Formation of a large singlet bipolaron: Application to high-temperature bipolaronic superconductivity

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We variationally determine the conditions for the formation of *large* singlet bipolarons within the adiabatic approximation. We find that, in two- and three-dimensional electronic systems with only a short-range electron-lattice interaction, the only bipolarons are small bipolarons. Furthermore, with only the long-range (Fröhlich) electron-lattice interaction characteristic of an ionic solid, we find the classical result that bipolarons will not form. However, with the presence of *both* short- and long-range components of the electron-lattice interaction, we find a *novel* domain within which large bipolarons can be formed. In particular, an exceptionally large ratio of the static to high-frequency dielectric constants ϵ_0 and ϵ_∞, respectively, is critical to the formation of large singlet bipolarons. The remaining conditions for the formation of large singlet bipolarons are much less stringent for electronic systems of two dimensions than for those of three dimensions. Therefore, with the high-temperature superconductors having $\epsilon_0 \gg \epsilon_\infty$, the notion that their charge carriers are singlet *large* bipolarons is a real possibility. Estimating the transition temperature for bipolaronic superconductivity as the temperature of the Bose-Einstein condensation, transition temperatures of the order of those found in the high-temperature superconductors are reasonably obtained. Furthermore, if, as envisioned in the CuO_2-based materials, the mass of the large bipolaron is dominated by the short-range interaction of the carrier occupying oxygen sites with the surrounding (relatively heavy) cations, there is only a slight dependence of the transition temperature on isotopic substitutions for the solid's oxygen atoms. Finally, the transition temperature increases linearly with the thickness of the disk-shaped bipolaron (the number of contiguous CuO_2 sheets) until a limiting value is achieved when the bipolaron's shape approaches three dimensionality. These findings are consistent with the general features of the high-temperature superconducting materials.

I. INTRODUCTION

The discovery of high-temperature superconductors[1-3] has increased interest in "novel" mechanisms of superconductivity. In particular, there has been revived interest in the notion of bipolaronic superconductivity.[4-12] Bipolarons form when, as a result of their interactions with the surrounding atoms, electrons pair to form a bosonlike entity. The basic idea of bipolaronic superconductivity is that, with the bipolarons acting as charged bosons, superconductivity will result below the temperature of the Bose-Einstein condensation.[4] Minimally, bipolaronic superconductivity requires that the charge carriers form bipolarons and that the bipolarons be mobile (rather than localized).

The self-trapping of a charge carrier to form a polaron and the pairing of carriers to form bipolarons result from the carrier's interactions with the atoms of the solid. Two types of electron-lattice interactions are generally envisioned. The fact that the energy of an electron at some location within a solid depends on the positions of the atoms in its immediate vicinity gives rise to a short-range electron-lattice interaction.[13] This short-range electron-lattice interaction is present in all materials. Additionally, in ionic materials a carrier interacts with the dipoles of the solid via a long-range electrostatic interaction.[14]

With only a short-range electron-lattice interaction, polarons in two or more dimensions are always "small."[15-17] That is, even in a perfect crystal, the local states that are combined to produce the Bloch-like small-polaronic eigenstates describe a carrier that is strongly localized within the potential well produced by the displacements of the atoms surrounding it from their carrier-free equilibrium positions. Here, with a "linear" electron-lattice interaction, atomic displacements about a "localized" carrier lower the system's energy by $E_b = A^2/2k$, where A is the electron-lattice force between a static carrier confined to a single atomic site and the surrounding atoms, and k is the stiffness constant associated with the atomic displacements.

For a small bipolaron to be energetically stable, the lowering of the polaronic energy, which results from having *two* charges occupy a single site rather than being at well-separated sites ($2^2E_b - 2E_b = 2E_b$), must overwhelm the carriers' mutual (single-site) Coulomb repulsion U.[18-20] Thus, small bipolaron formation is generally associated with significant atomic displacements $\simeq (U/k)^{1/2}$. As with a small polaron, for a *small* bipolaron to move coherently, this atomic-displacement pattern must tunnel with the paired carriers.[21] As a result, the bipola-

ronic bandwidth is greatly reduced from that characterizing pure electronic transfer [by a factor of about $\exp(-2U/\hbar\omega_0)$ even at $T=0$ K, where ω_0 is the characteristic atomic vibrational frequency]. For a small particle with such narrow energy bands, even a modest departure from perfect translational degeneracy should lead to localization of small bipolarons.[19,20,22,23] This conclusion is supported by the fact that carrier localization rather than superconductivity is observed in systems (e.g., the boron carbides) in which small bipolarons have been shown to exist.[24-27] Indeed, it is presumably because of the strong tendency toward localization that coherent ("bandlike") motion of small polarons, predicted to exist at low temperatures,[21] has not been observed. Thus, it seems unlikely that real *small*-bipolaronic systems will actually be superconducting.

Conversely, with only the long-range electrostatically based (Fröhlich) electron-lattice interaction, polarons are generally large rather than small. In these instances the polarons move as quasifree carriers. However, at least in a classical treatment, large polarons of the same sign always repel one another. In particular, the atomic displacements induced electrostatically by a pair of charges separated by the distance r only reduce the effective repulsion between the charges from $e^2/\epsilon_\infty r$ to $e^2/\epsilon_0 r$, where ϵ_∞ and ϵ_0 are the high-frequency and static dielectric constants, respectively. That is, these polarization effects will not produce an attractive interaction. Thus, long-range electrostatic interactions, by themselves, cannot induce the pairing of large polarons into bipolarons.

The present state of our knowledge of bipolaron formation can be succinctly summarized. With only a short-range electron-lattice interaction in a system of two or more dimensions, although small bipolarons can be formed, they tend to be localized rather than mobile. With only the long-range electrostatic interaction generally utilized in studying large polarons (the Fröhlich interaction), polarons are mobile but do not pair to form bipolarons.

In the present work, we consider the *combined* effect of the short- and long-range electron-lattice interactions on the formation of a large singlet bipolaron. We find that a large bipolaron can only be formed in multidimensional electronic systems if the ratio of the static dielectric constant to the high-frequency dielectric constant is uncommonly large: $\epsilon_0/\epsilon_\infty \gg 2$. In a three-dimensional electronic system, the formation of a large bipolaron also requires that the electronic bandwidth lie within a restricted range of values. Thus, the three-dimensional ($BaBiO_3$-based) high-temperature (up to about 30 K) superconductors[3] might support the formation of large bipolarons. Strikingly, we also find that with a two-dimensional electronic system, as occurs in the ionic CuO_2-based superconductors, large bipolarons may be formed over a very much wider range of energetic parameters. Since these novel superconductors are characterized by $\epsilon_0 \gg 2\epsilon_\infty$, it is reasonable to suspect that the charge carriers in these materials form large bipolarons.

Specifically, in this paper we consider a singlet *pair* of electrons in a deformable continuum with both short- and long-range electron-lattice interactions. Within the adiabatic limit, we derive an expression for the ground-state energy of this system. After simplifying the expressions for the electrons' kinetic energy and their direct Coulombic repulsion, we minimize the system's energy with respect to both the spatial extent of the self-trapped electrons R and to the interpolaron separation s. With only a short-range electron-lattice interaction, we find that the only bipolarons in systems of two or more dimensions are small bipolarons. With only the long-range Fröhlich interaction, we find that bipolaron formation will not occur. However, we find that with *both* the short- and long-range components of the electron-lattice interaction, a large-radius bipolaron *can* be formed.

We note then that, as with large polarons, large bipolarons move through a solid as quasifree charged particles. Thus, we view a finite density of large bipolarons in a solid as being analogous to a gas of mobile charged bosons. This circumstance is just that envisioned as producing bipolaronic superconductivity.[4] Following other studies, we estimate the transition temperature for the superconductivity as the Bose-Einstein condensation temperature.[4-12] Taking the density of large bipolarons to be comparable to the observed carrier density and presuming plausible values of the bipolaron's mass ($\simeq$twenty times the mass of a free electron), we obtain transition temperatures comparable to those characterizing the high-temperature superconductors. If the carrier density is raised sufficiently high so as to inhibit the formation of large bipolarons, the density of large bipolarons and, therefore, the superconducting transition temperature will decrease with increasing carrier density. Furthermore, with the holes in the CuO_2-based materials primarily occupying oxygen sites, the large bipolaron's effective mass is dominated by the holes' short-range electron-lattice interaction with acoustic phonons. Then the dependence of the superconducting transition temperature on the masses of the solid's atoms enters through the square of the material's sound velocities. Thus, there may only be a weak dependence of the transition temperature of the CuO_2-based materials on isotopic substitutions for the solid's oxygen atoms. Finally, associating a thickening of a quasi-two-dimensional large bipolaron with the contiguous stacking of CuO_2 sheets in the CuO_2-based superconductors, we find that the superconducting transition temperature increases linearly with the thickness of a disklike large bipolaron. This increase of the superconducting transition temperature with the bipolaron's thickness saturates when the bipolaron's thickness becomes comparable to its diameter. These expectations for the superconductivity of large bipolarons are consistent with observations on the high-temperature superconductors.

This paper is organized in the following manner. In Sec. II, we calculate the adiabatic ground-state energy of two electrons within a deformable medium with a linear electron-lattice interaction of arbitrary range. We restrict our considerations to the formation of a singlet bipolaron. The terms associated with the electronic kinetic energy, electron-lattice interaction, and direct electron-electron Coulomb-repulsion are subjected to simplifying assumptions concerning electronic polarization, correlation, and exchange effects. The resulting formula presents the

ground-state energy in terms of parameters related to the spatial extent R and separation s of the two self-trapped electrons. In Sec. III, we determine an explicit formula for the electron-lattice interaction function for a system in which the (standard) short- and long-range electron-lattice interactions coexist. In Sec. IV, this electron-lattice interaction function is combined with the general formula for the ground-state energy found in Sec. II to yield an explicit expression for the ground-state energy in terms of the size and separation of the two polarons. This formula is then analyzed to determine the situations in which small- and large-bipolaron formation is energetically favorable. In Sec. V, we consider issues related to the formation of large bipolarons. In particular, we review our approach, estimate the relevance of our calculation to real solids, and consider the approximations we employed. In Sec. VI, we describe a rudimentary theory of the superconductivity of large bipolarons. We note that if the atomic displacements about the bipolaron are primarily of acoustic character, bipolaronic superconductivity need not produce a significant isotope dependence of the transition temperature. In addition, we find a rapid increase of the transition temperature with the thickening of a disklike quasi-two-dimensional large bipolaron as might arise from the contiguous stacking of CuO_2 sheets in the CuO_2-based superconductors. These predictions are consistent with distinctive features observed in the CuO_2-based superconductors. The principal results of these studies and their relevance to the high-temperature superconductors are then very succinctly summarized in Sec. VII.

II. THE GROUND-STATE ENERGY WITHIN THE ADIABATIC APPROXIMATION

To determine the situations in which electrons can pair to form bipolarons, we study the ground state of two electrons within a deformable continuum. To proceed, we employ the adiabatic approximation. Within the adiabatic approximation, the electrons are viewed as moving sufficiently rapidly compared with the motion of the atoms so that the electrons adjust to the instantaneous positions of the atoms. That is, the kinetic energy of the arbitrarily slowly moving atoms may be neglected. In this limit the ground state corresponds to the minimum of the sum of electrons' ground-state energy, itself a function of the atomic positions, and the potential energy of the atoms.

The Hamiltonian of two electrons placed in a deformable continuum is

$$H_{\rm el}=(-\hbar^2/2m)(\nabla_{\mathbf{r}_1}^2+\nabla_{\mathbf{r}_2}^2) - \int d\mathbf{r}[Z(\mathbf{r}_1,\mathbf{r})+Z(\mathbf{r}_2,\mathbf{r})]\Delta(\mathbf{r})+e^2/\epsilon_\infty|\mathbf{r}_1-\mathbf{r}_2| . \quad (1)$$

The first term of Eq. (1) describes the kinetic energy of two particles of mass m with coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. The second term is the continuum analog of the electron-lattice interaction. This term portrays a linear dependence of the potential energy of the two electrons on deformations of the deformable continuum. Here, $\Delta(\mathbf{r})$ is the (dimensionless) deformation variable of the continuum at $\mathbf{r}$ and $Z(\mathbf{r}_1,\mathbf{r})$ gives the dependence of the electronic potential energy at $\mathbf{r}_1$ on the deformation of the continuum at $\mathbf{r}$. The final term of Eq. (1) is the electronically screened Coulomb repulsion of the two electrons. The presence of the high-frequency dielectric constant ϵ_∞ accounts for the electronic screening of the Coulomb repulsion. The electron-lattice interaction provides an explicit treatment of the screening of the Coulomb interaction arising from atomic displacements. With the ground-state electron eigenfunction being given by $\psi(\mathbf{r}_1,\mathbf{r}_2)$, the electronic energy of the ground state for a given atomic deformation is

$$E_{\rm el}[\Delta(\mathbf{r})]=\int d\mathbf{r}_1\int d\mathbf{r}_2\,\psi^*(\mathbf{r}_1,\mathbf{r}_2)H_{\rm el}\psi(\mathbf{r}_1,\mathbf{r}_2) . \quad (2)$$

Within Hooke's law, the strain energy associated with deforming the continuum is

$$E_{\rm st}=(k/2a)\int d\mathbf{r}\,\Delta^2(\mathbf{r}) , \quad (3)$$

where k is the Hooke's law stiffness constant and a is the interatomic separation.

