the five curves of Fig. 5.

	ω_1/Δ_0	ω_2/Δ_0	E/Δ_0
(a)	0.8861	0.8916	1.9180
(b)	0.8686	0.9090	1.8851
(c)	0.8201	0.9553	1.8110
(d)	0.7441	1.0	1.7520
(e)	0.6481	1.0	1.7336

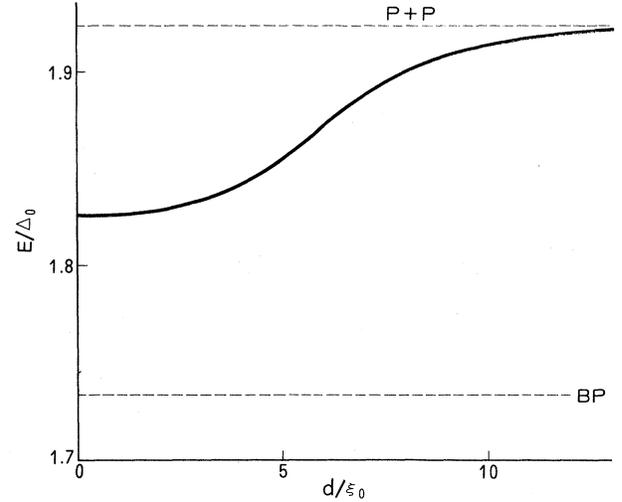


FIG. 6. Energy E plotted as a function of the separation d between two polarons for $\gamma=0.6$. The separation d is determined numerically as the distance between the two dips of $\Delta(x)$ given by Eq. (3.2). For small separations, it is meaningless to speak of "separation between two polarons," as the gap parameter becomes considerably distorted and loses its double-dip structure.

the bonding level $-\omega_2$. Thus the asymptotic form of the attractive potential at large d is given by

$$V(d) \simeq -2(\omega_2 - \omega_0) \simeq -(4\kappa_0^2 v_F^2 / \omega_0) \exp(-\kappa_0 d). \quad (3.11)$$

This expression does not depend on the confinement parameter γ , and it is valid for *trans*-PA as well for which it becomes

$$V(d) \simeq -2\sqrt{2} \Delta_0 \exp(-d/\sqrt{2} \xi_0), \quad (3.12)$$

since $\kappa_0 v_F = \omega_0 = \Delta_0 / \sqrt{2}$.

IV. REPULSIVE INTERACTION OF TWO BIPOLARONS

In this section we investigate the interaction between two bipolarons on a single PA chain.

The two-bipolaron system may be approached by making the same considerations as for two polarons. As two bipolarons approach each other, the energy levels $\pm\omega_0$ are each split into two levels. Therefore, the energy-level structure should be the same as for the two-polaron case. The only differences are the occupation numbers of the electrons in the discrete levels. In the case of two bipolarons, we have

$$N_1 = N_2 = 0, \quad (4.1)$$

as shown in Fig. 7. Except for this single difference, the results obtained in the preceding section apply to the present case of two bipolarons.

To see the interaction between two bipolarons, in Fig. 8 we draw the constant-energy lines given by Eq. (3.8) with (4.1). The cross in the figure represents two infinitely separated bipolarons. As may be seen from this figure, the cross point denotes the minimum-energy configura-

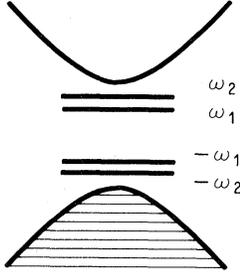


FIG. 7. Electron configuration of two-bipolaron system.

tion, and a repulsive interaction operates between the two bipolarons.

