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# Electron-hole asymmetric polarons

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In small polaron models the hopping amplitude for a carrier from a site to a neighboring site is reduced due to "dressing" by a background degree of freedom. Electron-hole symmetry is broken if this reduction is different for a carrier in a singly occupied site and one in a doubly occupied site. Assuming that the reduction is smaller in the latter case, the implication is that a gradual "undressing" of the carriers takes place as the system is doped and the carrier concentration increases. A similar "undressing" will occur at fixed (low) carrier concentration as the temperature is lowered, if the carriers pair below a critical temperature and as a result the "local" carrier concentration increases (and the system becomes a superconductor). In both cases the "undressing" can be seen in a transfer of spectral weight in the frequency-dependent conductivity from high frequencies (corresponding to non-diagonal transitions) to low frequencies (corresponding to diagonal transitions), as the carrier concentration increases or the temperature is lowered respectively. This experimental signature of electron-hole asymmetric polaronic superconductors as well as several others have been seen in high temperature superconducting oxides. Other experimental signatures predicted by electron-hole asymmetric polaron models remain to be tested.

## I. THE PHYSICS OF HIGH $T_C$ OXIDES

From the beginning of the high $T_c$ era there have been indications that small polarons may play an important role in the physics of these materials.[1–10] Among the workers that have not completely abandoned the Fermi liquid framework for this problem most would agree that the physics of the normal state may be described by heavily dressed quasiparticles.[11] There is little agreement however concerning the physical origin of this quasiparticle dressing, with proposed explanations ranging from strong electron-phonon interactions[1–6] to electron-spin interactions (magnetic polarons)[7–9] to electron-electron interactions (electronic polarons).[10]

When a high $T_c$ oxide is doped increasingly with holes the normal state becomes less "strange"[11], suggesting that the quasiparticles evolve from being heavily dressed to being lightly dressed, or undressed. In other words, a gradual undressing of carriers occurs as the carrier density increases. Direct evidence for this process is seen in optical absorption in the normal state: a transfer of spectral weight in the frequency-dependent conductivity occurs, from high energy excitations (in the 1 to 3 $eV$ range) to mid-infrared and lower energy (intra-band) excitations, as the carrier concentration increases.[12,13] Furthermore the band effective mass as inferred for example from resistivity is seen to decrease as the carrier concentration increases.

When a low carrier concentration system becomes superconducting the "local" carrier concentration around a given carrier will also increase, due to pairing, particularly if the pair wavefunction has a short spatial extent (coherence length). Thus one may expect that a similar "undressing" to what takes place in the normal state upon doping would occur at a fixed (low) carrier concentration as the temperature is lowered and the system becomes superconducting. Furthermore, assuming that it is this "undressing" that drives the superconducting transition one would conclude that superconductivity should disappear at high carrier concentration[14] because carriers are already undressed in the normal state. This physics is qualitatively depicted in Fig. 1.

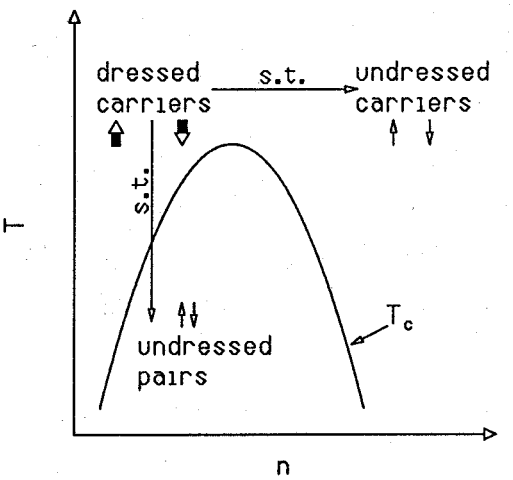


FIG. 1. Schematic depiction of the physics of electron-hole asymmetric polaron systems. Heavily dressed quasiparticles at low concentrations undress as the temperature is lowered or as the carrier concentration increases. *s.t.* denotes *s*pectral weight *t*ransfer, from high to low frequencies (in the direction of the arrows). Below the curve labeled $T_c$ the system is superconducting. The initial rise in $T_c$ versus $n$ is due to the increasing number of carriers.

