

Electron-correlation effects in one-dimensional large-bipolaron formation

David Emin

Sandia National Laboratories, Albuquerque, New Mexico 87185

Jun Ye and Charles L. Beckel

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

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We study the effects of electron correlation on the ground state of a one-dimensional large singlet bipolaron. The electron-lattice interaction is taken to be the short-range interaction of Holstein's molecular-crystal model. We represent the Coulomb repulsion with the Hubbard short-range repulsion. This adoption of the Hubbard model is equivalent to replacing a strict one-dimensional system that has a short-range logarithmic divergence of the Coulomb repulsion energy between overlapping charges, with a quasi-one-dimensional system of finite width. Two types of electronic correlation are considered. With "in-out" correlation, we permit one of the two self-trapped carriers of bipolaron to have a larger radius than the other. With "left-right" correlation, we permit the centroids of the self-trapped carriers to be displaced from one another. For both types of correlation, variational calculations are performed to determine the magnitudes of the correlation effects in the ground state. There are three parameters in the model: the electronic bandwidth parameter t , the electron-lattice coupling strength E_b , and the Hubbard repulsion, V_c . The electron-lattice interaction provides an indirect intercarrier attraction that fosters the coalescence of the two carriers. In opposition, the carriers' Coulomb repulsion and the kinetic energy required for carrier confinement foster the carriers spreading. With bipolaron formation the intercarrier attraction dominates the Coulomb repulsion. The electron-correlation effect on the bipolaron's binding depends explicitly on only V_c/E_b . The electron correlation also depends on the shape of the local functions presumed in the variational calculations. Of course, the effects of electron correlation on the bipolaron's ground state increase as the Coulomb repulsion between the carriers is increased. Strikingly, we also find that the dependence of the confinement energy on electronic correlation is critical to promoting electronic correlation in the bipolaron's ground state. This feature is discussed in detail. At a maximum ratio of V_c/E_b for which we have stable bipolarons, we find that electronic correlation can lower the ground-state energy of our bipolaron by up to 30%.

I. INTRODUCTION

A carrier is said to be self-trapped when it is bound within a potential well produced by displacements of the equilibrium positions of a solid's atoms from their carrier-free values. In the process of self-trapping the lowering of the carrier's energy due to its binding overcomes the strain energy required to displace atoms from their carrier-free equilibrium positions. Thus, with self-trapping the formation of the potential well in which the carrier is bound is stabilized by the carrier's occupation of a bound state. The quasiparticle comprising a self-trapped carrier and the associated atomic displacements is termed a polaron.

A bipolaron is formed when two carriers are self-trapped within a common potential well. Bipolaron formation can occur because the net electron-lattice interaction, the driving force that stabilizes the atomic displacements, increases as the number of carriers at a common site is increased. By itself this effect leads to a deepening of the self-trapping potential well as the number of carriers self-trapped within the well is increased. As a result, the deformation-related potential energy of each of the two carriers is lowered. Since this effect lowers the energy per carrier of each of the two self-trapped car-

riers, it fosters the coalescing of self-trapped carriers into a common potential well. Of course this driving force for merger of self-trapped carriers is opposed by the Coulomb repulsion between the carriers. Nonetheless, if the electron-lattice interaction is sufficiently strong compared with the Coulomb repulsion, two carriers will be bound in a common well, thereby forming a bipolaron. As illustrated by curve a in Fig. 1, if the energy of the bi-

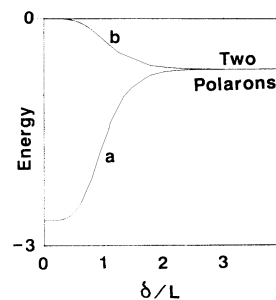


FIG. 1. The energy of two self-trapped carriers is plotted as a function of their separation, δ , divided by their characteristic size, L . In curve a, the bipolaron is stable with respect to dissociation into two separate polarons. In curve b, the bipolaron is unstable with respect to dissociation into two separate polarons.

polaron is lower than that of two separate polarons, the bipolaron will be stable with respect to dissociation. Alternatively, as curve b of Fig. 1 illustrates, a bipolaron will be unstable with respect to forming two separate polarons.

Since each of the self-trapped carriers of a bipolaron is a fermion, it is generally favorable for the self-trapped carriers to pair as a singlet in the lowest level of the self-trapping potential well rather than as a triplet with one of the carriers being promoted to an excited level of the self-trapping potential.¹ Furthermore, the Pauli principle also ensures that excited states of the self-trapping potential well must be occupied if more than two carriers share a common potential well.¹ This effect reduces the energetic favorability of carriers coalescing in units larger than pairs. In other words, this effect impedes the coalescence of polarons and bipolarons into grander polarons. Thus, we only consider the formation of singlet bipolarons.

There are two distinct types of polaron and bipolaron.² If the self-trapped state is confined to a single site, the polaron or bipolaron is referred to as small. For example, the small polaron formed by a hole in KCl, also called a V_K center, is associated with a bonding state centered between two Cl^- ions. If the self-trapped state extends over multiple sites, the polaron is referred to as large. For example, the large polarons formed by electrons in alkali halides have radii that are estimated to be between 5 and 10 Å.

Interest in the formation of both large and small bipolarons has been spurred by evidence that carriers in some systems (1) have a charge of magnitude twice that of an electron, and (2) lack a spin degree of freedom.¹ The question of bipolaron formation in ionic solids is also central to the question of superconductivity in these systems since the *collective* ground state of interacting mobile bipolarons superconducts.¹

The formation of polarons and bipolarons involves a feedback mechanism. That is, self-trapping is a nonlinear phenomenon. In particular, the depth and steepness of the stabilized self-trapping potential well increases as the severity of the carriers' localization is increased. However, the severity of the carriers' localization increases as the self-trapping potential well is deepened. As a result of this feedback mechanism, two distinct types of polaron solution are found. These two types of solution correspond to the formation of polarons and bipolarons that are small or large, respectively. A small polaron or bipolaron is formed when the carriers' energy falls monotonically as the carriers' spatial extent is reduced.^{2,3} The self-trapped state of a small polaron or bipolaron is that for which the carrier or carriers collapse to the smallest size compatible with atomicity, a single site (an atom or a bond). A large polaron or bipolaron forms when the size of a self-trapped state is determined by a competition between (1) the lowering of the carriers' potential energy that accompanies increased localization, and (2) the increase of the carriers' energy arising from carrier confinement.^{2,3}