An asymptotic expression for the repulsive potential can be obtained in a way similar to that for two polarons, although the origin of repulsion is less clear. The separation d between two bipolarons is related to the difference $\kappa_1 - \kappa_2$ by Eq. (3.5). We then expand the energy E in powers of $\kappa_1 - \kappa_0$ and $\kappa_2 - \kappa_0$. Linear terms vanish (when $N_1 = N_2 = 0$) because of bipolaron stability [Eqs. (2.17)]. [This is the reason why we could simply obtain Eq. (3.11) for the two-polaron system.] Hence the asymptotic potential, which is determined by second-order terms, becomes

$$V(d) \simeq \frac{16}{\pi} \left[1 + \frac{\gamma \Delta_0^2}{\omega_0^2} \right] \frac{v_F^3 \kappa_0^3}{\omega_0^2} \exp(-2\kappa_0 d). \quad (4.2)$$

This potential has a shorter range than that of polaron attraction, since κ_0 of the bipolaron is larger than κ_0 of the polaron, in addition to the factor 2 in the exponent of Eq. (4.2). The repulsion arises from the increase in both the deformation energy and the electron energies in the valence band.

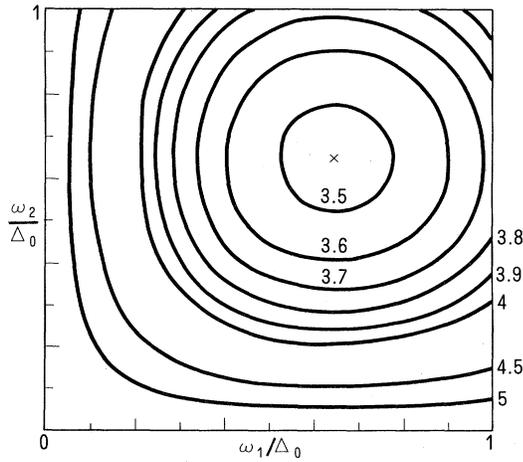


FIG. 8. Constant-energy contour of Eq. (3.8) for two bipolarons ($N_1 = N_2 = 0$). Confinement parameter γ is chosen to be 0.6. The numbers labeling the lines indicate the energy E in units of Δ_0 . The cross corresponds to the configuration of two bipolarons infinitely separated. The figure shows the stability of such a configuration.

V. COEXISTENCE OF A POLARON AND A BIPOLARON

In this section we study interaction between a polaron and a bipolaron coexisting on a single chain. We can expect such a coexistence in lightly doped PA. We find that neither attractive nor repulsive interactions work between them. This means that a polaron and a bipolaron can pass freely through each other.

The coexistence system is analyzed in the same way as the two-polaron case: We focus our attention on the energy-level structure generated by such a configuration. When a polaron and a bipolaron are sufficiently separated on a single chain, the system should have four discrete levels as shown in Fig. 9, where

$$\omega_1 = \omega_0 \text{ of bipolaron}, \quad (5.1)$$

$$\omega_2 = \omega_0 \text{ of polaron}.$$

The electron occupation numbers should be such that

$$N_1 = 0 \text{ and } N_2 = -1. \quad (5.2)$$

We therefore impose a requirement on $\Delta(x)$ that it should admit four discrete levels as shown in Fig. 9. Then $\Delta(x)$ can be constructed by solving the inverse problem of Eq. (2.3). We give the derivation in Appendix A and show here the result

$$\Delta(x) = \Delta_0 + \frac{(\kappa_1^2 - \kappa_2^2)v_F}{\kappa_1 \coth(\kappa_1 x - \beta_1) - \kappa_2 \tanh(\kappa_2 x - \beta_2)} - \frac{(\kappa_1^2 - \kappa_2^2)v_F}{\kappa_1 \coth(\kappa_1 x - \beta_3) - \kappa_2 \tanh(\kappa_2 x - \beta_4)}, \quad (5.3)$$

where

$$2\beta_1 = \alpha + \tanh^{-1}(\kappa_1 \xi_0), \quad 2\beta_3 = \alpha - \tanh^{-1}(\kappa_1 \xi_0), \quad (5.4)$$

$$2\beta_2 = -\alpha + \tanh^{-1}(\kappa_2 \xi_0), \quad 2\beta_4 = -\alpha - \tanh^{-1}(\kappa_2 \xi_0).$$

We have three independent parameters in all. The parameters κ_1 and κ_2 are related to the energies ω_1 and ω_2 of the discrete levels by Eq. (3.4). The parameter α is new, it was absent in the two-polaron case. In fact, the two-polaron solution (3.2) is obtained from Eq. (5.3) by setting $\alpha = 0$.