The ground state of the coupled system is that state for which the deformation pattern is such as to produce the lowest energy. To obtain the ground state, we therefore minimize $E_{\rm el}+E_{\rm st}$ with respect to variations of $\Delta(\mathbf{r})$. Using Eqs. (1)–(3), we readily find the minimization condition:

$$\Delta(\mathbf{r})=(a/k)\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2\,[Z(\mathbf{r}_1,\mathbf{r})+Z(\mathbf{r}_2,\mathbf{r})] . \quad (4)$$

The ground-state energy corresponding to this minimum is found by inserting the condition of Eq. (4) into Eqs. (2) and (3). After integrating the kinetic energy terms by parts, we find the ground-state energy to be

$$E=T+V_c-V_{\rm int} , \quad (5a)$$

where

$$T=(\hbar^2/2m)\int d\mathbf{r}_1\int d\mathbf{r}_2[|\nabla_{\mathbf{r}_1}\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 + |\nabla_{\mathbf{r}_2}\psi(\mathbf{r}_1,\mathbf{r}_2)|^2] , \quad (5b)$$

$$V_c=\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2(e^2/\epsilon_\infty|\mathbf{r}_1-\mathbf{r}_2|) , \quad (5c)$$

and

$$V_{\rm int}=(a/2k)\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2\int d\mathbf{r}_1'\int d\mathbf{r}_2'\,|\psi(\mathbf{r}_1',\mathbf{r}_2')|^2\int d\mathbf{r}[Z(\mathbf{r}_1,\mathbf{r})+Z(\mathbf{r}_2,\mathbf{r})][Z(\mathbf{r}_1',\mathbf{r})+Z(\mathbf{r}_2',\mathbf{r})] . \quad (5d)$$

Here, T represents the kinetic energy of the two electrons, V_c describes the Coulomb repulsion between the two electrons modified by the screening provided by the electronic polarization, and $-V_{\rm int}$ portrays the interaction of the two electrons with the atomic displacements.

Exploiting the indistinguishability of the two electrons, we combine the four terms of the integrand of $V_{\rm int}$ to obtain

$$V_{\rm int}=4\int d\mathbf{r}_1\int d\mathbf{r}_2\,|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 \times\int d\mathbf{r}_1'\int d\mathbf{r}_2'\,|\psi(\mathbf{r}_1',\mathbf{r}_2')|^2 I(\mathbf{r}_1,\mathbf{r}_1')\,, \tag{6}$$

where

$$I(\mathbf{r}_1,\mathbf{r}_1')=(a/2k)\int d\mathbf{r}Z(\mathbf{r}_1,\mathbf{r})Z(\mathbf{r}_1',\mathbf{r})\,. \tag{7}$$

Carrying out the $\mathbf{r}_2$ and $\mathbf{r}_2'$ integrations of Eq. (6), we then write

$$V_{\rm int}=4\int d\mathbf{r}_1P(\mathbf{r}_1)\int d\mathbf{r}_1'P(\mathbf{r}_1')I(\mathbf{r}_1,\mathbf{r}_1')\,, \tag{8}$$

where

$$P(\mathbf{r}_1)=\int d\mathbf{r}_2\,|\psi(\mathbf{r}_1,\mathbf{r}_2)|^2 \tag{9a}$$

and

$$P(\mathbf{r}_1')=\int d\mathbf{r}_2'\,|\psi(\mathbf{r}_1',\mathbf{r}_2')|^2\,. \tag{9b}$$

Thus, the electron-lattice interaction energy [Eq. (8)] depends nonlinearly on only the single-particle probability distributions $P(\mathbf{r}_1)$ and $P(\mathbf{r}_1')$ rather than on the two-particle probability distribution, $|\psi(\mathbf{r}_1',\mathbf{r}_2')|^2$. Furthermore, the interaction strength, $I(\mathbf{r}_1,\mathbf{r}_1')$ as defined in Eq. (7), of this self-energy term depends quadratically on the basic electron-lattice interaction $Z(\mathbf{r}_1,\mathbf{r})$.

To address the question of the pairing of the two electrons, we find it expedient to decompose the electronic probability distribution into two symmetric parts separated by the distance $|\mathbf{s}|=s$:

$$P(\mathbf{r})=[p(\mathbf{r}+\mathbf{s}/2,s)+p(\mathbf{r}-\mathbf{s}/2,s)]/2\,, \tag{10}$$

where each of the two components of the net probability distribution $P(\mathbf{r})$ is normalized to unity: $\int d\mathbf{r}P(\mathbf{r})=\int d\mathbf{r}p(\mathbf{r})=1$. Each probability distribution represents one of the system's two electrons. The dependence of $p(\mathbf{r}\pm\mathbf{s}/2,s)$ on s permits alteration of the shape of $p(\mathbf{r}\pm\mathbf{s}/2,s)$ as the interelectron separation s is varied. Of course, the arbitrariness of the axis of the distribution produces an orientational degeneracy.

Inserting Eq. (10) into Eq. (8) and dropping the superfluous subscripts, we find

$$V_{\rm int}=2\int d\mathbf{r}\int d\mathbf{r}'[p(\mathbf{r})p(\mathbf{r}')+p(\mathbf{r}+\mathbf{s}/2) \times p(\mathbf{r}'-\mathbf{s}/2)]I(\mathbf{r},\mathbf{r}')\,, \tag{11}$$

where we have combined two sets of equivalent terms. In addition, we neglected the dependence of the shape of each of the two peaks of the electron distribution on the interelectron separation: $p(\mathbf{r},s)\rightarrow p(\mathbf{r})$. The second term in the square brackets involves the overlap of the probability distributions of the two electrons. As such, the second term vanishes as $s\rightarrow\infty$ and becomes equal to the first term as $s\rightarrow 0$. Thus, the s-independent term of Eq. (11) gives the electron-lattice energy of two polarons that are infinitely far apart. In addition, Eq. (11) shows that the electron-lattice interaction energy is doubled when the two electrons pair about a common site, when $s=0$.

At this point, we simplify our expressions for the two other components of the ground-state energy (the electronic kinetic energy T and the Coulomb-repulsion energy V_c) in the same spirit as the simplification of $V_{\rm int}$ contained in Eq. (11). In particular, envisioning a singlet bipolaron, we write the kinetic energy of the two electrons as simply twice the kinetic energy of two independent electrons occupying the same spatial state:

$$T=2(\hbar^2/2m)\int d\mathbf{r}\,|\nabla_{\mathbf{r}}\phi(\mathbf{r})|^2\,, \tag{12}$$

where, as in the Heitler-London approximation, $\phi(\mathbf{r})$ is the one-electron wave function associated with one of two singlet-paired polarons that are separated arbitrarily far apart:

$$\lim_{s\rightarrow\infty}\psi(\mathbf{r}_1,\mathbf{r}_2)\rightarrow(2)^{-1/2}[\phi(\mathbf{r}_1+\mathbf{s}/2)\phi(\mathbf{r}_2-\mathbf{s}/2) +\phi(\mathbf{r}_1-\mathbf{s}/2)\phi(\mathbf{r}_2+\mathbf{s}/2)]\,. \tag{13}$$

In addition, we approximate the Coulomb repulsion energy [Eq. (5c)] by

$$V_c=\int d\mathbf{r}\int d\mathbf{r}'p(\mathbf{r}+\mathbf{s}/2)p(\mathbf{r}'-\mathbf{s}/2)(e^2/\epsilon_\infty|\mathbf{r}-\mathbf{r}'|)\,. \tag{14}$$

These approximations are all within the same spirit. Namely, these simplifications (1) ignore s-dependent changes of the electrons' kinetic energy T, (2) neglect the s-dependence of $V_{\rm int}$ arising from polarization of the electronic distribution, and (3) ignore correlation and polarization effects in the Coulomb repulsion energy V_c. The importance of these approximations will be discussed in Sec. V.

To address the problem of bipolaron formation, we must determine the nature of the ground state of the system comprising two electrons within a deformable medium. In particular, we wish to determine whether polarons are formed, whether the polarons are large or small, whether these polarons find it energetically favorable to pair into bipolarons, and whether these bipolarons are large or small. Thus, we must study the energy of the ground state as a function of both the spatial extent of the electronic wave functions and the separation between the electrons. The separation between the electrons already enters into our expressions for $V_{\rm int}$ and V_c [Eqs. (11) and (14)], through their dependence on the parameter s. Thus, we must introduce an explicit measure of the spatial extent of the electronic wave functions of the individual polarons into the problem.

To introduce a parameter related to the spatial extent of each peak of the electronic distribution, we scale the sizes of the electronic wave functions and probability distribution, the $\phi(\mathbf{r}\pm\mathbf{s}/2)$'s and the $p(\mathbf{r}\pm\mathbf{s}/2)$'s, while maintaining their shapes. In particular, we jointly (1) replace the arguments of the $\phi(\mathbf{r}\pm\mathbf{s}/2)$'s and the $p(\mathbf{r}\pm\mathbf{s}/2)$'s by $(\mathbf{r}\pm\mathbf{s}/2)/R$ and, to maintain the proper normalizations of these functions, (2) multiply these wave functions and probability distributions by $R^{-d/2}$ and R^{-d}, respectively, where d is the dimensionality of the electronic wave function.[17] Upon carrying out this scaling

procedure with the expressions for T, V_c, and $V_{\rm int}$ [Eqs. (12), (14), and (11), respectively], the three contributions to the ground-state energy become

$$T=2t/R^2\,, \tag{15}$$

$$V_c=v_c(s/R)/\epsilon_\infty R\,, \tag{16}$$

and

$$V_{\rm int}(R,s/R)=2\int d\mathbf{u}\int d\mathbf{u}'[p(\mathbf{u})p(\mathbf{u}')+p(\mathbf{u}+\mathbf{s}/2R)\times p(\mathbf{u}'-\mathbf{s}/2R)]I(\mathbf{u}R,\mathbf{u}'R)\,, \tag{17}$$

where

$$t=(\hbar^2/2m)\int d\mathbf{u}\,|\nabla_{\mathbf{u}}\phi(\mathbf{u})|^2 \tag{18}$$

and

$$v_c(s/R)=\int d\mathbf{u}\int d\mathbf{u}'p(\mathbf{u}+\mathbf{s}/2R)\times p(\mathbf{u}'-\mathbf{s}/2R)(e^2/|\mathbf{u}-\mathbf{u}'|)\,. \tag{19}$$

We note that, manifesting its Coulombic character, $v_c(s/R)$ is proportional to $1/s$ in the limit of arbitrarily large s.

It is now our task to find the minima of the ground-state energy for two electrons in a deformable continuum

$$E(R,s/R)=2t/R^2+v_c(s/R)/\epsilon_\infty R-V_{\rm int}(R,s/R)\,, \tag{20}$$

with respect to variations of R and s/R. However, to proceed, we require an explicit expression for $V_{\rm int}(R, s/R)$. We, therefore, must determine the electron-lattice interaction function, $I(\mathbf{u},\mathbf{u}')$, that enters into our expression for $V_{\rm int}(R,s/R)$ [Eq. (17)].

III. THE ELECTRON-LATTICE INTERACTION FUNCTION $I(\mathbf{u},\mathbf{u}')$

In this section we evaluate the electron-lattice interaction function that is defined in Eq. (7). In terms of the notation of Eq. (17), the interaction function is

$$I(\mathbf{u},\mathbf{u}')=(a/2k)\int d\mathbf{r}\,Z(\mathbf{u},\mathbf{r})Z(\mathbf{u}',\mathbf{r})\,, \tag{21}$$

where $\mathbf{u}$ and $\mathbf{u}'$ are electronic position vectors and $\mathbf{r}$ is the vector defining the location in the deformable continuum undergoing a dilatation. Thus, the strength and range of the electron-lattice interaction are determined by the magnitude and $|\mathbf{u}-\mathbf{r}|$ dependence of $Z(\mathbf{u},\mathbf{r})$.

The short-range component of the electron-lattice describes the dependence of the energy of an electron on a deformation of the deformable continuum in the immediate vicinity of the electron. Thus, we write the short-range component of the electron-lattice interaction as[17]

$$Z_S(\mathbf{u},\mathbf{r})=Aa\delta(\mathbf{u}-\mathbf{r})\,, \tag{22}$$

where A is the force associated with the short-range electron-lattice interaction. The long-range (Coulombic) component of the electron-lattice interaction describes the change of the potential energy of an electron at $\mathbf{u}$ in an ionic solid caused by altering an electric dipole at $\mathbf{r}$. This long-range portion of the electron-lattice interaction is described by[13,17]

$$Z_L(\mathbf{u},\mathbf{r})=(\beta e^2k/\pi^3a)^{1/2}|\mathbf{u}-\mathbf{r}|^{-2}\,, \tag{23}$$

where $\beta=(1/\epsilon_\infty-1/\epsilon_0)$ with ϵ_∞ and ϵ_0 being the high-frequency and static dielectric constants. Here, β measures the strength of the electronic polarizability of the medium arising from atomic displacements.