Whether the polarons or bipolarons formed in a *three-dimensional* system are large or small depends on the

range of the predominant electron-lattice interaction.^{2,3} In particular, a strong long-range electron-lattice interaction results from the Coulomb interactions of charge carriers with the cations and anions of an ionic solid. In addition, a short-range electron-lattice interaction (i.e., like the deformation-potential interaction) results even in covalent systems from the dependence of a carrier's energy on the interatomic separation. When the long-range interaction predominates, finite-size (large) polarons or bipolarons generally form. However, if the short-range interaction is dominant, carriers either do not self-trap or self-trap as small polarons or bipolarons.^{2,3}

Resolving the issue of whether polarons and bipolarons are large or small also depends critically on the dimensionality of the electronic system.^{2,3} In particular, in one-dimensional electronic systems with only short-range electron-lattice interactions (like idealized polymer chains) carriers generally form large polarons or bipolarons. Thus, large polaronic states form in ionic three-dimensional systems and in covalent one-dimensional systems. In fact, at least within the adiabatic approach, the problem of polaron formation in a one-dimensional system with a short-range electron-lattice interaction is isomorphic to that of polaron formation in a three-dimensional system with the long-range Fröhlich electron-lattice interaction.²

This paper addresses the role of electronic correlation in the formation of a large singlet bipolaron. Electron correlation effects occur in bipolaron formation when the interactions between the two carriers causes the presence of one carrier to alter the wave function of the other. Here, we specifically study large bipolaron formation in a one-dimensional system. In individual atoms correlation effects arise from the (direct) Coulomb interactions between charged particles. However, in condensed matter with bipolaron formation, correlation effects are also produced by the indirect interaction between electronic carriers that arises from their mutual interaction with atomic displacements. Electron correlation depends on three different tendencies. First, the atomic displacement-induced potential well that binds the self-trapped carriers is deepened as the *net* charge density of the carriers increases. Second, the (kinetic) energy associated with the confinement of a bound pair of carriers can be lowered by reducing their electronic overlap with one another. Third, the Coulomb repulsion between two carriers confined within a common well favors keeping the two electronic carriers of a bipolaron apart from each other. That is, their confinement energy and their Coulomb repulsion tends to reduce the carriers' overlap with one another while the electron-lattice interaction favors their merger. Thus, we ask if and how electron correlation manifests itself in the electronic state of a one-dimensional large singlet bipolaron.

The role of electronic correlation in bipolaron formation was broached previously in studying the ground state of a small bipolaron in a three-dimensional system with a short-range electron-lattice interaction.⁴ In that system carriers either remain free or self-trap as small polarons or small bipolarons. In our one-dimensional system, carriers either form large polarons or large bipolarons.

rons. Thus, we are addressing the question of electron correlation for a different type of bipolaron than that studied previously. In addition, our treatment of correlation, contained in our choice of variational wave function, differs from that of the earlier study.

We calculate the effects of electron correlation for a one-dimensional large bipolaron. We minimize the energy of a one-dimensional singlet large bipolaron within a model in which the self-trapped carriers are given the freedom to be correlated. We consider the “in-out-type” correlation analogous to that used to describe correlated motion of the two electrons in the ground state of a helium atom.⁵ Namely, we construct a trial wave function for the self-trapped carriers of a singlet bipolaron in which one carrier can move away from the core of the self-trapping potential when the other moves closer to the potential’s core. “Left-right-type” correlation is also considered. In left-right correlation one of the carriers moves to the left of the core of the self-trapping potential when the other carrier is to the right of the core of the self-trapping potential. For each type of correlation, we determine the magnitude of this electronic correlation in a variationally determined ground state of a singlet large bipolaron.

We perform our variational calculations with different functional forms being presumed for the ground-state wave function of the self-trapped carriers. As expected, the presence of the direct Coulomb repulsion between electronic carriers is necessary for correlation effects to be present. However, in all cases the dependence of the confinement energy on electronic correlation is also critical to promoting electronic correlation in the bipolaron’s ground state. In other words, we would find no correlation effects if we were to ignore this kinetic-energy effect. Thus, although correlation effects generally increase with the strength of the Coulomb repulsion, correlation effects should not be viewed as solely caused by the Coulomb repulsion between charges.

In Sec. II we present the formalism we use to address polaron and bipolaron formation in a deformable continuum within the adiabatic approximation. In Sec. III, analytic variational calculations are presented. The results of numerical calculations are described in Sec. IV. Finally, the meaning of our studies is summarized in Sec. V.

II. FORMALISM

To address polaron formation, we determine the ground state of an electron in a deformable continuum within the adiabatic approximation. To study bipolaron formation within the same spirit, we calculate the ground state of a singlet pair of electrons within a deformable medium within the adiabatic approximation. Employing the adiabatic approach means that we presume that the electrons may be regarded as always adjusting to the instantaneous configuration of the deformable continuum.

In the adiabatic approach the potential energy of the deformable continuum is the sum of the vibrational potential energy in the absence of charge carriers plus the electronic energy: $V_{\text{ad}} = V_{\text{vib}} + E_e$. The ground-state

configuration is that for which the net potential energy is a minimum.

A. Formation of a one-dimensional large polaron

The Hamiltonian for a carrier in a one-dimensional deformable chain whose linear coordinate x is expressed in units of the lattice constant is

$$H_{e1} = -t \frac{\partial^2}{\partial x^2} - F \Delta(x), \quad (1)$$

where t is the electronic transfer energy (a constant) associated with the carrier’s effective mass along the linear chain, $\Delta(x)$ is the deformation of the chain at x , and F is the force (a constant) between the deformed chain and the excess electron. Taking this interaction to be local means that we are presuming a short-range electron-chain interaction. With the ground-state wave function of the self-trapped electron being written as $\phi(x)$, the electronic energy is

$$E_{e1} = t \int dx \left| \frac{\partial \phi(x)}{\partial x} \right|^2 - F \int dx |\phi(x)|^2 \Delta(x). \quad (2)$$

The vibrational potential energy for the configuration of the deformed chain corresponding to the self-trapped state is

$$V_{\text{vib}} = (k/2) \int dx \Delta^2(x), \quad (3)$$

where k is the stiffness constant of the deformable strand. In the ground state the total adiabatic potential energy, $E_e + V_{\text{vib}}$, is at its minimum with respect to changes of the deformation, $\Delta(x)$. Minimizing the total adiabatic energy with respect to deformation, the displacement pattern corresponding to the ground state of the polaron is found to be

$$\Delta(x) = \frac{F |\phi(x)|^2}{k}. \quad (4)$$

The adiabatic energy of the ground state is therefore

$$E_{1\text{g.s.}} = t \int dx \left| \frac{\partial \phi(x)}{\partial x} \right|^2 - E_b \int dx |\phi(x)|^4, \quad (5)$$

where $E_b \equiv F^2/2k$.