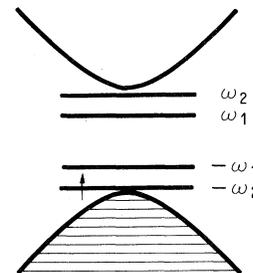


FIG. 9. Electron configuration of polaron-plus-bipolaron coexistence system. The discrete levels with energy $\pm\omega_1$ originate in the bipolaron P^{++} and those with $\pm\omega_2$ in the polaron P^+ .

In spite of the close similarity of Eq. (5.3) to Eq. (3.2), there is one important difference between the two cases: It is now the parameter α that determines the separation between the polaron and bipolaron. This can be seen from the asymptotic expression of Eq. (5.3) for large x . According to the analysis given in Appendix B, when α is positive and large, the bipolaron is located at

$$x_1 = (\frac{1}{2}\alpha + \theta)/\kappa_1, \quad (5.5)$$

and the polaron is located at

$$x_2 = -(\frac{1}{2}\alpha + \theta)/\kappa_2, \quad (5.6)$$

where

$$\theta = \tanh^{-1}(\kappa_2/\kappa_1). \quad (5.7)$$

Figure 10 shows the displacement pattern for various values of the parameter α . For large positive α , we have a polaron and a bipolaron which are separated. They approach each other as α is diminished. The pattern becomes considerably distorted as they pass each other, but they regain their identities after the passage.

To investigate the interaction between the polaron and bipolaron, we have to calculate the energy (2.5) of the system. As far as the energy is concerned we can use the result of Sec. III, because the parameter α has no influence on the energy-level structure [four discrete levels, $\pm\omega_1$ and $\pm\omega_2$, and continuum states $\pm E(k)$]. Therefore the energy of the polaron-plus-bipolaron system is given by Eq. (3.8), where Eq. (5.2) is understood.

Minimization of this energy with respect to the parameters ω_1 and ω_2 leads to the self-consistency equation (2.17) for the bipolaron ($j=1$, $N_1=0$) and polaron ($j=2$, $N_2=-1$). Thus the system has lowest energy when Eq. (5.1) is satisfied. The energy (3.8) is then simply a sum of the bipolaron-formation energy and polaron-formation energy, irrespective of the value of the parameter α , as seen from comparison with Eq. (2.20).

$$\Delta_e - \pi\lambda v_F \sum_j^{\text{occ}} \text{Re}[f_j^*(x)g_j(x)] = \Delta(x) + 4\lambda \sum_{j=1}^2 \left[\frac{\gamma v_F \kappa_j}{\omega_j} - \sin^{-1} \left(\frac{\omega_j}{\Delta_0} \right) - \frac{\pi}{4} N_j \right] \Delta_j(x), \quad (5.8)$$

where

$$\Delta_j(x) = v_F f_{+j}(x) g_{+j}(x) \quad (j=1,2)$$

is related to the wave functions (A13) of the bound states with energy $+\omega_j$. From this result and Eq. (2.17) we know that the system is stable when Eq. (5.1) is satisfied, irrespective of the value of α .

This stability means that the polaron and bipolaron pass each other freely without attractive or repulsive interactions. The energy levels $\pm\omega_1$ and $\pm\omega_2$ are fixed during the entire process of passage. The free passage guarantees that the bipolarons generated by polaron reactions will not disturb any further reaction of polarons into bipolarons.