We now combine the short- and long-range components of the electron-lattice interaction

$$Z(\mathbf{u},\mathbf{r})=Z_S(\mathbf{u},\mathbf{r})+Z_L(\mathbf{u},\mathbf{r})\,. \tag{24}$$

We insert Eq. (24) into Eq. (21), use the results contained in Eqs. (22) and (23), and perform the $\mathbf{r}$ intergrations in order to write the electron-lattice interaction function as

$$I(\mathbf{u},\mathbf{u}')=a^3E_b\delta(\mathbf{u}-\mathbf{u}')+(2E_b\beta e^2a^3/\pi^3)^{1/2}|\mathbf{u}-\mathbf{u}'|^{-2}+\beta e^2/2|\mathbf{u}-\mathbf{u}'|\,, \tag{25}$$

where we have used the definition of the small-polaron binding energy with only a short-range electron-lattice interaction, $E_b=A^2/2k$. The first two terms of Eq. (25) are obtained from $\mathbf{r}$ integrations over Dirac δ functions. The final term is obtained by noting that in a *three-dimensional* isotropic dielectric medium

$$\int d\mathbf{r}\,|\mathbf{u}-\mathbf{r}|^{-2}|\mathbf{u}'-\mathbf{r}|^{-2}=\pi^3/|\mathbf{u}-\mathbf{u}'|\,. \tag{26}$$

IV. BIPOLARONIC GROUND STATES

A. Formalism

We now determine the conditions under which a large bipolaron can be formed. In particular, we find the minimum of the ground-state energy $E(R,s/R)$ that corresponds to the formation of a large bipolaron.

To accomplish this, we first find an explicit expression for $V_{\rm int}(R,s/R)$ by incorporating our formula for the electron-lattice interaction function [Eq. (25)] into the general expression for $V_{\rm int}(R,s/R)$ [Eq. (17)]. As a result of this procedure, we can write $V_{\rm int}(R,s/R)$ as the sum of terms arising from (1) the short-range component of the electron-lattice interaction, (2) the long-range component of the electron-lattice interaction, and (3) the cross term arising from the combined presence of short- and long-range components of the electron-lattice interaction

$$V_{\rm int}(R,s/R)=2v_{\rm int}^{S,d}(s/R)/R^d+v_{\rm int}^{L}(s/R)/R+2v_{\rm int}^{SL}(s/R)/R^2\,, \tag{27}$$

where

$$v_{\rm int}^{S,d}(s/R)=(E_ba^3/l^{3-d})\int d\mathbf{u}[p^2(\mathbf{u})+p(\mathbf{u}+\mathbf{s}/2R)p(\mathbf{u}-\mathbf{s}/2R)]\,, \tag{28}$$

$$v_{\rm int}^{L}(s/R)=\beta[v_c(0)+v_c(s/R)]\,, \tag{29}$$

and

$$v_{\rm int}^{SL}(s/R)=(2E_b\beta e^2a^3/\pi^3)^{1/2}\int d\mathbf{u}\int d\mathbf{u}'[p(\mathbf{u})p(\mathbf{u}')+p(\mathbf{u}+\mathbf{s}/2R)p(\mathbf{u}'-\mathbf{s}/2R)]\,|\mathbf{u}-\mathbf{u}'|^{-2}. \tag{30}$$

In obtaining Eq. (27), we have noted that the power of R arising from the Dirac δ function depends on the dimensionality d of the electronic probability distribution $p(\mathbf{u}\pm\mathbf{s}/2R)$. In an electronic system of d dimensions $d\leq 3$, the integration over the Dirac δ function is suppressed in $3-d$ dimensions. This procedure introduces the factor of $1/l^{3-d}$ in Eq. (28), where l is the characteristic length of the electronic system perpendicular to the direction(s) in which the electronic wave function is large. In addition, Eq. (19) was utilized in obtaining Eq. (29). For future reference, we note from Eq. (30) that $v_{\rm int}^{SL}(s/R)-v_{\rm int}^{SL}(0)/2$ is proportional to $1/s^2$ as s becomes arbitrarily large.

Combining Eq. (27) with Eq. (20), we explicitly display the R dependence of the ground-state energy $E(R,s/R)$:

$$E(R,s/R)=\alpha_T(s/R)/R^2-\alpha_C(s/R)/R-\alpha_S(s/R)/R^d, \tag{31}$$

where

$$\alpha_T(s/R)=2[t-v_{\rm int}^{SL}(s/R)], \tag{32}$$

$$\alpha_C(s/R)=\beta v_c(0)-v_c(s/R)/\epsilon_0, \tag{33}$$

and

$$\alpha_S(s/R)=2v_{\rm int}^{S,d}(s/R). \tag{34}$$

In obtaining Eq. (33), we have utilized Eq. (29) and noted that $\beta=(1/\epsilon_\infty-1/\epsilon_0)$. It should be observed that the direct effect of the long-range component of the electron-lattice interaction on the term associated with the Coulomb repulsion, the second term of Eq. (33), is just to increase the dielectric constant associated with the screening from ϵ_∞ to ϵ_0. Hence, without the presence of the long-range component of the electron-lattice interaction, ϵ_0 in Eq. (33) is just ϵ_∞. Finally, we note that α_S is always positive while α_T and α_C may be of either sign.

In anticipation of their subsequent interest to us, we compare values of $\alpha_T(s/R)$, $\alpha_C(s/R)$, and $\alpha_S(s/R)$ at $s/R=0$ with those at $s/R=\infty$. To accomplish this, we exploit the fact that the overlap between $p(\mathbf{r}+\mathbf{s}/2R)$ and $p(\mathbf{r}-\mathbf{s}/2R)$ vanishes as s becomes infinite. We also infer from Eqs. (28) and (29) that $v_{\rm int}^{S,d}(\infty)=v_{\rm int}^{S,d}(0)/2$ and $v_{\rm int}^{L}(\infty)=v_{\rm int}^{L}(0)/2$, respectively. Incorporating these relationships into the definitions contained in Eqs. (32)–(34), we find

$$\alpha_T(\infty)=2t-v_{\rm int}^{SL}(0)=\alpha_T(0)+v_{\rm int}^{SL}(0), \tag{35}$$

$$\alpha_C(\infty)=\beta v_c(0)=\alpha_C(0)[(\epsilon_0-\epsilon_\infty)/(\epsilon_0-2\epsilon_\infty)], \tag{36}$$

and

$$\alpha_S(\infty)=v_{\rm int}^{S,d}(0)=\alpha_S(0)/2. \tag{37}$$

We now consider the dependence of the ground-state energy $E(R,s/R)$ on R and s. Since a solid is composed of discrete atomistic units, there is a minimum size of the electronic wave function below which the electron-lattice interaction saturates.[17] One means of incorporating this saturation effect into our considerations is to set a minimum value of R below which curves of $E(r,s/R)$ are discarded as unphysical.[15,17,20] We denote the value of R as R_s.

We first minimize the ground-state energy $E(R,s/R)$ with respect to R, the radius characterizing the electronic distribution functions. A minimum of $E(R,s/R)$ at $R=R_s$ indicates a self-trapped state with the smallest radius that is compatible with the discreteness of the lattice, i.e., the formation of two small polarons or a small bipolaron. A minimum at $R=\infty$ corresponds to the absence of any self-trapping, i.e., neither two polarons nor a bipolaron is formed. A finite-radius minimum corresponds to a self-trapped state of finite radius, i.e., the formation of either two large polarons or a large bipolaron. Since this paper is directed toward determining the conditions for the formation of large bipolarons, we shall direct our attention toward only the minima at finite R, $R=R_{\rm min}$. Having obtained the ground-state energy of such minima, $E_{\rm min}(s/R_{\rm min})=E(R_{\rm min},s/R_{\rm min})$, we shall ultimately study the s dependence of these minima in order to ascertain when they correspond to energetically stable finite-radius bipolarons. In particular, bipolaron formation will be energetically stable if the global minimum of $E_{\rm min}(s/R_{\rm min})$ occurs at $s<\infty$.

We sequentially minimize $E(R,s/R)$ with respect to R for electronic distributions of one, two, and three dimensions, respectively. With the electronic distribution being one dimensional, $d=1$, $E(R,s/R)$ [Eq. (31)] only has terms that vary as R^{-1} and R^{-2}:

$$E(R,s/R)=\alpha_T/R^2-(\alpha_C+\alpha_S)/R. \tag{38}$$

If α_T and $\alpha_C+\alpha_S$ are both positive, $E(R,s/R)$ of Eq. (38) has a single *finite-radius* minimum with respect to R at $R_{\rm min}=2\alpha_T/(\alpha_C+\alpha_S)$ with the energy of this minimum being

$$E_{\rm min}(s/R_{\rm min})=-(\alpha_C+\alpha_S)^2/4\alpha_T. \tag{39}$$

With the electronic distribution being two dimensional, $d=2$, we find from Eq. (31) that

$$E(R,s/R)=(\alpha_T-\alpha_S)/R^2-\alpha_C/R. \tag{40}$$

When $(\alpha_T-\alpha_S)$ and α_C are both positive, there is a finite-radius minimum at $R_{\rm min}=2(\alpha_T-\alpha_S)/\alpha_C$ with the ground-state energy

$$E_{\rm min}(s/R_{\rm min})=-\alpha_C^2/4(\alpha_T-\alpha_S). \tag{41}$$

With a three-dimensional electronic wave function $d=3$, the ground-state electronic energy of Eq. (31) becomes

$$E(R,s/R)=\alpha_T/R^2-\alpha_C/R-\alpha_S/R^3. \tag{42}$$

A finite-radius minimum of the ground-state energy at a positive value of R, the only physically meaningful situa-

tion, only exists if a_C and a_T are both positive and $a_T^2 > 3a_S a_C$. In these circumstances, this minimum occurs at

$$R_{\min} = (a_T/a_C)[1+(1-3a_S a_C/a_T^2)^{1/2}], \tag{43}$$

with the ground-state energy

$$E_{\min}(s/R_{\min}) = -(a_C^2/3a_T)\frac{1+2(1-3a_S a_C/a_T^2)^{1/2}}{[1+(1-3a_S a_C/a_T^2)^{1/2}]^2}. \tag{44}$$

B. Short-range electron-lattice interaction

We now discuss the physical significance of these results. First consider the situation in which there is only a short-range component of the electron-lattice interaction. With the vanishing of the long-range portion of the electron-lattice interaction, we have [from Eqs. (32) and (33) with ϵ_∞ replacing ϵ_0] $a_T = 2t$ and $a_C = -v_c(s/R)/\epsilon_\infty \leq 0$. Since a requirement for a finite-radius state in two- and three-dimensional electronic systems is that $a_C > 0$ [cf. the discussion below Eqs. (40) and (42)], finite-radius bipolarons are precluded in two- and three-dimensional systems with only a short-range electron-lattice interaction. However, in a one-dimensional electronic system the requirement for a finite-radius state $a_C + a_S > 0$ can be met even if a_C is negative since a_S is always positive. In particular, in the limit of the two electrons being infinitely far apart $s \to \infty$, where $a_C \to 0$ and $a_C + a_S$ is positive, we have two large polarons. This result agrees with the previously proved existence of a finite-radius polaron in one-dimensional electronic systems with only a short-range electron-lattice interaction.[13,17] Furthermore, if the electron-lattice interaction is sufficiently strong to overwhelm the Coulomb repulsion, a one-dimensional bipolaron can be formed. In particular, a large (finite-radius) bipolaron with both electrons centered at the same site, $s = 0$, will be energetically stable if $E_{\min}(0) < E_{\min}(\infty)$. Using Eq. (39) with Eqs. (35)–(37) with only a short-range electron-lattice interaction, this condition may be rewritten as

$$\begin{aligned} E_{\min}(0) - E_{\min}(\infty) &= [a_C(\infty)+a_S(\infty)]^2/4a_T(\infty) - [a_C(0)+a_S(0)]^2/4a_T(0) \\ &= \{[a_C(0)+v_c(0)/\epsilon_\infty + a_S(0)/2]^2 - [a_C(0)+a_S(0)]^2\}/4a_T(0) < 0, \end{aligned} \tag{45}$$

where we have recalled that ϵ_0 should be replaced by ϵ_∞ in the absence of a long-range component of the electron-lattice interaction. Comparing the squared terms, we finally find the condition for bipolaron formation in a one-dimensional electronic material to be that $v_c(0)/\epsilon_\infty < a_S(0)/2 = v_{\text{int}}^{S,1}(0)$. Thus, with only a short-range component of the electron-lattice interaction, large-radius bipolarons can be formed in quasi-one-dimensional electronic systems but not in electronic systems of higher dimensionality.