The physics just described arises in electron-hole asymmetric polaron models. Electron-hole asymmetry is a generic property of solids and in particular arises naturally in various models of small polarons, including the Holstein model[15] when slightly generalized. When electron-hole asymmetry is introduced in these models a new pairing mechanism arises and superconductivity can occur under conditions on the interaction parameters in the models that are vastly less restrictive than in their electron-hole symmetric counterparts. Put another way, possibly the most effective way to suppress superconductivity in a generic model of small polarons is to make it electron-hole symmetric.

There are many characteristic features of such electron-hole asymmetric polaron models. Several are seen in high $T_c$ oxide superconductors, others are still experimentally untested. In addition there are likely to be many other phenomena predicted by these models that have yet to be elucidated and quantified. Because electron-hole asymmetry can arise in any small polaron model, whether electronic, magnetic or electron-phonon, we hope that workers in these problems will be interested in exploring its consequences further.

## II. ELECTRON-HOLE ASYMMETRIC SMALL POLARONS

A small polaron model describes the propagation of a carrier (electron or hole) that carries with it a "cloud" describing the deformation of a local background degree of freedom by the carrier.[15–17]. This local degree of freedom may be an ionic coordinate, as in Holstein's model, an electronic degree of freedom (electronic polaron) or a spin degree of freedom (magnetic polaron). In the simplest realization there is one background degree of freedom associated with each lattice site. In a tight binding description, the possible ground states of a lattice site with different numbers of carriers are then:

$$|0>|0>\equiv|0\gg \tag{1a}$$

$$|\uparrow>|1>\equiv|\uparrow\gg \tag{1b}$$

$$|\downarrow>|1>\equiv|\downarrow\gg \tag{1c}$$

$$|\uparrow\downarrow>|2>\equiv|\uparrow\downarrow\gg \tag{1d}$$

On the left-hand side of Eq. (1) the first ket describes the electronic state and the second the background ground state: $|n>$ denotes the background state when there are $n$ carriers at the site. On the right-hand side we defined a "composite state" of electron and background state in its ground state and denote it with a double bracket.

Coherent motion of these small polarons occurs when the background degree of freedom remains in the ground state when the carrier hops from site to site (diagonal transitions).[15] It is assumed that the background state instantaneously relaxes from the ground state corresponding to the old number of carriers to that corresponding to the new number of carriers as the hopping occurs (anti-adiabatic limit). The possible hopping amplitudes for a carrier are then, depending on the number of carriers at the two sites involved in the hopping process

$$|\uparrow\gg|0\gg \overset{t_0}{\longleftrightarrow} |0\gg|\uparrow\gg \tag{2a}$$

$$|\uparrow\gg|\downarrow\gg \overset{t_1}{\longleftrightarrow} |0\gg|\uparrow\downarrow\gg \tag{2b}$$

$$|\uparrow\downarrow\gg|\downarrow\gg \overset{t_2}{\longleftrightarrow} |\uparrow\gg|\uparrow\downarrow\gg \tag{2c}$$

where the hopping amplitudes are obtained from the "bare" hopping amplitude $t$ by multiplying by appropriate overlap matrix elements of the background states:

$$t_0 = t<0|1>^2 \tag{3a}$$

$$t_1 = t<0|1><1|2> \tag{3b}$$

$$t_2 = t<1|2>^2 \tag{3c}$$

Our basic assumption is that

$$<0|1>\neq<1|2> \tag{4}$$

in general. Eq. (4) defines what we mean by electron-hole asymmetric polarons. It implies that the effective model describing the dressed quasiparticles is not electron-hole symmetric even if the "bare" model involving only the carriers was: since $t_0 \neq t_2$, the hopping amplitude for a single electron and a single hole will be different. We assume for definiteness that the carriers in Eq. (1) are electrons, and that

$$<0|1>><1|2> \tag{5}$$

so that holes are heavier than electrons. If the converse of Eq. (5) were to hold the subsequent discussion would still apply provided the words "electron" and "hole" are interchanged.

The assumption Eq. (5) implies that the deformation of the background state induced by the first electron is smaller than that induced by the second electron on a site. Conversely, the deformation induced by the first hole on a site is larger than that induced by the second hole. In a Holstein model for small polarons, this occurs if the equilibrium position of the oscillator changes by a different amount in adding the first and the second carrier to a site. This is schematically shown in Figure 2. Generalized Holstein models with this property will be discussed in Section V.