We now employ the Emin-Holstein (EH) scaling argument.² Specifically, we note that since $\phi(x)$ is the ground-state wave function, any alteration of $\phi(x)$ must necessarily increase the ground-state energy. In particular, the energy of the system must rise if the scale of $\phi(x)$ is altered by a dimensionless factor L : $\phi(x) \rightarrow \sqrt{1/L} \phi(x/L)$, where the presence of the prefactor preserves the wave function’s normalization. Therefore, we may obtain an expression for the ground-state energy by (i) introducing this scale transformation in Eq. (5), and (ii) minimizing the resulting expression with respect to L . Carrying out this two-step procedure with Eq. (5), we first obtain

$$E_{1\text{g.s.}} = c_1 t/L^2 - c_2 E_b/L, \quad (6)$$

where two dimensionless constants have been defined:

$$c_1 \equiv \int dx \left| \frac{\partial \phi(x)}{\partial x} \right|^2, \quad (7a)$$

and

$$c_2 \equiv \int dx |\phi(x)|^4. \quad (7b)$$

Minimizing Eq. (6) with respect to L yields

$$E_{1 \text{ g.s.}} = -[(c_2)^2/4c_1][(E_b)^2/t]. \quad (8)$$

Holstein has solved the one-dimensional adiabatic polaron problem exactly in the continuum limit we are considering. He obtains

$$\phi(x) = \sqrt{E_b/4t} \operatorname{sech}[(E_b/2t)(x-x_0)],$$

where x_0 is the centroid of the large polaron.⁶ With this wave function one finds that $(c_2)^2/c_1 = \frac{1}{3}$. We shall compare results of our variational approaches with this exact result.

B. Formation of a one-dimensional large bipolaron

With two polaronic carriers in our one-dimensional deformable medium, we consider the electronic Hamiltonian to be

$$H_{e2} = -t \left[\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right] - F[\Delta(x_1) + \Delta(x_2)] + V_c \delta(x_1 - x_2). \quad (9)$$

Here x_1 and x_2 are the positions of the two carriers and we represent the Coulomb interaction by a short-range Hubbard-type repulsion between the carriers. The electron-lattice interaction constant F and the electronic transfer energy t are both assumed to be unaltered by the presence of a second carrier.

The choice of a Hubbard-type Coulomb repulsion energy deserves some comment. In particular, since quantum-mechanical particles always have some overlap with one another, the integrand of the actual Coulomb repulsion energy between two overlapping charges in a strict one-dimensional system always has a nonintegrable (logarithmic) divergence at zero interparticle separation. That is, the Coulomb repulsion energy between the charged particles of a bipolaron always diverges for a strict one-dimensional system. For a quasi-one-dimensional system, a deformable strand of finite width, the Coulomb energy diverges as the system's width narrows to approach that of a strict one-dimensional system. In other words, as a system approaches one-dimensionality, the magnitude of the Coulomb interaction is determined by the system's geometry and is ultimately dominated by the short-range repulsion between charged particles. For this reason, we model the Coulomb repulsion of a quasi-one-dimensional system as short ranged: $V_c \delta(x_1 - x_2)$, where V_c is a constant and $\delta(x_1 - x_2)$ is the Dirac δ function.

With the ground-state wave function of the self-

trapped carriers being written as $\chi(x_1, x_2)$, the electronic energy is

$$E_{e2} = t \int \int dx_1 dx_2 \left[\left| \frac{\partial \chi(x_1, x_2)}{\partial x_1} \right|^2 + \left| \frac{\partial \chi(x_1, x_2)}{\partial x_2} \right|^2 \right] - F \int \int dx_1 dx_2 |\chi(x_1, x_2)|^2 [\Delta(x_1) + \Delta(x_2)] + \int \int dx_1 dx_2 V_c \delta(x_1 - x_2) |\chi(x_1, x_2)|^2. \quad (10)$$

To obtain the deformation pattern associated with the ground state, we minimize the sum of the electronic energy of Eq. (10) and the strain energy of Eq. (3) to obtain

$$\Delta(x) = \frac{F}{k} \left[\int dx_1 |\chi(x_1, x)|^2 + \int dx_2 |\chi(x, x_2)|^2 \right] = \frac{2F}{k} \int dx_1 |\chi(x_1, x)|^2, \quad (11)$$

where the indistinguishability of the two particles is utilized. Inserting the equilibrium displacement function, Eq. (11), into the expression for the electronic energy, Eq. (10), and adding the strain energy of Eq. (3), we find the total energy of the two-carrier ground state:

$$E_{2 \text{ g.s.}} = 2t \int \int dx_1 dx_2 \left| \frac{\partial \chi(x_1, x_2)}{\partial x_1} \right|^2 - 4E_b \int dx_1 \left[\int dx_2 |\chi(x_1, x_2)|^2 \right]^2 + V_c \int \int dx_1 dx_2 \delta(x_1 - x_2) |\chi(x_1, x_2)|^2. \quad (12)$$