Before concluding this section, we comment on self-consistency in the two-polaron and two-bipolaron solutions. In the case of two polarons, we have Eq. (3.10). The second pair of terms on the right-hand side of Eq.

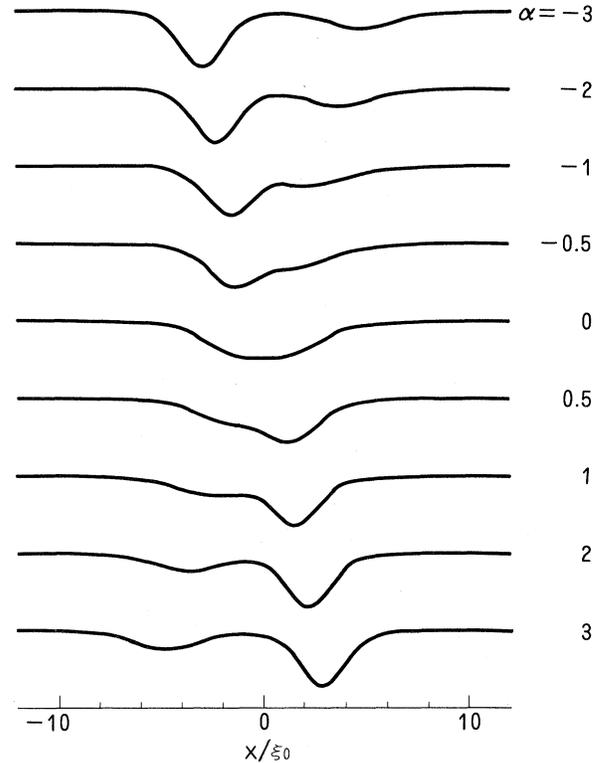


FIG. 10. Behavior of the gap parameter $\Delta(x)$ in the polaron-plus-bipolaron system. The parameter α determines the separation between the polaron and bipolaron.

Stability of the solution can also be confirmed by direct inspection of the self-consistency equation (2.6). We can calculate the right-hand side of Eq. (2.6), using the wave functions obtained in Eqs. (A13)–(A15) of Appendix A, and we obtain

(5.8) vanish when

$$\omega_1 = \omega_0 \text{ of bipolaron and } \omega_2 = \Delta_0,$$

which exactly corresponds to the bipolaron state. Hence, the self-consistency is satisfied only in the final, bipolaron state. This is what we naturally anticipate; intermediate states of chemical reaction will not satisfy such a stability requirement.

In the case of two bipolarons, we have Eq. (4.1). The second terms vanish only when

$$\omega_1 = \omega_2 = \omega_0 \text{ of bipolaron.}$$

Thus the two-bipolaron system is stable only when the bipolarons are infinitely separated.

VI. DISCUSSION

The results obtained in the preceding three sections may be summarized as follows.

Within the framework of the continuum model of *cis*-PA, we have presented exact analytic solutions to three configurations—two polarons, two bipolarons, and a polaron and a bipolaron coexisting on a single chain. We have found that two polarons attract each other with a long-range potential, which reflects large spatial extension of the polaron. The driving force of such attraction is attributed to the electron configuration as depicted in Fig. 3, namely bonding-antibonding splitting of the electron levels and accommodation of two electrons in the lower level constitutes the origin of the attraction. The attracted free polarons will then form a bipolaron. We have thus explained the mechanism of reaction process (3.1).

Two bipolarons have been shown to repel each other. The range of the repulsion is much shorter than that of polaron attraction. The bipolaron repulsion means that the ideal ground state of doped *cis*-PA is the bipolaron lattice.

Finally, we have found that a polaron and a bipolaron can pass freely through each other with neither attractive nor repulsive interactions. The displacement pattern becomes considerably distorted just when they pass each other, but they keep their identities before and after the passage (see Fig. 10). This behavior is similar to the free passage of a soliton through a polaron in *trans*-PA.¹⁹ The free passage implies that even when a bipolaron [which, by itself, has been generated by the reaction (3.1)] happens to exist between two polarons, it will not exert an influence on the reaction of those two polarons into a bipolaron.