C. Long-range electron-lattice interaction

With only a long-range component of the electron-lattice interaction, a finite-radius state can be formed provided that a_C is positive. In electronic systems of all dimensionalities, the energy of such a state is $E_{\min}(s/R_{\min}) = -a_C^2/4a_T$ regardless of dimensionality since $a_S = 0$. Observing [from Eq. (32) with $v_{\text{int}}^{SL}(s/R) = 0$] that a_T is independent of the interelectron separation and [from Eq. (33) and (19)] that a_C decreases as s decreases, we see that these large polarons always repel one another. If the polarons are brought sufficiently close together so that a_C vanishes, $R_{\min}$ tends toward infinity, signifying the decomposition of the polarons. Thus, we find that bipolarons cannot be formed with only a long-range component of the electron-lattice interaction.

With the independent existence of *either* a short- or long-range component of the electron-lattice interaction, we find that large bipolarons do not exist in systems with an electronic dimensionality of two or three. We now successively discuss the formation of large bipolarons in systems of $d = 1$, 2, and 3 with *both* components of the electron-lattice interaction.

D. Short- and long-range electron lattice interaction with $d = 1$

With the electronic charge distribution being one dimensional, the energy of a large-radius polaronic state for a pair of electrons is given by Eq. (39): $E_{\min}(s/R_{\min}) = -(a_C+a_S)^2/4a_T$. Pairing is favored and a large bipolaron is stabilized if $E_{\min}(s/R_{\min})$ decreases as the interelectron separation s decreases. As noted previously, because of the Coulomb repulsion between the two electrons, a_C generally decreases as s decreases. However, because $v_{\text{int}}^{S,1}(s/R)$ increases when the two electrons are brought sufficiently close together so that their charge distributions overlap, a_S [Eq. (34)] generally increases as s decreases. If the increase of a_S as s decreases dominates the decrease of a_C with decreasing s, $a_C + a_S$ will increase as s decreases. The cross term between the short- and long-range electron-lattice interaction produces an additional effect. As a result of the presence of $v_{\text{int}}^{SL}(s/R)$, $a_T = 2[t - v_{\text{int}}^{SL}(s/R)]$ generally falls as s decreases since $v_{\text{int}}^{SL}(s/R)$ generally increases as s decreases. Since $E_{\min}(s/R_{\min}) = -(a_C+a_S)^2/4a_T$, we see that bipolaron formation in a one-dimensional system is facilitated not only by $a_C + a_S$ increasing with decreasing s, but also by a_T decreasing with decreasing s. Put in more physical terms, while a large bipolaron is possible in a one-dimensional electronic system with only a short-range component of the electron-lattice interaction, the added presence of a long-range component of the electron-lattice interaction further assists the formation of a bipolaron. In particular, the presence of the long-range component of the electron-lattice interaction assists large bipolaron formation in two ways. First, its presence increases a_C by enhancing the screening of the Coulomb repulsion (con-

verting ϵ_∞ to ϵ_0). Second, through the presence of the cross term between both components of the electron-lattice interaction, the effective kinetic energy α_T is reduced.

E. Short- and long-range electron-lattice interaction with $d=2$

With a two-dimensional electronic distribution, a large-radius polaronic state can be formed with $E_{\min}(s/R_{\min}) = -\alpha_C^2/4(\alpha_T-\alpha_S)$ [Eq. (41)], if α_C and $\alpha_T-\alpha_S$ are both positive. With only a short-range component of the electron-lattice interaction, large-radius states cannot form since then α_C is negative [cf. Eq. (33) with $\beta=0$ and $\epsilon_0 \rightarrow \epsilon_\infty$]. With only a long-range component of the electron-lattice interaction, bipolarons cannot form since $E_{\min}(s/R_{\min})$ then rises with decreasing s. This behavior occurs in this instance because the total s dependence of $E_{\min}(s/R_{\min})$ arises from the decreasing of α_C with decreasing s caused by the Coulomb repulsion of the two electrons [cf. Eq. (33)]. However, with the combined presence of short- and long-range components of the electron-lattice interaction, large-radius bipolarons may be formed. In particular, then α_C can be positive and the decrease of $\alpha_T-\alpha_S$ as s decreases may be sufficient to drive the minimum of $E_{\min}(s/R_{\min})$ to be at $s<\infty$.

To determine the conditions under which a large-radius bipolaron will form, we consider the s dependence of the ground-state energy $E_{\min}(s/R)$. We first observe that as two carriers are brought together from infinite separation, they initially repel one another, thereby opposing bipolaron formation. This feature is deduced by observing that the dominant s-dependence of $E_{\min}(s/R_{\min})$ when s is arbitrarily large is that of $\alpha_c(s/R_{\min})$. In particular, due to the s dependence of $v_c(s/R_{\min})$ caused by the electron-electron repulsion, $\alpha_C(s/R_{\min})$ falls from its limiting value at infinity as $1/s$ [cf. the discussion below Eq. (19)]. The other terms in the expression for $E_{\min}(s/R_{\min})$ [Eq. (41)] fall off more rapidly with increasing s. In particular, due to the s dependence of $v_{\rm int}^{SL}(s/R_{\min})$, $\alpha_T(s/R_{\min})$ falls from its value at infinity as $1/s^2$. In addition, the decline of $\alpha_S(s/R_{\min})=2v_{\rm int}^{S,d}(s/R_{\min})$ with increasing s, caused by the declining overlap between the separated electrons as s increases, is presumably faster than algebraic. As a result, in the limit of very large s, the s dependence of α_C dominates the s dependence of the ground-state energy $E_{\min}(s/R_{\min})$ and produces the long-range (large s) interelectron repulsion.

Despite the fact that $E_{\min}(s/R_{\min})$ rises as s is decreased from infinity, there may be a minimum of $E_{\min}(s/R_{\min})$ at a sufficiently small value of s. To investigate the possibility of a large bipolaron associated with $s=0$, we compare $E_{\min}(0)$ with $E_{\min}(\infty)$. If $E_{\min}(0)<E_{\min}(\infty)$, it is energetically favorable to bind two large polarons to form a large bipolaron with both electrons being centered at the same site. Using Eq. (41), we write this energetic condition as

$$[\alpha_C(0)/\alpha_C(\infty)]^2 > [\alpha_T(0)-\alpha_S(0)]/[\alpha_T(\infty)-\alpha_S(\infty)] . \tag{46}$$

Employing relations between the values of these functions at $s=0$ and at $s=\infty$, Eqs. (35)–(37), the inequality of Eq. (46) is reexpressed as

$$[(\epsilon_0-2\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)]^2 > [\alpha_T(\infty)-v_{\rm int}^{SL}(0)-2\alpha_S(\infty)]/[\alpha_T(\infty)-\alpha_S(\infty)] = 1-[v_{\rm int}^{SL}(0)+\alpha_S(\infty)]/[\alpha_T(\infty)-\alpha_S(\infty)] . \tag{47}$$

Rearranging the terms of Eq. (47), the energetic requirement for the formation of large bipolarons in two-dimensional electronic systems becomes

$$[v_{\rm int}^{SL}(0)+\alpha_S(\infty)/[\alpha_T(\infty)-\alpha_S(\infty)] > 1-[(\epsilon_0-2\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)]^2 . \tag{48}$$

We recall, from below Eq. (40), that the existence of a large-radius state in a two-dimensional electronic system requires that $\alpha_T-\alpha_S>0$ and $\alpha_C>0$. In particular, the existence of a large-radius state at $s=0$ requires that

$$\alpha_T(0)-\alpha_S(0)=\alpha_T(\infty)-v_{\rm int}^{SL}(0)-2\alpha_S(\infty)>0$$

and $\epsilon_0>2\epsilon_\infty$ [cf. Eqs. (35)–(37)]. Using the requirement that $\alpha_T(\infty)-\alpha_S(\infty)>0$ if there are to be large polarons at $s=\infty$, we reexpress the two conditions for a $s=0$ large-radius state as

$$1>[v_{\rm int}^{SL}(0)+\alpha_S(\infty)]/[\alpha_T(\infty)-\alpha_S(\infty)]$$

and $\epsilon_0>2\epsilon_\infty$. Incorporating the first requirement into Eq. (48), we obtain the conditions under which a large bipolaron with $s=0$ can exist and be energetically stable with respect to two well-separated, $s=\infty$, large polarons:

$$1>[v_{\rm int}^{SL}(0)+\alpha_S(\infty)]/[\alpha_T(\infty)-\alpha_S(\infty)] > 1-[(\epsilon_0-2\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)]^2 , \tag{49a}$$

with

$$\epsilon_0>2\epsilon_\infty . \tag{49b}$$

To understand the physical significance of Eqs. (49a) and (49b), we first note that elimination of the long-range portion of the electron-lattice interaction corresponds to the replacement of ϵ_0 by ϵ_∞. Hence, we confirm from Eqs. (49a) and (49b) that the $s=0$ large-bipolaron cannot form without the presence of the long-range portion of the electron-lattice interaction. Furthermore, since $v_{\rm int}^{SL}(0)$ and $\alpha_S(\infty)$ both vanish with the elimination of the short-range component of the electron-lattice interaction, we see from Eq. (49a) that a sufficiently large short-range component of the electron-lattice interaction is a requirement for the large-radius bipolaron. In other words, it is only with the combined presence of both the short- and long-range components of the electron-lattice interaction that large bipolarons with $s=0$ can be stable. Finally, we note

that when $\epsilon_0 > 2\epsilon_\infty$, the reduction of the potential energy arising from two electrons of "radius" R centered at the same site $s=0$, forming large polarons, $-2(\epsilon_\infty^{-1}-\epsilon_0^{-1})v_c(0)/R$, exceeds the potential energy of the (unscreened) Coulomb repulsion of the two electrons, $v_c(0)/\epsilon_\infty R$; that is, $-(\epsilon_\infty^{-1}-2\epsilon_0^{-1})v_c(0)/R<0$. Thus, there cannot be a large-radius bipolaron with both electrons sharing a common centroid unless $\epsilon_0 \geq 2\epsilon_\infty$.

To better appreciate the constraints imposed by the conditions for large bipolaron formation, it is useful to rewrite Eq. (49a) in terms of more fundamental physical quantities. To this end, we use Eqs. (35) and (37) to rewrite $a_T(\infty)$ and $a_S(\infty)$ of Eq. (49a) in terms of $v_{\rm int}^{SL}(0)$ and $v_{\rm int}^{S,2}(0)$. After some algebra, we obtain

$$1+(\epsilon_0-2\epsilon_\infty)^2/2\epsilon_\infty(2\epsilon_0-3\epsilon_\infty) > t/[v_{\rm int}^{SL}(0)+v_{\rm int}^{S,2}(0)] > 1 , \quad (50)$$

with $\epsilon_0 \geq 2\epsilon_\infty$. Here we see that the requirements for large-bipolaron formation contained in Eq. (50) restrict the permitted values of the ratio of the single-carrier electronic kinetic energy t to a combination of electron-lattice coupling energies, $v_{\rm int}^{SL}(0)+v_{\rm int}^{S,2}(0)$. As will be demonstrated later, the numerator and denominator of this ratio are frequently of the same order of magnitude. Thus, a regime in which large bipolarons can be formed in a two-dimensional electronic system is conceivable if the ratio of static- to high-frequency dielectric constants is sufficiently large, $\epsilon_0 \gg 2\epsilon_\infty$. In the CuO_2-based superconducting solids, the static dielectric constants are very large while the high-frequency dielectric constants are modest, $\epsilon_0 \gg 2\epsilon_\infty$. For example, the static dielectric constants reported for a single crystal of insulating La_2CuO_4 are about 50 with values of 85 and 22 for directions parallel and perpendicular to the CuO planes, respectively.[28] In addition, the high-frequency dielectric constant in the CuO_2-based superconducting materials is typically only between 3 and 5.[29] These experimental results suggest that the regime for two-dimensional bipolaron formation may be exceptionally large in the CuO_2-based superconducting materials.

F. Short- and long-range electron-lattice interaction with $d=3$

We now consider whether stable large bipolarons may be formed in three-dimensional electronic systems. With a three-dimensional electronic distribution, a large-radius state can be formed with the energy $E_{\rm min}(s/R_{\rm min})$ given by Eq. (44) if $a_C>0$, $a_T>0$, and $a_T^2>3a_S a_C$. For a bipolaron to be formed, there must be a minimum of $E_{\rm min}(s/R_{\rm min})$ with respect to s at a value of s less than infinity. The expression for $E_{\rm min}(s/R_{\rm min})$ given by Eq. (44) is especially complex. However, we can simplify the analysis of the s dependence of $E_{\rm min}(s/R_{\rm min})$ by noting from Eq. (44) that $E_{\rm min}(s/R_{\rm min})$ only decreases from $-a_C^2/4a_T$ to $-a_C^2/3a_T$ as a_S is increased from 0 to its maximum value, $a_T^2/3a_C$. In particular, we exploit the weak dependence of $E_{\rm min}(s/R_{\rm min})$ on the value of a_S in approximating $E_{\rm min}(s/R_{\rm min})$ by $-a_C^2/4a_T$, its value of $a_S=0$.