To proceed, the two-electron ground-state wave function is written in terms of one-electron functions in a manner that incorporates correlation. That is, the spatial extents or centroids of the two one-electron functions, defined as $\psi_+(x)$ and $\psi_-(x)$, are permitted to differ from one another. With each of the one-electron functions being normalized, the normalized spatial factor of the two-electron wave function for a singlet bipolaron is written as

$$\chi(x_1, x_2) = \frac{[\psi_+(x_1)\psi_-(x_2) + \psi_-(x_1)\psi_+(x_2)]}{\sqrt{2(1+|S|^2)}}, \quad (13)$$

where

$$S \equiv \int dx [\psi_+(x)]^* \psi_-(x). \quad (14)$$

The bipolaron's ground-state energy is then expressed in terms of these one-electron functions by incorporating Eq. (13) into Eq. (12):

$$\begin{aligned}
E_{2\text{g.s.}} = & \frac{t}{(1+|S|^2)} \int dx \left[\left| \frac{\partial \psi_+(x)}{\partial x} \right|^2 + \left| \frac{\partial \psi_-(x)}{\partial x} \right|^2 + 2S \frac{\partial \psi_+(x)}{\partial x} \frac{\partial \psi_-(x)}{\partial x} \right] \\
& - \frac{E_b}{(1+|S|^2)^2} \int dx [|\psi_+(x)|^2 + |\psi_-(x)|^2 + 2S \psi_+(x) \psi_-(x)]^2 \\
& + \frac{2V_c}{(1+|S|^2)} \int dx |\psi_+(x)|^2 |\psi_-(x)|^2, \tag{15}
\end{aligned}$$

where the one-electron functions are taken to be nondegenerate and real. Without electron-correlation effects, the two one-electron functions equal one another, $\psi_+(x) = \psi_-(x) = \psi(x)$ and $S = 1$. Alternatively, in the limit of a very strong electron-correlation effect, S approaches zero.

In the absence of Coulomb interactions between carriers, the form of the equations governing the formation of a large bipolaron are analogous to those for large polaron formation. For example, with $V_c = 0$ and uncorrelated (product) wave functions, Eq. (12) has the same form as Eq. (5). Equation (12) then only differs from Eq. (5) in that $2t$ replaces t and $4E_b$ replaces E_b . Thus, we know that the adiabatic large bipolaron eigenfunction in this limit is of the same form as the adiabatic large polaron eigenfunction obtained by Holstein.⁶

III. VARIATIONAL STUDIES

To study the electron-correlation effects we minimize $E_{2\text{g.s.}}$, Eq. (15), with respect to spatial parameters of trial one-electron functions. Two reasonable trial functions are $\psi(x) = \sqrt{1/2L} \operatorname{sech}(x/L)$ and

$$\psi(x) = (1/\sqrt{\pi L})^{1/2} \exp(-x^2/2L^2).$$

As shown in Fig. 2, the spatial extent of the first type of trial wave function is broader than that of the Gaussian for the same values of the L . The first of these functions is of the form of the exact solution of the one-dimensional large polaron problem in the continuum limit. The second of these functions is a convenient *ad hoc* choice that is qualitatively similar to the first function.

To treat an "in-out-type" correlation the spatial extents of the two local functions are allowed to differ from one another: $\psi_{\pm}(x) = \sqrt{1/2L_{\pm}} \operatorname{sech}(x/L_{\pm})$ or

$$\psi_{\pm}(x) = (1/\sqrt{\pi L_{\pm}})^{1/2} \exp(-x^2/2L_{\pm}^2).$$

For a "left-right-type" correlation, the centroids of the local functions differ from one another: $\psi_{\pm}(x) = \sqrt{1/2L} \operatorname{sech}[(x \pm \delta)/L]$ or

$$\psi_{\pm}(x) = (1/\sqrt{\pi L})^{1/2} \exp[-(x \pm \delta)^2/2L^2].$$

A. In-out correlation: Gaussian approximation

We begin by studying the in-out-type correlation. To quantify this type of correlation, we define the dimensionless correlation parameter, $r \equiv L_+/L_-$. The correlation parameter r is unity when there is no correlation effect

and rises to infinity when the correlation effects are maximized. In the strong-correlation limit, one of the carriers is a large polaron while the other carrier is nearly free.

Using the Gaussian trial wave function and the definition $r \equiv L_+/L_-$, we find that Eq. (15) becomes

$$E_{2\text{g.s.}} = \frac{tc_1(r)}{(L_-)^2} - \frac{E_b c_2(r)}{L_-} + \frac{V_c c_3(r)}{L_-}, \tag{16}$$

where

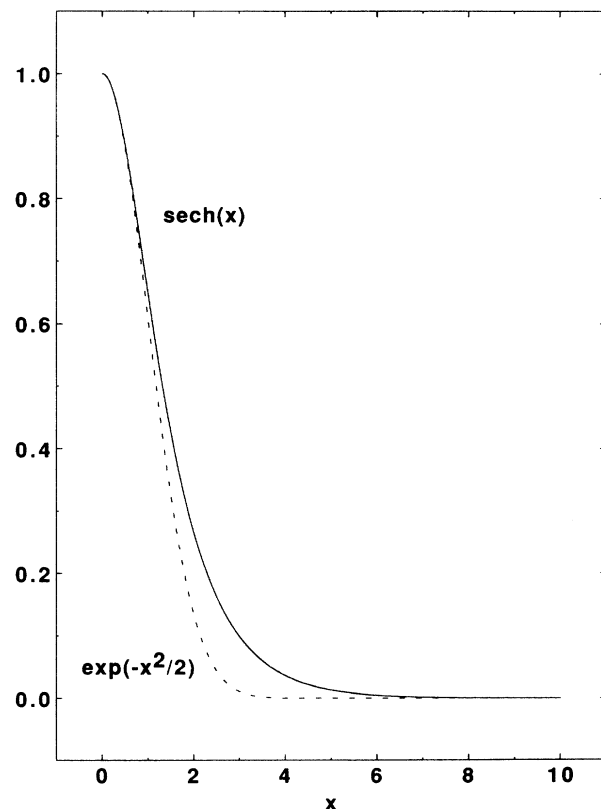


FIG. 2. The unnormalized wave function for a one-dimensional large polaron is $\operatorname{sech}(x)$. This function is plotted as a solid line. The Gaussian approximation to the $\operatorname{sech}(x)$, the dashed line, is valid at small x . Since the Gaussian function is more compact than the secant function, its normalization factor is larger than that for the secant function by the factor $(4/\pi)^{1/4} = 1.06$.