Here, we would like to stress the static nature of the above conclusion. The interaction of a polaron and a bipolaron shown in Fig. 10 reminds us of soliton collisions in nonlinear evolution equations.²⁴ However, here we have adopted the adiabatic approximation and entirely neglected the kinetic energy of carbon atoms. Therefore, the free passage mentioned above cannot mean dynamical collision of a fast polaron and a bipolaron. Our conclusion on the free passage refers only to the limit of slow velocities.

In the above theoretical development, we have entirely neglected effects of Coulomb interactions. In polarons and bipolarons, which have electric charge, the Coulomb attraction of ionized dopants will be substantial. Polarons (and bipolarons) cannot be free; they are pinned onto ionized dopants. In the case of charged solitons in *trans*-PA, the binding energy is estimated¹ to be 0.3 eV using the macroscopic dielectric constant $\epsilon \approx 10$ suggested by Fincher *et al.*²⁵ The binding energy of the polaron will be smaller because of larger spatial extension, but it cannot be neglected except at very high temperatures. If polarons (and bipolarons) are strongly pinned on fixed ionized dopants, they cannot move. On the other hand, if dopant diffusion takes place rapidly, polarons (and bipolarons) can move together with the ionized dopants on which they are pinned. Neglect of the pinning potential becomes then unessential. The above-summarized theoretical results may be understood in light of this.

Although no direct experimental data are available on such dopant diffusion, some indirect evidence seems to exist that suggests relatively rapid dopant diffusion. First,

in optical-absorption spectra of lightly doped *trans*-PA, the intensity of soliton absorption is far stronger than that of polarons.^{12,13} In *trans*-PA, the elementary process of doping is considered to be polaron formation rather than soliton formation. If the polarons are fixed and cannot move, they cannot decay in pairs into charged solitons. Then polaron absorption should predominate over soliton absorption. Consequently, the above experiment suggests that, on the contrary, dopant diffusion takes place rapidly along chain,¹³ promoting polaron reactions into charged solitons.

In addition to this, optical measurements on *cis*-rich PA showed that dopants preferentially enter *trans* regions.²⁶ This presumably means that a dopant that first entered a *cis* region and generated a polaron on a *cis*-PA chain diffuses along the chain together with the polaron until it reaches a *trans* region. Hence this experiment also suggests dopant diffusion. Furthermore, the intercalation model of Baughman and co-workers, according to which dopants enter PA in columns or in layers,²⁷ favorably accounts for the ease of dopant diffusion. The light translational mass and large spatial extension of the polaron will help in such diffusion.

The above-mentioned preferential doping on *trans* regions entails a difficulty in the experimental detection of polarons in *cis*-PA. The *cis* films available at present appear to have a small amount (about 10%) of *trans*-PA (Ref. 20) owing to thermal isomerization. Diffusion of dopants into the *trans* regions suppresses polarons in the *cis* region. Polarons in *cis*-PA can survive only in pure-*cis* samples. In addition, the overwhelming predominance of soliton absorption over polaron absorption in *trans*-PA (Refs. 12 and 13) suggests that the corresponding reaction (3.1) in *cis*-PA proceeds quite efficiently owing to rapid dopant diffusion. The amount of surviving polarons will be small as in *trans*-PA.

As for bipolarons, the above inference indicates that doping of pure *cis*-PA generates, finally, a large amount of bipolarons. Therefore bipolarons will be detected in optical measurements if they are stable.