We now investigate the s dependence of $E_{\rm min}(s/R_{\rm min}) \approx -a_C^2/4a_T$. The net s dependence of $E_{\rm min}(s/R_{\rm min})$ results from the s dependences of a_C and a_T. Reflecting the Coulombic repulsion of charges of like sign, $a_C(\infty)-a_C(s) \propto 1/s$ as $s\rightarrow\infty$. In addition, as in the two-dimensional situation, $a_T(\infty)-a_T(s) \propto s^{-2}$ as $s\rightarrow\infty$. Thus, the s dependence of a_C dominates that of a_T in the limit of arbitrarily large s. As a result, at arbitrarily large values of s, $E_{\rm min}(s/R_{\rm min})$ rises as s decreases indicating a long-range interelectronic repulsion.

Despite the initial increase of the energy of two polarons as they are brought toward each other from infinite separation, they may ultimately find it energetically favorable to pair to form a bipolaron. To investigate this possibility, we compare the energy for $s=0$ with that for $s=\infty$. If $E_{\rm min}(0)<E_{\rm min}(\infty)$, it is energetically favorable for two large polarons to coalesce into a large bipolaron that has both carriers centered at the same site. With $E_{\rm min}(s/R_{\rm min})=-a_C^2/4a_T$, the energetic stability of such a bipolaron requires that

$$[a_C(0)/a_C(\infty)]^2 > a_T(0)/a_T(\infty) . \quad (51)$$

Exploiting the relationships between $a_T(0)$, $a_T(\infty)$, $a_C(0)$, and $a_C(\infty)$ contained in Eqs. (35) and (37), the energetic requirement for bipolaron formation, Eq. (51) is rewritten as

$$v_{\rm int}^{SL}(0)/a_T(\infty) > 1-[(\epsilon_0-2\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)]^2 . \quad (52)$$

We now recall from below Eq. (42) that a large-radius state only exists if a_T and a_C are positive. Using Eqs. (35) and (36), we observe that these requirements for the $s=0$ and $s=-\infty$ situations stipulate that $1>v_{\rm int}^{SL}(0)/a_T(\infty)$, $a_T(\infty)>0$, and $\epsilon_0>2\epsilon_\infty$. Writing the first of these condition along with Eq. (52), we have

$$1 > v_{\rm int}^{SL}(0)/a_T(\infty) > 1-[(\epsilon_0-2\epsilon_\infty)/(\epsilon_0-\epsilon_\infty)]^2 . \quad (53)$$

We now use Eq. (35) to replace $a_T(\infty)$ in Eq. (53) with quantities that are physically more meaningful. Specifically, after some algebra, we convert Eq. (53) to

$$1+(\epsilon_0-2\epsilon_\infty)^2/2\epsilon_\infty(2\epsilon_0-3\epsilon_\infty) > t/v_{\rm int}^{SL}(0) > 1 , \quad (54)$$

with $\epsilon_0 \geq 2\epsilon_\infty$.

In a three-dimensional electronic system the formation of a large bipolaron is constrained by yet another condition. In particular, in a three-dimensional electronic system, a large-radius bipolaron must be dynamically stable against collapse into a small-radius state (corresponding to a small bipolaron or to two separated small polarons). From above Eq. (43), we recall that this requirement is that $a_T^2(0)>3a_S(0)a_C(0)$. With Eqs. (32)–(34), this condition may be reexpressed as

$$t/v_{\rm int}^{SL}(0) > 1+\left[\frac{3v_{\rm int}^{S,3}(0)v_c(0)(\epsilon_0-2\epsilon_\infty)}{2[v_{\rm int}^{SL}(0)]^2\epsilon_0\epsilon_\infty}\right]^{1/2} . \quad (55)$$

Combining the relations of Eqs. (54) and (55), we find that the formation of a large-radius bipolaron in an electronically three-dimensional system requires that

$$1+(\epsilon_0-2\epsilon_\infty)^2/2\epsilon_\infty(2\epsilon_0-3\epsilon_\infty) > t/v_{\rm int}^{SL}(0) > 1+\{3v_{\rm int}^{S,3}(0)v_c(0)(\epsilon_0-2\epsilon_\infty)/2[v_{\rm int}^{SL}(0)]^2\epsilon_0\epsilon_\infty\}^{1/2}. \quad (56)$$

We compare the requirements for forming an energetically favorable large bipolaron in a three-dimensional electronic system, Eq. (56), with that for forming a large bipolaron in a two-dimensional electronic system Eq. (50). The limitations on the electronic parameter t are more restrictive for a three-dimensional electronic system than for a two-dimensional electronic system. In particular, the difference between the upper and lower limits of Eq. (56) is smaller than the corresponding difference in Eq. (50). In addition, the denominator of the central term of the two inequalities of the three-dimensional restrictions [Eq. (56)] is smaller than that for the central term of the two-dimensional restrictions [Eq. (50)].

V. SUMMARY AND DISCUSSION OF THE FORMATION OF A LARGE BIPOLARON

The discovery of "very high-temperature superconductors" has rekindled interest in "novel" mechanisms for superconductivity. In particular, one might wonder if these materials are manifesting the long-sought-for bipolaronic superconductivity predicted for mobile bipolarons.[4]

Nonetheless, it has been uncertain if mobile bipolarons can form in the two- and three-dimensional electronic systems that characterize these superconductors. In particular, *small* bipolarons, bipolarons for which the spatial extent of the wave function is less than or comparable to an interatomic separation, are generally found to be localized rather than mobile. This is not surprising since the large atomic displacements required for binding two electrons into a small bipolaron also produce a huge enhancement of the effective mass of a small bipolaron. With the very small sizes and very large effective masses characteristic of small bipolarons, and even small polarons, these carriers are readily localized by even the modest disorder of a typical crystal. Thus, for bipolarons to result in bipolaronic superconductivity they must be large. That is, these bipolarons should extend over multiple sites.

Here, we investigate the conditions under which large singlet bipolarons can be formed. In particular, we study the adiabatic ground state of two electrons within a deformable medium. Within the adiabatic approach, the electrons are presumed to move sufficiently rapidly so as to adjust to the instantaneous positions of the atoms of the solid. Although we envision the electrons to be within a three-dimensional deformable medium, we consider the electronic states to be either one, two, or three dimensional. This model encompasses a situation that is roughly analogous to that of the CuO_2-based superconducting materials. In particular, in these solids the carriers (holes) are presumed to reside within the CuO_2 sheets. Therefore, if the width of contiguous CuO_2 sheets is sufficiently small compared to the large bipolaron's diameter, the electronic system may be regarded as having a two-dimensional character. Furthermore, the large ($\gg 10$) static dielectric constants both parallel and perpendicular to the CuO_2 sheets[28] indicate that atoms may be significantly displaced in all three directions. In addition, with displaceable ions present through the solid, the CuO_2-based materials may be approximated as a three-dimensional deformable medium.

As is common, we consider a linear electron-lattice interaction. That is, the energy of an electron is presumed to depend linearly on the displacements of the atoms of the solid from their carrier-free equilibrium positions. Furthermore, the electron-lattice interaction is composed of two components. The short-range component of the electron-lattice interaction described a linear dependence of an electron's energy on the displacements of the atoms it overlaps. The long-range component of the electron-lattice interaction describes the linear dependence of the energy of an electron that arises from its Coulombic interactions with small displacements of the anions and cations of an *ionic* solid from their carrier-free equilibrium positions. The strain energy of the carrier-free lattice is presumed to obey Hooke's law.

To make our general expressions for the adiabatic energy amenable to analytic analysis, we ignore the effects of electronic polarization and correlation on the electron-lattice interaction energy, the two-electron electronic kinetic energy and the interelectron Coulombic repulsion [Eqs. (11), (12), and (14), respectively]. We then employ a variational scheme. This procedure enables us to describe the energy of the adiabatic ground state in terms of the (dimensionless) radius of the wave functions of the two equivalent electrons R and the interelectron separation s. We then examine large-radius minima of the energy to determine the conditions under which they correspond to the formation of a large singlet bipolaron that is energetically stable with respect to decomposition into two separate large polarons.

With only the presence of the classical long-range (Fröhlich) electron-lattice interaction, we regain the classical result that bipolarons are always energetically unstable with respect to decomposition into separate large polarons. In other words, the presence of the two electrons classically induces displacements of the anions and cations of an ionic solid that reduce the effective Coulomb interaction between electrons separated by the distance r from $e^2/\epsilon_\infty r$ to $e^2/\epsilon_0 r$, where ϵ_∞ and ϵ_0 are the high-frequency and static dielectric constants, respectively. However, despite the screening provided by the atomic displacements, the two electrons do not experience an attraction for one another, since the dielectric constant remains positive.

With only the short-range component of the electron-lattice interaction, a large bipolaron can only be produced in a one-dimensional electronic system. Only *small* bipolarons can be formed in two- and three-dimensional systems with only a short-range component of their electron-lattice interaction. In particular, *small* bipolarons will be energetically stable in two- and three-dimensional electronic systems if the energy of the two electrons paired at a site $-4E_b+U$ is less than that of two well-separated small polarons $-2E_b$.[18–20] Here, E_b is the small-polaron

binding energy and U is the on-site Coulomb repulsion between the two electrons.

With the *combined* presence of both the long- and short-range components of the electron-lattice interaction, large singlet bipolarons *can* exist in one-, two-, and three-dimensional electronic systems. The mechanism via which bipolaron formation is fostered by the collateral presence of both components of the electron-lattice interaction differs in systems of different electronic dimensionality. Specifically, in one-dimensional electronic systems, the addition of the long-range portion of the electron-lattice interaction to the short-range component facilitates bipolaron formation by providing additional screening of the Coulomb repulsion of the two electrons. In two-dimensional electronic systems, the presence of the long-range component of the electron-lattice interaction is necessary for the formation of a large-radius ground state (e.g., large polarons or large bipolarons). In addition, the short-range component of the electron-lattice interaction is required to produce the attractive interaction between large polarons that leads to the formation of a large bipolaron. In three-dimensional electronic systems, as in two-dimensional electronic systems, the presence of the long-range component of the electron-lattice interaction is essential to the formation of a large-radius ground state. However, it is only the "cross term" involving the product of the coupling constants associated with the long- and short-range components of the electron-lattice interaction that produces the attraction that can cause the formation of a large bipolaron. These cross terms arise with two components of the electron-lattice interaction because the polaronic energy depends on the square of the electron-lattice interaction [cf. Eq. (7)].

The requirements for forming a large singlet bipolaron become increasingly stringent as the dimensionality of the electronic state increases. In a one-dimensional electronic system, polarons and bipolarons are generally large. In two-dimensional electronic systems, a large bipolaron is only possible if (1) the material's atoms are sufficiently displaceable, $\epsilon_0 > 2\epsilon_\infty$, and (2) the electronic parameters related to the electronic bandwidth and the two components of the electron-lattice interaction fall within a specified range [cf. Eq. (50)]. In passing from a two-dimensional electronic system to a three-dimensional electronic system, $v_{\rm int}^{SL}(0)+v_{\rm int}^{S,2}(0)$ is replaced by $v_{\rm int}^{SL}(0)$ in the energy ratio contained in the condition for the formation of large bipolarons [compare Eqs. (50) and (56)]. As a result, the upper bound on t, arising from requiring stability of the large bipolaron against decomposition into two separate large polarons, is smaller for a three-dimensional electronic system than for a two-dimensional electronic system. In particular, with $v_{\rm int}^{S,2}(0) \gg v_{\rm int}^{SL}(0)$, the upper limit on an electron's kinetic energy t for the formation of large bipolarons is considerably smaller in a three-dimensional electronic system than in a two-dimensional electronic system.