$$c_1(r) \equiv \frac{(1+r^2)}{2(1+r)^2} \left[1 + \frac{1}{r^2} + \frac{8r}{(1+r^2)^2} \right], \quad (17a)$$

$$c_2(r) \equiv \frac{1}{\sqrt{2\pi}} \frac{(1+r^2)^2}{(1+r)^4} \left[1 + \frac{1}{r} + 4r \left[\frac{2}{1+r^2} \right]^{3/2} + 2 \left[\frac{2}{1+r^2} \right]^{1/2} + 8 \left[\frac{2}{1+r^2} \right]^{1/2} \left[\frac{r}{(1+3r^2)^{1/2}} + \frac{1}{(3+r^2)^{1/2}} \right] \right], \quad (17b)$$

and

$$c_3(r) \equiv 2(1+r^2)^{1/2} / \sqrt{\pi}(1+r)^2. \quad (17c)$$

The coefficients $c_1(r)$ and $c_2(r)$ are plotted in Figs. 3 and 4. For weak correlation, $r-1 < 1$, $c_1(r) = 1 - (r-1) + (r-1)^2$, and

$$c_2(r) = 4[1 - (r-1)/2 + 15(r-1)^2/32] / \sqrt{2\pi}.$$

In the strong-correlation limit, $r \rightarrow \infty$, one finds that $c_1(\infty) = \frac{1}{2}$ and $c_2(\infty) = 1/\sqrt{2\pi}$. These values of c_1 and c_2 are those of a solitary one-dimensional large polaron in the Gaussian approximation. The ground-state energy of this large polaron is proportional to $(c_2)^2/c_1$. With the values of c_1 and c_2 obtained in the Gaussian approximation at $r = \infty$, $(c_2)^2/c_1$ equals $1/\pi$, a value comparable to that of Holstein's exact solution, $\frac{1}{3}$. It is also noted that the coefficients $c_1(r)$ and $c_2(r)$ for the bipolaron ($r=1$) and polaron ($r=\infty$) are related in the customary manner: $c_1(1)/c_1(\infty) = 2$ and $c_2(1)/c_2(\infty) = 4$. In addition, we note that

$$c_3(r) \approx [1 - (r-1)/2 + 5(r-1)^2/8] / \sqrt{2\pi} \quad \text{for } (r-1) \ll 1.$$

Examining the dependence of $c_2(r)$ on r , we find that the potential energy associated with self-trapping energy rises as correlation is imposed. Of course, the Coulomb repulsion energy falls with increased electronic correlation. Combining these two potential-energy effects through second order in the $(r-1)$ expansion, we find that for sufficiently strong electron-lattice interaction such that $4E_b > V_c$, the net potential energy rises as correlation is imposed. By contrast, from the behavior of $c_1(r)$ as r is increased from unity, we see that the imposition of electronic correlation reduces the confinement energy. Whether or not it is energetically favorable for a bipolaron to assume a correlated state depends upon whether the correlation-related fall of the kinetic energy overwhelms the rise of the net potential energy. We now investigate this question.

Minimizing $E_{2\text{g.s.}}$ of Eq. (16) with respect to L_- , we find

$$E_{2\text{g.s.}}(r) = -[E_b c_2(r) - V_c c_3(r)]^2 / 4t c_1(r). \quad (18)$$

To find the minimum of $E_{2\text{g.s.}}$ near $r=1$, we insert expansions of $c_1(r)$, $c_2(r)$, and $c_3(r)$ about $r=1$ into Eq. (18). To second order in $(r-1)$, we find

$$\begin{aligned} E_{2\text{g.s.}} &= \frac{(4E_b - V_c)^2}{4t(2\pi)} \frac{1 - (r-1) + (r-1)^2(19 - 6V_c/E_b)/4(4 - V_c/E_b)}{1 - (r-1) + (r-1)^2} \\ &= -\frac{(4E_b - V_c)^2}{4t(2\pi)} \left[1 + \frac{(r-1)^2}{4} \frac{3 - 2V_c/E_b}{4 - V_c/E_b} \right]. \end{aligned} \quad (19)$$

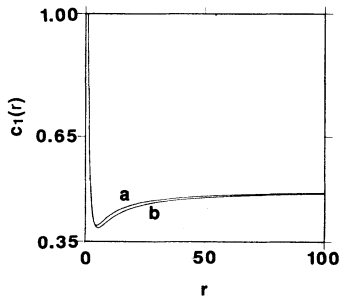


FIG. 3. Curve a is the confinement energy coefficient $c_1(r)$ obtained with the Gaussian approximation plotted against the in-out correlation parameter r . Curve b is a plot of $3c_1(r)/2$ against r obtained with the secant approximation.

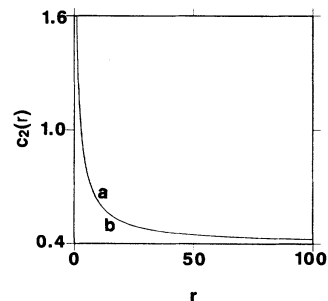


FIG. 4. Curve a is the deformation energy coefficient $c_2(r)$ obtained with the Gaussian approximation plotted against the in-out correlation parameter r . Curve b is a plot of $3c_2(r)/\sqrt{2\pi}$ against r obtained with the secant approximation. In this instance, curves a and b are virtually identical.

The correlation dependences of the potential-energy terms provide the r dependence of the numerator of the r -dependent fraction that follows the first equality of Eq. (19). By itself, the correlation dependence of the potential-energy terms gives a minimum at $r=1$, corresponding to the absence of electronic correlation. The r dependence of the confinement energy is contained in the denominator of the r dependent fraction that follows the first equality of Eq. (19). This factor fosters a minimum at $r > 1$, corresponding to the presence of electronic correlation. As indicated after the second equality of Eq. (19), the r dependence of the confinement energy may be sufficient to stabilize a correlated state. In particular, if $(3-2V_c/E_b)/(4-V_c/E_b) > 0$, the minimum is at $r > 1$. Further comments on this minimum are deferred to Sec. IV where numerical results are presented.

A bipolaron's energy must be less than that of two separate large polarons for the bipolaron to be stable: $E_{2\text{g.s.}} < 2E_{1\text{g.s.}}$. From Eq. (16) with $r = \infty$ and $V_c = 0$ one finds the energy of a large polaron to be

$$E_{1\text{g.s.}} = -\frac{(E_b)^2}{2t(2\pi)}. \quad (20)$$

Thus, for example, a quasi-one-dimensional bipolaron at $r = 1$ is stable when $E_b > V_c/2$.