The stability of bipolarons is quite certain in the Brazovskii-Kirova model, as has been shown in Sec. IV. However, further considerations, to see if the stability is absolute or only metastable, is merited. Among the two isomers of PA, *cis*-PA and *trans*-PA, the latter is known to have lower energy. Isomerization from *cis* to *trans* isomers occurs through two channels—by heating²⁸ and by doping.²⁶ The mechanism of either isomerization process has not yet been clarified. However, a model has been proposed^{29,17} in which a bipolaron is an important factor in initiating isomerization by doping. In that event, bipolaron excitation will be metastable rather than stable excitation.

In this context, it would be of much theoretical interest to explore the possibility of a unified model that describes both *cis*- and *trans*-PA. The Brazovskii-Kirova model (2.2) is insufficient for this purpose. If we assume the same electron-lattice coupling constant λ for both isomers, then *cis*-PA will have a lower ground-state energy than *trans*-PA on account of its larger band-gap energy, in contradiction to the established stability of the *trans*

isomer. This is indicative of some missing factor to be included in the existing theoretical model. Construction of such a unified model and elucidation of the isomerization process is quite a challenging problem.

ACKNOWLEDGMENTS

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APPENDIX A: CONSTRUCTION OF THE FUNCTION $\Delta(x)$

In this appendix we derive an explicit expression for the gap-parameter function $\Delta(x)$ in two-polaron (two-bipolaron) and polaron-plus-bipolaron systems. The procedure is almost parallel to that described elsewhere¹⁹ for soliton-polaron coexistence in *trans*-PA. As mentioned in the text, we require $\Delta(x)$ to admit four discrete levels with energies $\pm\omega_1$ and $\pm\omega_2$. In addition, $\Delta(x)$ is taken to be reflectionless. The "reflectionless" condition arises from minimization of the total energy with respect to the electron-reflection coefficients.^{9,30} Throughout this and the following appendixes, we take $\Delta_0 = \xi_0 = 1$ for simplicity.

The eigenvalue problem (2.3) is transformed to decoupled Schrödinger equations,

$$\left[-\frac{\partial^2}{\partial x^2} + U_e(x) \right] f_j(x) = \lambda_j f_j(x), \quad (A1)$$

$$\left[-\frac{\partial^2}{\partial x^2} + U_o(x) \right] g_j(x) = \lambda_j g_j(x),$$

for even- and odd-site wave functions f_j and g_j . The "potentials" $U_e(x)$ and $U_o(x)$ are related to $\Delta(x)$ by

$$U_{e,o}(x) = [\Delta(x)]^2 \mp \frac{\partial \Delta(x)}{\partial x} - 1, \quad (A2)$$

and the "energy" λ_j is

$$\lambda_j = \epsilon_j^2 - 1. \quad (A3)$$

From the requirement on $\Delta(x)$ mentioned above, both $U_e(x)$ and $U_o(x)$ should be reflectionless potentials with two bound states ($\lambda = -\kappa_1^2$ and $-\kappa_2^2$). Such a potential and corresponding wave functions are constructed by means of the inverse scattering method³¹ or by Bargmann's direct method.³² The potential, called the Bargmann potential,²⁴ is

$$U_{e,o}(x) = -2 \frac{d^2}{dx^2} \ln w_{e,o}(x), \quad (A4)$$

where

$$w_e(x) = \kappa_1 \cosh(\kappa_1 x - \beta_1) \cosh(\kappa_2 x - \beta_2) - \kappa_2 \sinh(\kappa_1 x - \beta_1) \sinh(\kappa_2 x - \beta_2), \quad (A5)$$

$$w_o(x) = \kappa_1 \cosh(\kappa_1 x - \beta_3) \cosh(\kappa_2 x - \beta_4) - \kappa_2 \sinh(\kappa_1 x - \beta_3) \sinh(\kappa_2 x - \beta_4). \quad (A6)$$