To appreciate the relative difficulty of forming large singlet bipolarons in electronic systems of two and three dimensions, first note that the range of electronic parameters within which large bipolaron formation can occur is determined by the values of the static and high-frequency dielectric constants. In particular, for the formation of large bipolarons with $s=0$, it is necessary that $\epsilon_0 > 2\epsilon_\infty$. In addition, in a quasi-two-dimensional electronic system, large-bipolaron formation is only possible when a dimensionless function of various electronic parameters lies between 1 and $1+f$, where $f=(\epsilon_0-2\epsilon_\infty)^2/2\epsilon_\infty(2\epsilon_0-3\epsilon_\infty)$ [see Eq. (50)]. Here, f is about unity for $\epsilon_0/\epsilon_\infty=6$ and is about 2 for $\epsilon_0/\epsilon_\infty=10$. The electronic quantities of Eq. (50) [defined in Eqs. (18), (28), and (30), respectively] may be estimated as $t \approx \hbar^2/2mL^2$, $v_{\rm int}^{S,2}(0) \approx 2E_b a^3 l/L^2$, and $v_{\rm int}^{SL}(0) \approx 2(2E_b\beta e^2/\pi^3 a)^{1/2} a^2/L^2$, where L is the characteristic size of the bipolaron. With these estimates, the ratio of energies that determines whether a large bipolaron will form in a *two-dimensional* electronic system is

$$t/[v_{\rm int}^{S,2}(0)+v_{\rm int}^{SL}(0)] \approx J/\{2[E_b+(2E_b\beta e^2/\pi^3 a)^{1/2}]\} ,$$

where we have recognized $J(=\hbar^2/2ma^2)$ as the electronic transfer energy of tight-binding theory. For simplicity, we have set $l=a$. Typically E_b is several tenths of an electron volt and $2\beta e^2/\pi^3 a < 0.1$ eV $\ll E_b$. Then, with the ratio of electronic parameters ($\approx J/2E_b$) being constrained to lie between 1 and $1+f$, the overall electronic bandwidth W ($W=2zJ$, where z is the number of nearest neighbors) is limited by the approximate relation $16E_b < W < 16E_b\ (1+f)$ for a two-dimensional square array of sites ($z=4$). These conditions are frequently satisfied with typical estimates of it parameters. In this sense, this limitation seems to pose little practical restriction on the width of the electron energy band for a two-dimensional electronic system. However, the situation is quite different for a three-dimensional electronic system. In a *three-dimensional* electronic system, the ratio of electronic energies that is constrained to be less than $1+f$ is $t/v_{\rm int}^{SL}(0) \approx J/[2(2E_b\beta e^2/\pi^3 a)^{1/2}]$. Because of the relatively small value of the denominator of this ratio, the width of a three-dimensional electronic energy band is generally constrained to be moderately narrow, e.g., $\lesssim 4$ eV. In addition, the lower bound on t that is contained in Eq. (56) can pose another serious limitation on the value of t. Thus, these considerations suggest that the formation of large bipolarons is more likely in a two-dimensional electronic system than in a three-dimensional electronic system. In particular, for a two-dimensional electronic system the principal requirement is only that the system be ionic with ϵ_0 being significantly larger than $2e_\infty$. However, in a three-dimensional electronic system, the formation of a large bipolaron also requires moderately narrow electronic energy bands and appropriate values of $v_{\rm int}^{d,3}(0)$, $v_c(0)$, and $v_{\rm int}^{SL}(0)$ as indicated in Eq. (56).

We have studied the large-radius minimum of the ground-state adiabatic energy in order to ascertain the conditions under which a large bipolaron is stable against decomposition into two separated large polarons. When, as in one- and two-dimensional electronic systems, there is only one minimum of the adiabatic ground-state energy, this procedure is adequate to determine when large bipolarons are energetically stable. However, in a three-dimensional electronic system, a small polaron or small-bipolaron minimum can coexist with the large-radius minimum. Noting that a small polaron or a small bipola-

ron minimum corresponds to R being at its saturation value R_s the minimum physically allowed value of R, we express the energies, $E(R,s/R)$, corresponding to two small polarons and to a small bipolaron as $E(R_s,\infty)$ and $E(R_s,0)$, respectively. Thus, for the large bipolaron to be the stable state, its energy $E_{\min}(0)$ must be lower than $E(R_s,\infty)$ and $E(R_s,0)$. These conditions impose additional restrictions on the formation of large bipolarons in three-dimensional electronic systems that do not apply to systems of lower electronic dimensionality. There is no unambiguous way of choosing R_s, the cutoff value of R in a continuum model below which the continuum approach fails. Thus, within the framework of the present calculations, we can only note that, in a three-dimensional electronic system, the establishment of the stability of a large-radius bipolaron against decomposition into separate large polarons does not guarantee the energetic stability of the large-radius bipolaron with respect to forming either a small bipolaron or two separated small polarons.

Despite two polarons finding it energetically favorable to pair into a singlet bipolaron, we find that two polarons always repel one another in the limit of large interelectron separations. This long-range repulsion occurs because the $1/s$ Coulomb repulsion is the dominant force at large separations, as $s\rightarrow\infty$. Thus, even when a bipolaron is energetically stable with respect to two widely separated polarons, with decreasing interelectron separation s the energy of the two-electron system rises before it falls. In other words, we find a *barrier to the formation of bipolarons.*

With only a short-range component of the electron-lattice interaction, large-radius self-trapped states in electronic systems of two and three dimensions will not form.[15–17,19] However, we have shown herein that a large-radius self-trapped state can exist with the presence of both short- and long-range components of the electron-lattice interaction. Thus, the long-range component of the electron-lattice interaction plays a critical role in the formation of such states. Nonetheless, the short-range portion of the electron-lattice interaction can provide the dominant contribution to the deformational energy of such a state. To show this feature, we compare the deformational energies associated with the short- and long-range components of the electron-lattice interaction for a two-dimensional ($s=0$) large bipolaron. From Eq. (27), we see that these deformational energies are $2v_{\rm int}^{S,2}(0)/R^2$ and $v_{\rm int}^{L}(0)/R$, respectively. We also note, from the text below Eq. (40), that the value of R at the large-radius minimum is $2[\alpha_T(0)-\alpha_S(0)]/\alpha_C(0)$. Therefore, the ratio of the deformational energies of the short- to long-range components of the electron-lattice interaction for a large-radius state is

$$v_{\rm int}^{S,2}(0)\alpha_C(0)/[\alpha_T(0)-\alpha_S(0)]v_{\rm int}^{L}(0)\,.$$

Recalling from Eqs. (29) and (32)–(34) that $v_{\rm int}^{L}(0)=2(\epsilon_\infty^{-1}-\epsilon_0^{-1})v_c(0)$, $\alpha_C(0)=(\epsilon_\infty^{-1}-2\epsilon_0^{-1})v_c(0)$, $\alpha_T(0)\approx 2t$, and $\alpha_S=2v_{\rm int}^{S,2}(0)$, we find that this ratio of deformational energies will exceed unity if $v_{\rm int}^{S,2}(0)>4t/5$, where we have taken $\epsilon_0\gg\epsilon_\infty$. Using the estimation procedure employed in an earlier paragraph of this section, this condition becomes $E_b(a/l)>W/20$, where W is the two-dimensional electronic bandwidth. Performing an analogous estimate for a three-dimensional system yields the condition that $E_b[v_c(0)/\epsilon_\infty]>2(W/12)^2$, where W is now the width of a three-dimensional electronic band. This condition is expected to be less likely to be fulfilled than that for the quasi-two-dimensional electronic system. Thus, we find that with an electronic band of modest width and a short-range component of the electron-lattice interaction of typical size, the *short-range component of the electron-lattice interaction can provide the dominant contribution to the deformational energy of the quasi-two-dimensional large-radius bipolaron.*

We have determined conditions for the formation of large singlet bipolarons in deformable systems whose electronic distributions are one, two, and three dimensional within the adiabatic approximation. However, we neglected electron exchange and correlation effects in obtaining Eqs. (12) and (14). These directly enter into the kinetic energy and Coulomb terms. In addition, we assumed that the shape of the probability distribution $p(\mathbf{r}-\mathbf{s}/2)$ does not change as s is varied. Thus, the adjustment of the wave function of one electron induced by the presence of the other has been ignored. Each of these electronic effects tends to reduce the effective Coulomb repulsion between the electrons. Therefore, their inclusion in the theory would make the formation of large bipolarons more likely. Our conditions for large bipolaron formation are therefore overly restrictive. Indeed, our calculation yields the classical result that bipolarons cannot be formed with only the long-range component of the electron-lattice interaction. However, some variational calculations indicate that, with some inclusion of correlation and exchange effects, large bipolarons (often weakly bound) may be formed over some (usually very limited) domain of parameters with only the long-range component of the electron-lattice interaction.[22,30–33] Although polarization, correlation and exchange effects will not alter the R dependences of the basic physical quantities of the theory, displayed in Eq. (31), these effects can alter the s dependence of the parameters of the theory and thereby introduce additional situations in which there can be pairing.

In Sec. IV of this paper, we find that, with only a short-range electron-lattice interaction, no large-radius polarons or bipolarons are possible in two- or three-dimensional electronic systems. The proof of this feature can be generalized so as to not involve the simplifications contained in Eqs. (11), (12), and (14). In particular, we adopt a universal scaling procedure[17] in which all distances [$\mathbf{r}_1$ and $\mathbf{r}_2$ of Eq. (5)] are scaled together with a single scaling parameter, designated as R', rather than with the two scaling parameters R and s used in the body of the paper. Then, with only a short-range component of the electron-lattice interaction, the general expression for the ground-state adiabatic energy, given in Eq. (5) and subsidiary equations, can be used to find the ground-state energy as a function of R'. This energy is of the form $E(R')=T/R'^2-v_{\rm int}^{S,2}/R'^d+v_C/R'$, where T, $v_{\rm int}^{S,2}$, and v_C are all positive. Since this energy has no minima at finite R' for $d\geq 2$, we conclude that, within the adiabatic regime, large polarons or bipolarons are not possible in electronic systems of two or three dimensions when there is only a

short-range component of the electron-lattice interaction.

The fundamental physics of the formation of a large singlet bipolaron is independent of the approximations of this paper. In particular, an essential finding is that, with ther *combined* presence of the long-range (Fröhlich) component of the electron-lattice interaction and the short-range component of the electron-lattice interaction, large-radius bipolarons *can* be formed in electronic systems of one, two, and three dimensions. The long-range portion of the electron-lattice interaction is necessary to ensure that a large-radius polaron state exists in two- and three-dimensional electronic systems. The additional presence of the short-range portion of the electron-lattice interaction is necessary to modify the effective kinetic energy so as to provide the interpolaron attraction that binds a pair of large polarons into a large bipolaron. The formation of a large bipolaron requires having an ionic system for which ϵ_0 is significantly greater than $2\epsilon_\infty$. In addition, bipolaron formation imposes restrictions on the system's electronic parameters. For a three-dimensional electronic system, these additional restrictions can be severe. Minimally, moderately narrow electronic energy bands are required for the formation of three-dimensional large bipolarons. However, in a two-dimensional electronic system, the analogous restrictions are generally much milder. Indeed, ionic materials for which $\epsilon_0 \gg 2\epsilon_\infty$ with two-dimensional electronic systems are prime candidates for the formation of large bipolarons. In light of this finding, the question of whether large singlet bipolarons can exist in the CuO_2-based high-temperature superconductors is answered affirmatively. Indeed, all the high-temperature superconducting materials have the unusual feature of satisfying the requirement that $\epsilon_0 \gg 2\epsilon_\infty$.[28,29,34]

VI. BIPOLARONIC SUPERCONDUCTIVITY

To address the superconductivity of large bipolarons, we must first consider how a large bipolaron moves. Since the radius of a large bipolaron is much larger than the lattice constant, we treat the solid through which the carrier moves as though it were a continuum. Furthermore, we address the motion of the large bipolaron within the adiabatic or strong-coupling limit. This step is justified by noting that the coupling constant for the short-range component of the electron-lattice interaction (e.g., $E_b/\hbar\omega_D$, where ω_D is the Debye frequency) is typically sufficiently large compared with unity so as to correspond to the strong-coupling regime.[35] In addition, because of the large difference between the static and high-frequency dielectric constants in the novel superconductors,[28,29,34] the coupling constant of the long-range portion of the electron-lattice interaction is also large. In particular, with such values of the dielectric constants, α, the coupling constant that is often used to discuss the long-range portion of the electron-lattice interaction,[36] is typically much greater than unity. For example, we find $\alpha \approx 5$ for a carrier with an electronic effective mass equal to the free-electron mass and an optical phonon temperature even as high as 900 K.