B. "Left-right" correlation: Gaussian approximation

To consider left-right type correlation rather than in-out-type correlation, we consider trial functions of the form

$$\psi_{\pm}(x) = (1/\sqrt{\pi L})^{1/2} \exp[-(x \pm \delta)^2/2L^2].$$

Using these functions in Eq. (15), we find that

$$E_{2\text{g.s.}} = \frac{td_1(\delta/L)}{L^2} - \frac{E_b d_2(\delta/L)}{L} + \frac{V_c d_3(\delta/L)}{L}, \quad (21)$$

where

$$d_1(\delta/L) = 1 - 2(\delta/L)^2 / \{ \exp[2(\delta/L)^2] + 1 \}, \quad (22a)$$

$$d_2(\delta/L) = \frac{2\{1 + 2\exp[-4(\delta/L)^2] + 4\exp[-5(\delta/L)^2/2] + \exp[-2(\delta/L)^2]\}}{\sqrt{2\pi}\{1 + \exp[-2(\delta/L)^2]\}^2}, \quad (22b)$$

and

$$d_3(\delta/L) = \frac{2}{\sqrt{2\pi}\{1 + \exp[2(\delta/L)^2]\}}. \quad (22c)$$

It should be noted that the kinetic-energy coefficient approaches unity both as δ/L approaches the value corresponding to an uncorrelated large bipolaron, $\delta/L = 0$, and as δ/L approaches the value corresponding to two separate large polarons, $\delta/L = \infty$. Between these limits $d_1(\delta/L)$ has a minimum. Thus, the confinement energy is reduced as correlation is increased from zero: as δ/L rises from zero. This kinetic-energy effect, by itself, tends to foster correlation. With sufficiently strong electron-lattice coupling, this tendency is opposed by the potential energy. Specifically, if $2E_b > V_c$ the potential energy rises as δ/L is increased from zero. Again, to find out if electron correlation is favored energetically, we ask whether or not the correlation-induced lowering of the kinetic energy exceeds the raising of the potential energy.

Minimizing $E_{2\text{g.s.}}$ of Eq. (21) with respect to L and expanding about $\delta/L = 0$, we find that

$$\begin{aligned} E_{2\text{g.s.}} &= -\frac{(4E_b - V_c)^2}{4t(2\pi)} \\ &\times \frac{1 - [2(2 - V_c/E_b)/(4 - V_c/E_b)](\delta/L)^2}{1 - (\delta/L)^2} \\ &= -\frac{(4E_b - V_c)^2}{4t(2\pi)} \left[1 + (\delta/L)^2 \frac{V_c/E_b}{4 - V_c/E_b} \right]. \quad (23) \end{aligned}$$

The correlation dependences of the potential-energy terms produce the (δ/L) dependence of the numerator of the (δ/L) -dependent fraction that follows the first equality of Eq. (23). By itself, the correlation dependence of the potential-energy terms favors a minimum at $\delta=0$, corresponding to the absence of electronic correlation. The (δ/L) dependence of the confinement energy is contained in the denominator of the (δ/L) -dependent fraction that follows the first equality of Eq. (23). This factor fosters a minimum at $\delta \neq 0$, corresponding to the presence of electronic correlation. As indicated after the second equality of Eq. (23), the (δ/L) dependence of the confinement energy may be sufficient to stabilize a correlated state. In particular, for $V_c > 0$, the minimum value of $E_{2\text{g.s.}}$ is not at the uncorrelated value of δ , that is, at $\delta=0$. It is stressed that the minimum would be at $\delta=0$ were it not for the decrease of $d_1(\delta/L)$ from unity as δ/L is increased from zero. Thus, as in the case of in-out-type correlation, the dependence of the confinement energy on electronic correlation is critical to establishing electronic correlation in this example.

To analytically determine the location and depth of the minimum of $E_{2\text{g.s.}}$, we keep terms up to fourth order in δ/L in the expansion of Eq. (23). The algebra is messy, so only the result is quoted here. The minimum is found at

$$\delta/L = \frac{V_c(4E_b - V_c)}{36(E_b)^2 - 19E_b V_c + 2(V_c)^2}$$

with an energy of

$$E_{2\text{g.s.}}(\text{min}) = -\frac{(4E_b - V_c)^2}{4t(2\pi)} \left[1 + \frac{(V_c/E_b)^2}{2[36 - 19V_c/E_b + 2(V_c/E_b)^2]} \right]. \quad (24)$$

To estimate the size of these effects, we consider $V_c/E_b = 2$. This choice corresponds to the largest value of V_c for which the uncorrelated large bipolaron remains stable with respect to separating into two large polarons. Then, with this choice of parameter, $\delta/L = \frac{2}{3}$, a value corresponding to nonminimal overlap between the two separate local functions. At this value of δ/L the curly bracketed factor of Eq. (24) has risen to a value of $1 + \frac{1}{3}$. That is, even with this relatively large value of V_c/E_b ($=2$), the increased binding of the bipolaron that arises from electronic correlation is about 30%.

C. Two noninteracting particles in a harmonic potential well

To understand the competing effects of electron correlation on the confinement energy and the potential energy, we treat a well-known (nonpolaron) problem with our procedure. We consider two *noninteracting* particles placed in a harmonic potential well of spring constant κ . The potential energy of the two particles is

$$V(x_1, x_2) \equiv (\kappa a^2/2)[(x_1)^2 + (x_2)^2],$$

where a is the length scale and x_1 and x_2 are dimensionless. Using our correlated wave function, given in Eq. (13), and taking the local functions to be Gaussians,

$$\psi_{\pm}(x) = (1/\sqrt{\pi}L)^{1/2} \exp[-(x \pm \delta)^2/2L^2],$$

we obtain the expectation value of the potential energy:

$$\begin{aligned} \langle V \rangle &= (\kappa a^2 L^2/2) f(\delta/L) \\ &\equiv (\kappa a^2 L^2/2)[1 + 2(\delta/L)^2/(1+S^2)], \end{aligned} \quad (25)$$

where $S = \exp[-(\delta/L)^2]$. The confinement energy with our correlated wave function is just that of the bipolaron problem with left-right-type correlation: $td_1(\delta/L)/L^2$. The net variational energy for the two noninteracting particles in the harmonic oscillator well is then

$$E_{\text{var}}[L, \delta/L] = \frac{td_1(\delta/L)}{L^2} + \frac{\kappa a^2 L^2 f(\delta/L)}{2}, \quad (26)$$

where $t \equiv \hbar^2/2ma^2$ and m is the mass of each particle. Minimizing this energy with respect to the variational parameter L , we obtain

$$E_{\text{var}}[L_{\text{min}}, \delta/L] = \hbar\omega \sqrt{f(\delta/L)d_1(\delta/L)}, \quad (27)$$

where $\omega \equiv \sqrt{\kappa/m}$.