We construct $\Delta(x)$ from potentials U_e and U_o in the

following way. From Eqs. (A2) we have

$$\frac{d}{dx} \Delta(x) = \frac{1}{2} (U_o - U_e), \quad (A7)$$

$$\Delta(x)^2 = 1 + \frac{1}{2} (U_o + U_e). \quad (A8)$$

Integration of Eq. (A7) with the boundary condition

$$\Delta(x) \rightarrow 1 \quad \text{as } x \rightarrow \pm \infty$$

gives the expression for $\Delta(x)$,

$$\Delta(x) = 1 + \frac{d}{dx} \ln \left[\frac{w_e(x)}{w_o(x)} \right], \quad (A9)$$

which is the solution for polaron-plus-bipolaron system (5.3). The other relation, (A8), leads to

$$\frac{w_e''}{w_e} + \frac{w_o''}{w_o} - 2 \frac{w_e' w_o'}{w_e w_o} + 2 \frac{w_e'}{w_e} - 2 \frac{w_o'}{w_o} = 0,$$

which is satisfied for arbitrary x , if and only if

$$\tanh(\beta_1 - \beta_3) = \kappa_1, \quad \tanh(\beta_2 - \beta_4) = \kappa_2. \quad (A10)$$

The translational symmetry of the system now allows us one free choice of the parameters β_j . We therefore choose

$$\beta_1 + \beta_2 + \beta_3 + \beta_4 = 0.$$

To express the parameters in a symmetric form, we set

$$\beta_1 + \beta_3 = \alpha, \quad \beta_2 + \beta_4 = -\alpha. \quad (A11)$$

Equations (A10) and (A11) determine the parameters β_j as shown in Eq. (5.4). Thus the $\Delta(x)$ of Eq. (A9) contains three parameters, κ_1 , κ_2 , and α . It has the symmetry

$$\Delta(x, -\alpha) = \Delta(-x, \alpha), \quad (A12)$$

which is manifest in Fig. 10.

In two-polaron and two-bipolaron solutions, we take $\alpha = 0$ because $\Delta(x)$ should be an even function in x . This gives the result shown in Eqs. (3.2) and (3.3).

For $\Delta(x)$ of Eq. (A9), the normalized wave functions are as follows. For the bound states with energy $\pm\omega_1$,

$$f_{\pm 1}(x) = A_1 \cosh(\kappa_2 x - \beta_2) / w_e(x), \quad (A13)$$

$$g_{\pm 1}(x) = \pm A_1 \cosh(\kappa_2 x - \beta_4) / w_o(x),$$

and for $\pm\omega_2$,

$$f_{\pm 2}(x) = A_2 \sinh(\kappa_1 x - \beta_1) / w_e(x), \quad (A14)$$

$$g_{\pm 2}(x) = \pm A_2 \sinh(\kappa_1 x - \beta_3) / w_o(x),$$

where the normalization constants are

$$A_j = [\kappa_j (\kappa_1^2 - \kappa_2^2) / 4]^{1/2} \quad (j = 1, 2).$$

The wave functions of the continuum states with energy $\epsilon = \pm E(k)$ are

$$f_k(x) = A_k e^{ikx} [k^2 - \frac{1}{2} ika_e(x) + \frac{1}{4} b_e(x)], \quad (A15)$$

$$g_k(x) = \pm A_k e^{ikx} [k^2 - \frac{1}{2} ika_o(x) + \frac{1}{4} b_o(x)] e^{i\phi(k)},$$

where

$$\phi(k) = \tan^{-1}(k\xi_0),$$

$$A_k = \left[2(k^2 + \kappa_1^2)(k^2 + \kappa_2^2) \left[L + \frac{d\delta(k)}{dk} \right] \right]^{-1/2},$$

in terms of the phase shift $\delta(k)$ defined by Eq. (3.6). The auxiliary functions $a(x)$ and $b(x)$ are³²

$$a_{e,o}(x) = -2 \frac{d}{dx} \ln w_{e,o}(x),$$

$$b_{e,o}(x) = 2 \left[\kappa_1^2 + \kappa_2^2 - \frac{w''_{e,o}(x)}{w_{e,o}(x)} \right].$$