Within the adiabatic regime the electronic carriers instantaneously adjust to the positions of the solid's atoms and thereby follow the atomic motions. Therefore, a bipolaron can only move if the atoms surrounding it alter their positions. Since the motion of a carrier is contingent on the motion of atoms, the effective mass of the adiabatic large bipolaron is related to the atomic masses and the displacements the atoms must execute so that the electronic carrier can move. In particular, with a bipolaron that moves a distance $\delta\mathbf{r}$ in a time δt, we define the mass tensor of the bipolaron $\overline{M}_{\rm BP}$ through its kinetic energy, $(\delta\mathbf{r}/\delta t \cdot \overline{M}_{\rm BP} \cdot \delta\mathbf{r}/\delta t)/2$. The bipolaron only moves a distance $\delta\mathbf{r}$ if the solid undergoes an appropriate change of its atomic displacement pattern $\delta\mathbf{d}(\mathbf{u})$, where $\mathbf{u}$ is a position vector within the deformable continuum. Neglecting the mass of the bipolaron's two electrons in comparison with the atomic masses, we write that

$$(\delta\mathbf{r}/\delta t \cdot \overline{M}_{\rm BP} \cdot \delta\mathbf{r}/\delta t) = \rho \int d\mathbf{u} \sum_j (\delta x_j/\delta t) \sum_{j'} (\delta x_{j'}/\delta t) \sum_i [\partial d_i(\mathbf{u})/\partial x_j][\partial d_i(\mathbf{u})/\partial x_{j'}] . \quad (57)$$

where d_i is a component of the atomic displacement pattern vector $\mathbf{d}(\mathbf{u})$ and x_j is a component of $\mathbf{r}$, the position vector denoting the bipolaron's location. The density ρ is a generalization of the solid's density. Specifically, the mass that enters into this density is the reduced mass appropriate to the atomic displacements $d(\mathbf{r})$ that are being considered. We now express the bipolaron's effective-mass tensor as

$$\overline{M}_{\rm BP} = \rho \int d\mathbf{u} \sum_i [\partial d_i(\mathbf{u})/\partial x_j][\partial d_i(\mathbf{u})/\partial x_{j'}]$$

$$= \rho \int d\mathbf{u} \sum_i [\partial d_i(\mathbf{u})/\partial u_j][\partial d_i(\mathbf{u})/\partial u_{j'}] . \quad (58)$$

The second equality results from taking the change of the atomic displacement at a point $\mathbf{u}$ associated with moving the bipolaron a distance $\delta\mathbf{r}$ to equal the difference between the atomic displacement patterns at positions $\mathbf{u}$ and $\mathbf{u}-\delta\mathbf{r}$. A one-dimensional version of Eq. (58) has also been derived by field-theoretic means.[35]

We now determine the mass of our large bipolaron. Specifically, we observe that as a result of the long-range component of the electron-lattice interaction, the bipolaron is associated with optic-type atomic displacements beyond the spatial extent of the electronic distribution, at $u > R_{\rm BP}$, where $R_{\rm BP}$ is the "radius" of the bipolaron. These atomic displacements involve altering the distance between the anions and cations of an ionic solid. In addition, the short-range component of the electron-lattice interaction generally produces both optic- and acoustic-type atomic displacements within the region of the electronic distribution, at $u < R_{\rm BP}$. We now consider the effect of these three types of atomic displacements on the mass of

the large bipolaron.

The long-range component of the electron-lattice interaction is associated with relative displacements of the anions and cations of an ionic solid. In this situation, the atomic displacements parameter $\mathbf{d}(\mathbf{u})$ refers to the relative displacements of anions and cations located about the position $\mathbf{u}$ from their carrier-free equilibrium positions. At a sufficiently large distance away from the center of the bipolaron, the atomic displacement pattern becomes radial with the magnitude $d(u)$. In terms of the model of the long-range component of the electron-lattice interaction that we employ in Eq. (23), $d(u)=a\Delta(u)$. To determine $d(u)$, we insert the long-range electron-lattice interaction function of Eq. (23) into the general expression for the deformation variable $\Delta(\mathbf{u})$ given by Eq. (4). Since we are focusing our attention on the atomic displacement pattern outside of the region in which the two electrons are confined, we make the standard approximation[36] of regarding the atomic displacement pattern as being that which would surround point charges. That is, we treat the electronic wave function that occurs in Eq. (4) as only being nonzero at the origin of our coordinate system. We then find that $d=2a(\beta e^2 a/\pi^3 k)^{1/2}u^{-2}$. We insert this result into Eq. (58) and integrate over the region outside the domain of the electronic charge distribution of the large bipolaron. In particular, we characterize a bipolaron of electronic dimensionality d by a length $R_{\rm BP}$ in d directions and by the length l transverse to the bipolarons longer direction(s), $l<R_{\rm BP}$. This procedure yields the effective mass of the bipolaron arising from the long-range (LR) optic-type electron-lattice interaction:

$$M_{\rm BP}^{\rm LR,opt}\propto(\omega_0 a)^{-2}(\beta e^2/a)(a/R_{\rm BP})^3 \tag{59}$$

for $d=3$, where ω_0 is the characteristic optic-mode frequency. For one- and two-dimensional electronic systems in the limit that $l\ll R_{\rm BP}$, the factor $(a/R_{\rm BP})^3$ in Eq. (59) should be replaced by $(a/l)^3$. This dimensionality dependence occurs because the $\mathbf{u}$ integration is dominated by the smallest permitted value of u. There is uncertainty and ambiguity in assigning values to the physical parameters that enter into the expressions for the various contributions to the bipolaron's effective mass, such as Eq. (59). Therefore, in describing these contributions we shall consistently ignore all numerical constants and just display the dependence of the various contributions on physical quantities. Finally, we note that, despite different notation, the result contained in Eq. (59) for $d=3$ is the known result for the "strong-coupling" limit of the Fröhlich large polaron.[36,37]

We now determine the contribution to the bipolaron's effective mass arising from short-range optic-type atomic deformations. We consider the situation in which each optic-type atomic displacement is independent of the others. This circumstance corresponds to the model described by Eq. (22) in which the optic-type atomic displacements may be described by a scalar deformation parameter, $d(\mathbf{u})=a\Delta(\mathbf{u})$.[13] Inserting Eq. (22) into Eq. (4) and carrying out the integration over the Dirac δ function, we find that $d(\mathbf{u})=2a^3(A_{\rm opt}/k)P(\mathbf{u})$, where $P(\mathbf{u})$ is the electronic probability distribution defined in Eq. (9). Estimating the integral that remains after inserting this result into Eq. (58), we find that the component of the bipolaron's effective mass associated with short-range optic-type atomic displacements depends on whether the bipolaron's motion is parallel or perpendicular to a longer direction of the bipolaron. Specifically, we find that

$$M_{\rm BP}^{\rm SR,opt}(\text{parallel})\propto(\omega_0 a)^{-2}(E_b^{\rm opt})(a/R_{\rm BP})^{d+2}(a/l)^{3-d}\quad\text{for } d=1,2,3 \tag{60a}$$

and

$$M_{\rm BP}^{\rm SR,opt}(\text{perpendicular})\propto(\omega_0 a)^{-2}(E_b^{\rm opt})(a/R_{\rm BP})^{d}(a/l)^{5-d}\quad\text{for } d=1,2, \tag{60b}$$

where $E_b^{\rm opt}=A_{\rm opt}^2/2k$. For a three-dimensional electronic system, the effective mass is given by Eq. (60a) with $d=3$. For electronic systems of one and two dimensions, the adiabatic effective mass of the bipolaron is anisotropic. The effective mass is smaller for motion parallel to a direction in which the bipolaron is extended [Eq. (60a)] than for the motion transverse to directions of the bipolaron's greatest spatial extent [Eq. (60b)]. In particular, the effective mass is inversely proportional to the volume of the large bipolaron, $R_{\rm BP}^d l^{3-d}$, and inversely proportional to the square of the distance characterizing the relevant motion: $R_{\rm BP}$ for parallel motion and l for transverse motion. The fact that the mass of the adiabatic bipolaron is inversely proportional to the volume of the bipolaron's state is a general feature of polaron theory with a short-range electron–electron-lattice interaction. It has its origin in the nonlinearity of self-trapping. Specifically, the distortion that traps the electronic carrier is proportional to the probability distribution of the carrier, Eq. (4).

We now determine the atomic displacement pattern arising from short-range (SR) acoustic-type atomic displacements. We first observe that the deformation parameter for acoustic-type atomic displacements is the strain of the system, $\partial\mathbf{d}(\mathbf{u})/\partial\mathbf{u}$. Within our continuum model, the scalar dilatation $\Delta(\mathbf{u})$ replaces the strain tensor as the deformation parameter for the short-range interaction between electrons and the acoustic phonons. Therefore, after using the short-range component of the electron-lattice interaction of Eq. (22) in Eq. (4) to find that $\Delta(\mathbf{u})=2a^2(A_{\rm ac}/k)P(\mathbf{u})$, we replace $\partial\mathbf{d}(\mathbf{u})/\partial\mathbf{u}$ in Eq. (58) by $\Delta(\mathbf{u})$. Carrying out the integration of Eq. (58) then yields

$$M_{\rm BP}^{\rm SR,ac}\propto c_s^{-2}(E_b^{\rm ac})(a/R_{\rm BP})^d(a/l)^{3-d}, \tag{61}$$

where $E_b^{\rm ac}=A_{\rm ac}^2/2k$ and c_s is the speed of sound. With $d=1$ and $l=a$, this result agrees with the result obtained in Ref. (35) for the one-dimensional case.

For a quasi-two-dimensional electronic system, $d=2$, we observe from Eq. (61) that the acoustic component of

the bipolaron's mass varies inversely as the thickness of the disklike bipolaron l where $l < R_{BP}$. This feature manifests the dependence of the large bipolaron's mass on its size. As the size of the large bipolaron is increased, the severity of the atomic displacements with which it is associated decreases. As a result, the effective mass of the large bipolaron decreases.

It is important to recognize that the mass of the solid's atoms only affects the adiabatic *motion* of a polaron or bipolaron through the frequencies of the vibrations that are associated with the atomic distortions that self-trap the carrier. In particular, the energies that enter into the expressions for the bipolaron's effective mass [Eqs. (59)–(61)] are determined in a static, albeit deformed, solid. Therefore, these energies are independent of the masses of the system's atoms. Thus, the acoustic component of the bipolaron's effective mass only garners a dependence on the masses of the solid's atoms through the dependence of the acoustic component of the bipolaron's effective mass on the speed of sound c_s. Similarly, the optic components of the bipolaron's effective mass only depend upon the masses of the atoms of the solid through the dependence of the optical frequency ω_0 on the masses of the solid's atoms.

As might be expected from the fact that its motion is contingent on the motion of the atoms of the solid, the adiabatic mass of a large polaron or bipolaron is generally much greater than the mass of a free electron.[35,38–40] Nonetheless, it is well known empirically that large polarons move with moderate mobilities.[41] Indeed, barring exceptionally narrow vibrational dispersion, general theoretical considerations imply that a large polaron or bipolaron will move through a solid as almost a free particle.[35] In particular, Schüttler and Holstein explicitly show that a massive large acoustic polaron suffers little effective scattering as it moves through a solid.[35] This behavior occurs because a large polaron is most effectively scattered by phonons of a wavelength close to the polaron's characteristic length, $R_{BP} \gg a$. Thus, a large acoustic polaron only interacts with long wavelength acoustic phonons. Since long wavelength acoustic phonons have small energies and momenta, they cannot effectively scatter a massive large polaron. In other words, phonons are reflected off the large polaron with the large polaron experiencing little change of momentum. As a result, the large polaron moves with relatively high mobility. In fact, the mobility of a large acoustic polaron can be similar in magnitude and temperature dependence to that produced by the scattering of a free electron by acoustic phonons.[35] To establish this result, Schüttler and Holstein show that the scattering time for the large polaron τ is proportional to the polaron mass, M_P. Therefore, the mobility of the large polaron $\mu = e\tau/M_P$ is independent of M_P! Thus, we see that an acoustic large polaron or large bipolaron is a massive entity that nearly moves as a free particle. In particular, with the two spins of its electrons paired, we view an acoustic large bipolaron as a charged free boson.

Employing the simplest version of the theory of the superconductivity of charged bosons (bipolarons),[4] the superconducting transition temperature is the temperature of the Bose-Einstein condensation with the particle mass being the mass of the large bipolaron. The temperature of the Bose-Einstein condensation temperature is $T_c = A\hbar^2 d_{BP}^{2/3}/M_{BP}k_B$, where A is a numerical constant and d_{BP} is the density of large (mobile) bipolarons. For an isotropic three-dimensional system, $A = 3.31$.[42] Of course, we have no *a priori* detailed knowledge of the magnitude of the effective mass of a large bipolaron. The effective mass of a large bipolaron must therefore be deduced from experiment. However, at this point, we can consider the consequences if the mass of the large bipolaron were greater but of the same order of magnitude of those determined for large strongly coupled polarons: 10 to 200 times the mass of an electron.[38–40] For example, with a density of bipolarons comparable to the carrier density at the highest transition temperatures in the CuO_2-based materials, 10^{21} cm^{-3}, and a mass of the bipolaron of 20 times the electron mass, one obtains $T_c \approx 130$ K. Therefore, we see that rather high superconducting transition temperatures result from plausible values of the effective mass and density of bipolarons.

The formula for the superconducting transition temperature given in the preceding paragraph is that of the Bose-Einstein condensation temperature in an isotropic system. We now address the effects of electronic anisotropy on the transition temperature. This is a critical issue since the Bose-Einstein condensation temperature vanishes for strict one- or two-dimensional systems. Generally, electronic anisotropy can affect the shape, effective mass, and scattering of a large bipolaron. Within the adiabatic approximation employed throughout this work, we have already observed that electronic anisotropy determines the shape of a large bipolaron. A quasi-one-dimensional bipolaron is cigar shaped, a quasi-two-dimensional bipolaron is disklike, and a three-dimensional bipolaron is a spheroid. We have also seen in Eqs. (59)–(61) that, although the shape of the bipolaron affects the magnitude of its effective mass, only those components of the adiabatic effective mass that are associated with optic phonons become anisotropic for an anisotropic electronic system. The component of the bipolaron's effective mass arising from a carrier's short-range interaction with acoustic phonons remains isotropic even with an anisotropic electronic system. Thus, if the predominant contribution to the bipolaron's effective mass is associated with the (deformational-potential-like) short-range acoustic component of the electron-lattice interaction, its effective mass remains isotropic even in an anisotropic electronic system. In this circumstance, the formula for the superconducting transition temperature may be applied even to anisotropic electronic systems. Finally, we observe that these conclusions are only valid within the adiabatic regime. In the limit that the electronic transfer energy in the "hard" direction(s) becomes sufficiently small, the adiabatic approach will fail for motion in the "hard" direction(s). Then, ultimately the carrier's effective mass must become highly anisotropic and the transition temperature falls toward zero. Finally, we note that even with an isotropic effective mass, the scattering, and hence the normal-state motion, of a large-bipolaron with an anisotropic shape will be anisotropic.