To look for the minimum value of $E_{\text{var}}[L_{\text{min}}, \delta/L]$ with respect to a variation in δ/L , we expand S and the two functions contained within the radical of Eq. (27) for small δ/L :

$$f(\delta/L) = 1 + (\delta/L)^2 + (\delta/L)^4, \quad (28)$$

and

$$d_1(\delta/L) \approx 1 - (\delta/L)^2 + (\delta/L)^4. \quad (29)$$

Correlation has opposing effects on the two contributions to the energy. The confinement energy, proportional to $d_1(\delta/L)$, falls as δ/L is increased from zero, while the expectation value of the potential energy, proportional to $f(\delta/L)$, rises with increasing δ/L . Incorporating Eqs. (28) and (29) into Eq. (27), we see that the net energy rises with increasing δ/L :

$$E_{\text{var}}[L_{\text{min}}, (\delta/L)] \approx \hbar\omega \sqrt{1 + (\delta/L)^4}. \quad (30)$$

Thus, as is well known, the minimum energy of two noninteracting particles within a harmonic well is just the value obtained without correlation effects, (when $\delta/L = 0$) $\hbar\omega$. The absence of correlation in the ground state of this problem may be viewed as due to the correlation-induced lowering of the confinement energy being overwhelmed by the increase of the potential energy. One should note that the term that drives the minimum to $\delta/L = 0$ is only of fourth order in δ/L . That is, there is a near cancellation of the effects of correlation on the kinetic and potential energies. Thus, even in this problem the kinetic energy plays a significant role in determining the instability of the correlated state. In addition, this example indicates the great sensitivity of correlation effects to the choice of variational wave function. In particular, using a variational wave function that did not reduce to the exact solution, one could readily find the spurious result that electron correlation is significant even in the absence of interaction between the particles.

IV. NUMERICAL STUDIES

In addition to the analytical studies with the Gaussian-based trial wave functions described in the previous section, we have carried out numerical studies with the secant-based trial wave function. In these calculations, integrations are performed numerically. Here we present our findings in a form similar to that used to describe our analytical results.

For the case of in-out correlation with $\psi_{\pm}(x) = \sqrt{1/2L_{\pm}} \text{sech}(x/L_{\pm})$ we computed the coefficients $c_1(r)$ and $c_2(r)$ that are to be used in the energy expression of Eq. (16). The values of these coefficients found using the secant expression are smaller than the corresponding values found with the Gaussian approximation since the Gaussian function is a more compact function. In particular, with the secant function the values of the confinement coefficient $c_1(r)$, at $r=1$ and at $r=\infty$, are smaller than those obtained with the Gaussian function by the factor $\frac{2}{3}$. Similarly, the values of the deformation coefficient $c_2(r)$, at $r=1$ and at $r=\infty$, ob-

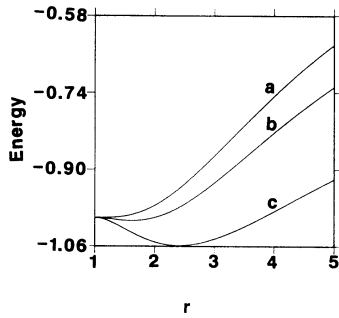


FIG. 5. A bipolaron's ground-state energy, $E_{2g.s.}$, in units of $(4E_b - V_c)^2/8\pi t$, obtained with the secant approximation, is plotted against the in-out correlation parameter r for $V_c/E_b = 0, 1, \text{ and } 2$ in curves a, b, and c, respectively. For $V_c \approx 2E_b$ the large bipolarons become unstable with respect to separating into two independent large polarons.

tained with the secant function are smaller than those obtained with the Gaussian function by the factor $\sqrt{2\pi}/3$. To facilitate comparison of the r dependence of the coefficients $c_1(r)$ and $c_2(r)$ obtained with the secant functions with those obtained with the Gaussian functions, we multiply the coefficients obtained with the secant functions by the factors $\frac{3}{2}$ and $3/\sqrt{2\pi}$, respectively. Thus, in Figs. 3 and 4 we plot $3c_1(r)/2$ and $3c_2(r)/\sqrt{2\pi}$ with the values of $c_1(r)$ and $c_2(r)$ obtained with secant functions along with the values of $c_1(r)$ and $c_2(r)$ found with the Gaussian functions. Figures 3 and 4 illustrate the similarity of the r dependences of the coefficients obtained with the two different trial functions.

In Fig. 5, the ground-state energy obtained with the secant function, in units of $(4E_b - V_c)^2/8\pi t$, is plotted against the in-out correlation parameter r for three values of V_c/E_b . For values of V_c/E_b that are larger than about 2, the large bipolaron becomes unstable with respect to separation into two widely separated large polarons. We see that as V_c/E_b is increased, correlation effects become increasingly significant. In particular, as V_c/E_b is increased, a minimum is produced at $r > 1$. Having the energy minimum at a value of r greater than unity corresponds to having a ground state in which elec-

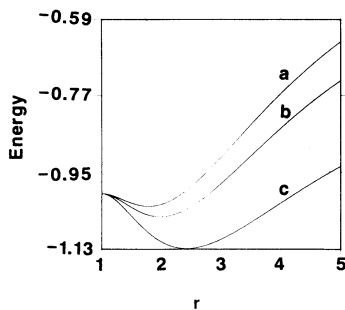


FIG. 6. A bipolaron's ground-state energy, $E_{2g.s.}$, in units of $(4E_b - V_c)^2/8\pi t$, obtained with the Gaussian approximation, is plotted against the in-out correlation parameter r for $V_c/E_b = 0, 1, \text{ and } 2$ in curves a, b, and c, respectively.

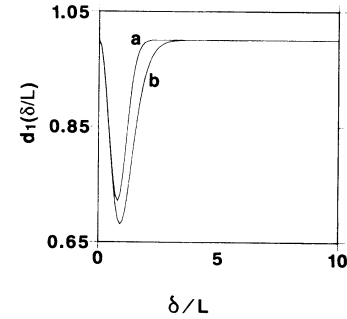


FIG. 7. Curve a is the confinement energy coefficient $d_1(\delta/L)$ obtained with the Gaussian approximation plotted against the left-right correlation parameter δ/L . Curve b is a plot of $3d_1(\delta/L)/2$ vs δ/L obtained with the secant approximation.

tronic correlation tends to keep the two charges somewhat apart from one another.