The usual cyclic boundary condition imposed on the wave functions (A15) yields Eq. (2.16).

$$\begin{aligned} \Delta(x) &= 1 + \frac{\kappa_1^2 - \kappa_2^2}{\kappa_1 \coth(\kappa_0 x - \beta_0) - \kappa_2 \tanh(\kappa_0 x - \beta_0)} - \frac{\kappa_1^2 - \kappa_2^2}{\kappa_1 \coth(\kappa_0 x + \beta_0) - \kappa_2 \tanh(\kappa_0 x + \beta_0)} \\ &= 1 + \kappa_0 [\tanh(\kappa_0 x - \beta_0 - \psi) + \tanh(\kappa_0 x - \beta_0 + \psi)] - \kappa_0 [\tanh(\kappa_0 x + \beta_0 - \psi) + \tanh(\kappa_0 x + \beta_0 + \psi)]. \end{aligned}$$

The parameter ψ is defined by

$$\tanh \psi = (\kappa_2 / \kappa_1)^{1/2}.$$

Comparing the above expression with Eq. (2.11), we find that it describes two separated polarons. Since the two polarons are located at $x_p = \pm \psi / \kappa_0$, the separation d is given by Eq. (3.5).

2. Polaron-plus-bipolaron system

To obtain an asymptotic expression of Eq. (5.3) at large separation, let α be positive and large. We can then set

$$\tanh(\kappa_2 x - \beta_2) = \tanh(\kappa_2 x - \beta_4) = 1 \quad \text{for } x > 0,$$

because of the negative sign of β_2 and β_4 . The right-hand side of Eq. (5.3) then becomes

$$\begin{aligned} \Delta(x) &= 1 + \frac{\kappa_1^2 - \kappa_2^2}{\kappa_1 \coth(\kappa_1 x - \beta_1) - \kappa_2} - \frac{\kappa_1^2 - \kappa_2^2}{\kappa_1 \coth(\kappa_1 x - \beta_3) - \kappa_2} \\ &= 1 + \kappa_1 \tanh(\kappa_1 x - \beta_1 - \theta) - \kappa_1 \tanh(\kappa_1 x - \beta_3 - \theta), \end{aligned}$$

where θ is defined by Eq. (5.7). This expression indicates that the bipolaron is located at

$$x_1 = \frac{1}{\kappa_1} \left[\frac{\beta_1 + \beta_3}{2} + \theta \right] = \frac{1}{\kappa_1} \left(\frac{1}{2} \alpha + \theta \right).$$

APPENDIX B: ASYMPTOTIC EXPRESSION OF $\Delta(x)$

In this appendix we derive the asymptotic expression of the gap-parameter function $\Delta(x)$ from Eq. (A9) and confirm that it correctly describes two excitations coexisting at large separation. Although the two-polaron (two-bipolaron) and polaron-plus-bipolaron systems are described by the same function, (A9), their asymptotic behavior is entirely different and calls for a separate treatment.

1. Two polarons (and two bipolarons)

As mentioned in the text, two polarons are infinitely separated when $\kappa_1 = \kappa_2 = \kappa_0$. Consequently, for two polarons sufficiently separated, we set $\kappa_1 = \kappa_2 = \kappa_0$ and $\beta_1 = \beta_2 = \beta_0$ in hyperbolic functions of Eq. (3.2), where

$$\beta_0 = \frac{1}{2} \tanh^{-1}(\kappa_0 \xi_0) = \kappa_0 x_0.$$

Then we have

Similarly, for $x < 0$, we may set

$$\tanh(\kappa_1 x - \beta_1) = \tanh(\kappa_1 x - \beta_3) = -1,$$

because of the positive sign of β_1 and β_3 . Analogous calculation, as above, yields the polaron location (5.6). In the case of negative α , one may use the symmetry (A12).

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