The transition temperature depends critically on the density of large bipolarons. Hence, we must consider how the density of large bipolarons depends upon the overall carrier density. In particular, even if it is energetically favorable for two carriers to pair to form a large bipolaron, the formation of large bipolarons becomes destabilized as the carrier density becomes sufficiently high. This destabilization arises from two sources. First, the atomic-displacement patterns surrounding different bipolarons begin to interfere with one another when the carrier density becomes too large. Depending on the geometry, the atomic displacements associated with different carriers interfere constructively or destructively with one another. For example, Fig. 8 of Ref. 19 contains an illustration of the interference of the deformation patterns about two small polarons. If the bipolarons primarily compete to displace the same atoms in different directions, the energy of the bipolarons is raised as they are brought toward one another. Concomitantly, the effective mass ascribed to a single bipolaron will be reduced. In particular, with bipolarons within the CuO_2 sheets in the CuO_2-based superconductors, bipolaronic atomic displacements parallel to the CuO_2 sheets will interfere destructively with one another. When there is sufficient overlap between such bipolarons, these bipolarons will be destabilized with respect to forming a collection of nonpolaronic carriers. Screening of the long-range (Coulombic) component of the electron-lattice interaction by mobile large bipolarons provides a second reason to expect the destabilization of large bipolarons at sufficiently high densities. Thus, a simple qualitative picture of the dependence of the density of bipolarons, and, therefore, the superconducting transition temperature, on the carrier density emerges. At sufficiently low carrier densities the superconducting transition temperature rises with the carrier density as carriers predominantly form large bipolarons. However, as the carrier density becomes sufficiently large that the bipolarons lose stability, the density of bipolarons, and, hence, the superconducting transition temperature, will fall with increasing carrier density.

We now consider the effect on T_c of a change of the mass of some of the solid's atoms brought about by isotropic substitution. The transition temperature will only be affected by such isotopic changes through a change in the effective mass of the large bipolaron. If the predominant atomic displacements induced by the presence of the electronic carriers involve the light atoms, then the electron-lattice interaction mainly involves the optic modes. In this situation, the dependence of the transition temperature on isotopic substitution will reflect the change of the optic phonon frequency with isotopic substitution. For example, an isotopic change of the oxygen atoms in the CuO_2-based materials should then produce a significant shift of M_{BP} (proportional to the shift of ω_0^2). However, if the predominant atomic displacements induced by the presence of the carrier involve displacing heavy atoms, then the electron-lattice interaction primarily involves acoustic-type atomic displacements. In this case, the change of the mass of the large bipolaron will only arise through shifting the speed of sound c_s. Then, an isotopic substitution for the solid's light atom (e.g., the oxygen atoms were linked by comparable stiffness constants, then an isotopic substitution for the system's oxygen atoms would only alter the superconducting transition temperature by the fractional amount that the isotopic substitution alters the material's density. Furthermore, if the large static dielectric constants of the CuO_2-based materials were associated with loosely bound oxygen atoms outside of the CuO_2 sheets, isotopic changes of these atoms would have a reduced effect on the sound velocity at finite frequencies and hence on $M_{BP}^{SR,ac}$.

We have seen [Eqs. (59)–(61)] that the mass of an isolated large bipolaron falls as the volume of the bipolaron is increased. Since the superconducting transition temperature is inversely proportional to the mass of the bipolaron, increasing the size of the bipolaron increases the superconducting transition temperature. We envision the large bipolaron in the CuO_2-based superconducting materials to have a quasi-two-dimensional (disklike) morphology. This picture is consistent with the large bipolaron being contained primarily within the CuO_2 sheets of these solids. Combining these sheets so as to make a thicker bipolaron decreases the bipolaron's mass and thereby increases the superconducting transition temperature. Therefore, the superconducting transition temperature rises with the number of contiguous sheets. In fact, as indicated by Eqs. (59)–(61), the transition temperature for bipolaronic superconductivity in a solid that is electronically quasi-two-dimensional can be greatly enhanced by combining sheets so as to form thicker bipolarons. As the shape of the bipolaron becomes more like a spheroid than a disk, the effect of adding more sheets slows and ultimately saturates when the bipolaron's thickness becomes comparable to its diameter. Therefore, the onset of saturation can provide a very rough estimate of the bipolaron's radius. Finally, if the number of contiguous sheets becomes sufficiently great so that the polaron is truly three dimensional, the conditions for the formation of a large bipolaron become the more stringent conditions that characterize a three-dimensional system. In this case, a large bipolaron may no longer form. Therefore, as the number of contiguous CuO_2 sheets increases the superconducting transition temperature should increase. The increase of the transition temperature with the number of contiguous CuO_2 sheets should saturate when the bipolaron's thickness approaches its diameter. With a further increase in the number of contiguous CuO_2 sheets, the transition temperature should either remain nearly constant or fall to zero depending on whether or not the three-dimensional large bipolaron is stable. The superconducting transition temperature of the CuO_2-based superconductors has been observed to rise to a saturation value with increasing the number of contiguously stacked CuO_2 sheets.[1,2] Thus, these observations are consistent with the predicted effect of the thickening of disklike bipolarons on the transition temperature for bipolaronic superconductivity.

Two striking predictions emerge from our theory if the predominant contribution to the effective mass of the large bipolaron were to be the acoustic component. First, the superconducting transition temperature can be only *weakly* dependent on *isotopic substitutions* for the solid's

oxygen atoms. Second, thickening of disklike large bipolarons would increase the transition temperature with the number of contiguous equivalent CuO_2 sheets until the bipolaron's thickness l becomes comparable to the in-plane bipolaronic diameter, $2R_{BP}$. Both of these features have been observed experimentally.

With regard to the dominance of the acoustic component of the bipolaron's effective mass, we note that the very high-temperature superconducting materials present us with an unusual situation. In most transition-metal oxides the charge carriers reside on the (heavy) cation sites. This circumstance suggests that the short-range electron-lattice interaction in these instances is associated with displacing the (relatively light) oxygen atoms adjacent to the cation. With this being the case, the short-range electron-lattice interaction in such circumstances is primarily of optic character. The situation in the CuO_2-based system appears to be reversed. In particular, a hole is thought to primarily reside on bonding orbitals of the oxygen atoms rather than on the cations.[43,44] Thus, we might envision a strong short-range electron-lattice interaction to be associated with the displacements of the (relatively heavy) copper-atom neighbors about an oxygen site. In such a situation, the short-range electron-lattice interaction is of acoustic character. This feature provides some rationale for presuming that the short-range electron-lattice interaction of a large bipolaron in the CuO_2-based materials has primarily an acoustic character.

VII. SUMMARY OF RESULTS AND DISCUSSION OF EXPERIMENTS

In summary, we have found that *large* singlet bipolarons can be formed in ionic solids when the *combined* presence of the short- and long-range components of the electron-lattice interaction is considered. A necessary condition for this occurrence is that the static dielectric constant greatly exceeds the high-frequency dielectric constant. For materials that are three-dimensional electronically, the remaining conditions for the formation of large bipolarons generally restrict their formation to ionic solids with narrow electronic bands and appropriate values of the electron-lattice coupling constants [Eq. (56)]. However, the limitations on the electronic bandwidth are considerably less restrictive in systems that are electronically two dimensional. Since these conditions are conceivably met in the high-temperature superconducting materials, we consider the formation of large bipolarons a real possibility in these solids. With its large size and large mass, an acoustic bipolaron moves through a solid as a classical particle. Treating these large singlet bipolarons as charged bosons results in bipolaronic superconductivity with the superconducting transition temperature being roughly the temperature of the Bose-Einstein condensation of a gas of large bipolarons.[4] The adiabatic mass of the large bipolaron is typically a small fraction of the mass of a nucleon. Masses of such magnitudes result in transition temperatures comparable to those observed in the high-temperature superconductors. Furthermore, for acoustic bipolarons, isotopic changes in the solid at most affect the mass of the bipolaron through a change of the solid's density. In this circumstance, there is only a very weak dependence of the transition temperature on isotopic changes of the solid's atoms. Finally, we find that the thickening of a quasi-two-dimensional large bipolaron produces a large increase of the superconducting transition temperature.

We now summarize the relevance of the considerations of this paper to the recently discovered high-temperature superconductivity. The high-temperature superconductors have (1) dielectric constants that satisfy the requirement that $\epsilon_0 \gg 2\epsilon_\infty$ (Refs. 28, 29, and 34) and (2) electronic-energy bands that are narrow to moderate in width. In addition, the CuO_2-based superconductors possess the electronic quasi-two-dimensionality that fosters the formation of large bipolarons. Furthermore, the low carrier densities ($\simeq 10^{21}$ elementary charges per cm^3 in the CuO_2-based materials)[45–47] in the superconducting materials are consistent with a gas of mobile large bipolarons centered at less than 10% of the sites. Thus, the high-temperature superconductors generally meet the requirements for the formation of a collection of large bipolarons.

Recent experiments provide evidence that charge carriers in the insulating parents of the CuO_2-based superconductors form large polarons or large bipolarons. In particular, with the optically induced generation of charge carriers in La_2CuO_4 and $YBa_2Cu_3O_{6.25}$, additional infrared absorption bands develop.[48] These bands are associated with carrier-induced atomic displacements. The masses of the carriers, large polarons or bipolarons, are roughly estimated to be at least an order of magnitude greater than the free-electron mass. Furthermore, the mass deduced for $YBa_2Cu_3O_{6.25}$ is found to be about half that found for La_2CuO_4. Thus, materials whose carriers have smaller effective masses have higher superconducting transition temperatures. The smaller carrier masses in the CuO_2-based materials with contiguous CuO_2 sheets and the inverse correlation of these masses with the superconducting transition temperatures are in accord with the predictions of this paper. Finally, it is striking to note that a photoinduced change in the infrared absorption is *not* observed in La_2NiO_4, a material that, while structurally and electronically similar to La_2CuO_4, does *not* display superconductivity. This fact is consistent with the hypothesis that the formation of large polarons or large bipolarons in the insulating parents of the superconducting materials is related to the carrier-laden materials becoming superconductors.

Reflectivity studies of samples of $YBa_2Cu_3O_{7-\delta}$ that have a sufficient carrier density ($\simeq 0.6\times 10^{21}$ cm^{-3}) so as to be superconducting also indicate large effective masses and long conductivity relaxation times.[49] Furthermore, these measurements suggest that the energies of the excitations that dress the carriers are several hundredths of an eV, comparable to phonon energies. Doubling the mass and halving the carrier density determined in this study so as to account for a collection of *bi*polarons rather than singly charged carriers, the temperature of the Bose-

Einstein condensation (57 K) is found to be comparable to the observed superconducting transition temperature in these samples (50 K). Thus, these results are also consistent with the expectations of bipolaronic superconductivity.

Furthermore, distinctive features of having large-bipolaronic superconductivity are observed in the CuO_2-based superconductors. First, the very weak dependence of the superconducting transition temperatures of the CuO_2-based superconductors on isotopic substitutions for oxygen is consistent with predictions of our treatment of the superconductivity associated with *large* bipolarons if the carriers primarily reside on light (oxygen) atoms. Furthermore, the strong dependence of the superconducting transition temperature in the $BaBiO_3$ system on isotopic substitutions for oxygen atoms[50,51] also follows from our model if the carriers in this system are centered on the (heavy) cations rather than on the light (oxygen) atoms. Second, the striking increase of the superconducting transition temperatures of the CuO_2-based superconductors with the addition of continuous CuO_2 sheets is consistent with the effect of thickening quasi-two-dimensional large bipolarons. Third, as described in Sec. VI of this paper, the observed increase and eventual decline of the superconducting transition temperature with carrier density[52] is also expected of the superconductivity of large bipolarons. Fourth, the observed values of the superconducting transition temperature emerge from our formula with plausible, albeit uncertain, values of the physical parameters.

Thus, although this work ignores many of the complexities of the real materials, such as their magnetic interactions, we feel that the picture of large-bipolaronic superconductivity is a cogent model that provides a plausible explanation for a number of the distinctive features of the novel high-temperature superconductors. As such, the bipolaronic superconductivity of *large* bipolarons is a real possibility.

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