The ground-state energy obtained with the Gaussian model with in-out correlation, shown in Fig. 6, yields a correlation effect, a minimum at $r > 1$, even when $V_c = 0$. However, as noted at the end of Sec II, the secant function reduces to the exact for our model in the limit of $V_c = 0$. Therefore, we take the presence of a small correlation effect in the Gaussian model even in the absence of Coulomb repulsion to be an artifact of the Gaussian approximation to the local wave function. Thus, the differences that exist between the coefficients obtained in the two approximations are sufficient to introduce a spurious minimum in the Gaussian approximation.

Computations have also been performed for the case of left-right correlation with secant-based trial wave functions: $\psi_{\pm}(x) = \sqrt{1/2L} \operatorname{sech}[(x \pm \delta)/L]$. In analogy with the procedure described above, we again augment the confinement coefficient, $d_1(\delta/L)$ and the deformation coefficient $d_2(\delta/L)$ by the factors that are required to facilitate a direct comparison of the δ/L dependences of these coefficients with those obtained with the Gaussian approximation. In Figs. 7 and 8, the augmented confinement coefficient $3d_1(\delta/L)/2$ and the augmented deformation coefficient $3d_2(\delta/L)/\sqrt{2\pi}$ obtained with the

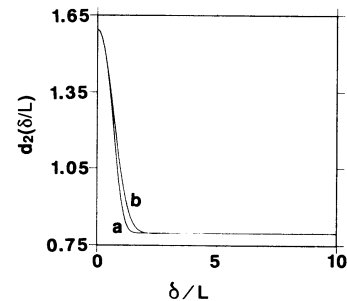


FIG. 8. Curve a is the deformation energy coefficient $d_2(\delta/L)$ obtained with the Gaussian approximation plotted against the left-right correlation parameter δ/L . Curve b is a plot of $3d_2(\delta/L)/\sqrt{2\pi}$ against δ/L obtained with the secant approximation.

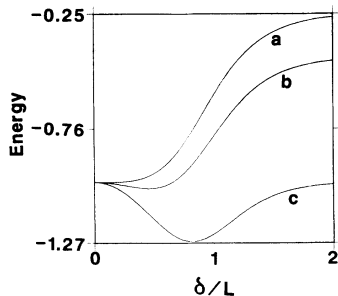


FIG. 9. A bipolaron's ground-state energy, $E_{2\text{g.s.}}$, in units of $(4E_b - V_c)^2/8\pi t$, obtained with the secant approximation, is plotted against the left-right correlation parameter δ/L for $V_c/E_b = 0, 1, \text{ and } 2$ in curves a, b, and c, respectively.

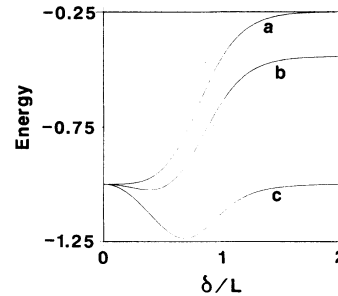


FIG. 10. A bipolaron's ground-state energy, $E_{2\text{g.s.}}$, in units of $(4E_b - V_c)^2/8\pi t$, obtained in the Gaussian approximation, is plotted against the left-right correlation parameter δ/L for $V_c/E_b = 0, 1, \text{ and } 2$ in curves a, b, and c, respectively.

secant functions are plotted along with $d_1(\delta/L)$ and $d_2(\delta/L)$ obtained with the Gaussian functions. The δ/L dependences of the coefficients obtained with both procedures are very similar to one another.

The ground-state energies of the bipolaron using secant functions is plotted against the correlation parameter for left-right correlation in Fig. 9. For comparison, the results for left-right correlation in the Gaussian model are shown in Fig. 10. The results with both approximations are very close to one another. The increase of correlation effects as V_c/E_b is increased is evident in both figures.

V. SUMMARY

Bipolarons form when the indirect attraction between charge carriers that results from the electron-lattice interaction overwhelms the Coulomb repulsion between the carriers. Then, two carriers find it energetically favorable to be bound within the same potential well. Despite the carriers' Coulomb repulsion being exceeded by their indirect attraction for one another, electron-correlation effects are found to occur for a one-dimensional singlet large bipolaron. That is, even though the carriers have a net attraction for one another, their ground-state energy can be lowered by separating the carriers somewhat from one another.

We consider correlated singlet wave functions involving states with different spatial extents (in-out correlation) and different centroids (left-right correlation). By themselves the potential-energy contributions to the total energy do *not* make a correlated ground state energetically favorable. Nonetheless, since our correlated states have greater spatial extents than the uncorrelated states, their adoption reduces the energy required to confine the carriers within their common potential well. This kinetic-energy effect is found to be *essential* to the energetic stabilization of a correlated ground state.

Correlation effects in an energetically stable bipolaron result from the competition between (1) the drive for coalescence of the carriers produced by the potential energy, and (2) the tendency for charge to disperse associated with the kinetic energy. Altering the form of variational wave functions generally shifts the relative contributions of the competing terms. Because of the delicacy of the competition, spurious results may be readily obtained. For example, the two functional forms presumed in the correlated wave function, the Gaussian function and the secant function, are seen in Fig. 1 to be similar to one another. In addition, with both functions the dependences of the correlation coefficients on the correlation parameters, r for in-out correlation and δ/L for left-right correlation, are seen in Figs. 3, 4, 7, and 8 to be similar to one another. Nonetheless, for in-out correlation the Gaussian approximation gives a correlated ground state even for $V_c = 0$, Fig. 6, while the secant wave function, the exact wave function in this limit, does not. Thus, we emphasize the sensitivity of the results to details of the trial wave functions.

Ground-state correlation vanishes when the on-site Coulomb repulsion V_c vanishes and the magnitudes of correlation effects increase with increasing V_c/E_b , where E_b is the electron-lattice coupling strength. However, V_c/E_b cannot become greater than about 2 without destabilizing our large bipolaron with respect to separating into two separate large polarons. At a maximum ratio of V_c/E_b for which we have stable bipolarons, we find that correlation effects can lower the ground-state energy of our singlet bipolaron by up to 30%.

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