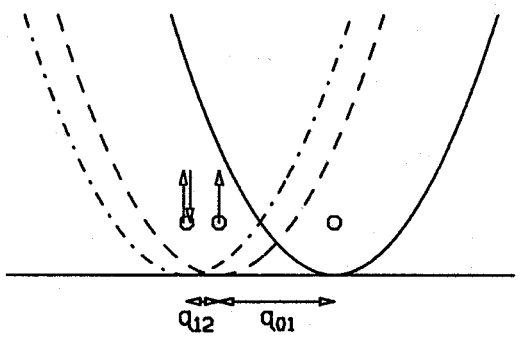


FIG. 2. Schematic depiction of potential wells for electron-hole asymmetric Holstein model. The full, dashed and dash-dotted lines show the oscillator potential when the site has zero, one and two holes respectively (indicated by vertical arrows on the circles centered at the respective equilibrium positions). $q_{01}$ and $q_{12}$ denote the difference in equilibrium positions when the site has zero and one hole, and one and two holes, respectively; $q_{01} > q_{12}$. In the electron-hole symmetric model $q_{01} = q_{12}$.

The hopping amplitude for a single hole in such a system is $t_2$. For a system with hole density $n$ per site the average hopping amplitude is

$$t(n) = t_2(1-n) + t_1 n \equiv t_2 + n\Delta t \tag{6a}$$

$$\Delta t = t_1 - t_2 \tag{6b}$$

since $n$ is the probability that another hole of opposite spin will occupy one of the two sites involved in the hopping process. Eq. (6) is correct only to lowest order in $n$ but is sufficient for our purpose since we will be interested in systems with low carrier concentration only.

The conductivity sum rule states that the integrated optical absorption for intra-band processes is given by

$$\int_0^{\omega_m} d\omega \sigma_1(\omega) = \frac{\pi e^2 n}{2m^*} \tag{7}$$

with $\sigma_1$ the frequency-dependent real part of the conductivity (per site), $n$ the number of carriers per site and $m^*$ the effective mass. $\omega_m$ is a high frequency cutoff that allows only for intra-band processes. The effective mass in a tight binding model is

$$m^* = \frac{\hbar^2}{2ta^2} \tag{8}$$

with $a$ the lattice spacing (we assume a simple hypercubic lattice). In our case, the hopping amplitude Eq. (6) varies with carrier concentration so that the integrated optical absorption

$$\int_0^{\omega_m} d\omega \sigma_1(\omega) = \frac{\pi e^2 a^2 t(n) n}{\hbar^2} \tag{9}$$

increases faster than linearly with carrier concentration. The extra spectral weight in the intra-band spectrum arises from a decrease in the spectral weight of nondiagonal transitions: hopping processes where the background degrees of freedom end up in excited states rather than the ground state.

Thus, an essential feature of electron-hole asymmetric polarons is that as a function of doping a transfer of spectral weight in the frequency-dependent conductivity from non-diagonal to diagonal transitions occurs. Such behavior is seen in high $T_c$ oxides doped with holes:[12,13] the intra-band spectral weight increases more rapidly than linear with hole concentration, and the absorption in the visible range (1 to 3 eV) decreases correspondingly. This indicates that the carriers gradually undress as the hole concentration increases.

## III. SUPERCONDUCTIVITY FROM ELECTRON-HOLE ASYMMETRIC POLARONS

The hopping amplitude for a hole polaron of spin $\sigma$ between sites $i$ and $j$ can be written as

$$t_{ij}^{\sigma} = t_2 + \Delta t(n_{i,-\sigma} + n_{j,-\sigma}) \tag{10}$$

with $n_{i,-\sigma}$ the number of holes of opposite spin at site $i$ and $\Delta t$ given by Eq. (6b). Eq. (10) ignores the possibility of holes of opposite spin being present at both sites $i$ and $j$, but this will be unimportant at low hole concentration. A Hamiltonian that describes the low-energy physics of these small polarons is then

$$H = -\sum_{\substack{<ij> \\ \sigma}} t_{ij}^{\sigma}(c_{i\sigma}^{\dagger} c_{j\sigma} + h.c.) + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{<ij>} n_i n_j \tag{11}$$

with $U$ and $V$ repulsive on-site and nearest neighbor interactions.[18] For a dilute system of hole carriers, this Hamiltonian can be accurately studied within the BCS framework,[19] and leads to superconductivity if the parameters satisfy the condition

$$\frac{\Delta t}{t_2} > \sqrt{(1+\frac{U}{2zt_2})(1+\frac{V}{2t_2})} - 1 \tag{12}$$

with $z$ the number of nearest neighbors to a site. If the single hole hopping amplitude $t_2$ is very small compared to $t_1$ we have $t_2 << \Delta t$ and Eq. (12) simplifies to

$$\Delta t > \sqrt{\frac{UV}{4z}} \tag{13}$$

The physics leading to superconductivity is gain of kinetic energy: when polarons pair their mobility increases and the energy is lowered. The mobility of a bound pair can be calculated explicitely and is found to be always larger than 1/2 the single particle mobility.[20] In other

words, a polaron pair is lighter than the sum of its individual components.

Figure 3 shows the critical temperature resulting from this model for a typical set of parameters. It also shows the pair coherence length and the single particle effective mass in the normal state (Eqs. (6a), (8)). The coherence length increases monotonically with hole doping, and the single particle effective mass decreases. Thus a cross-over occurs from a strong coupling regime at low hole doping to a weak coupling regime at high hole doping, where conventional behavior in all properties should be seen. In particular, the BCS gap ratio attains the weak coupling value 3.53 for large hole doping and is larger for low hole doping.[19]

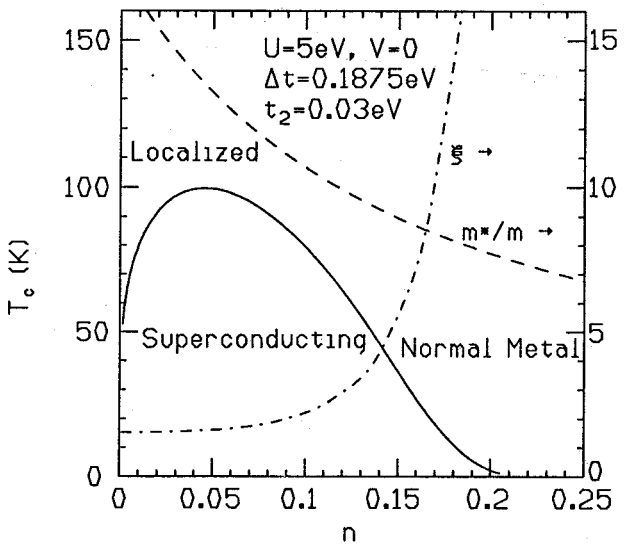


FIG. 3. Critical temperature versus hole concentration (solid line) for parameters given in the figure. Also shown is the coherence length (dash-dotted line) and the effective mass enhancement ( dashed line) versus hole concentration.

The quasi-particle energy in this model is given by the usual form

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} \tag{14}$$

with $\mu$ the chemical potential and $\epsilon_k$ the single particle band energy. The gap function $\Delta_k$ is only a function of band energy and of the form

$$\Delta_k = \Delta_m \left( \frac{-\epsilon_k}{D/2} + c \right) \equiv \Delta(\epsilon_k) \tag{15}$$

with

$$D = 2zt(n) \tag{16}$$

the bandwidth (that increases with hole doping) and $\Delta_m$ and $c$ parameters obtained from solution of the BCS equations. Analytic forms for these as well as for the critical temperature can be found in the weak and strong coupling limits.[19]

The quasiparticle energy can be rewritten as

$$E_k = \sqrt{a^2(\epsilon_k - \mu - \nu)^2 + \Delta_0^2} \tag{17a}$$

$$a = \sqrt{1 + \left( \frac{\Delta_m}{D/2} \right)^2} \tag{17b}$$

$$\Delta_0 = \frac{\Delta(\mu)}{a} \tag{17c}$$

$$\nu = \frac{1}{a} \frac{\Delta_m}{D/2} \Delta_0 \tag{17d}$$

Figure 4 shows the behavior of the quasiparticle energy, gap function and coherence factors

$$u_k^2 = \frac{1}{2} \left( 1 + \frac{\epsilon_k - \mu}{E_k} \right) \tag{18a}$$

$$v_k^2 = \frac{1}{2} \left( 1 - \frac{\epsilon_k - \mu}{E_k} \right) \tag{18b}$$

versus band energy. Because the minimum in the quasiparticle energy is shifted from $\mu$ to $\mu + \nu$, various characteristic features arise in tunneling and photoemission experiments.[19] In particular, tunneling characteristics exhibit an asymmetry of universal sign, and a thermoelectric voltage (also of universal sign) appears across a tunnel junction when the quasiparticles on both sides obey different distribution functions.[21] These effects should be experimentally observable.

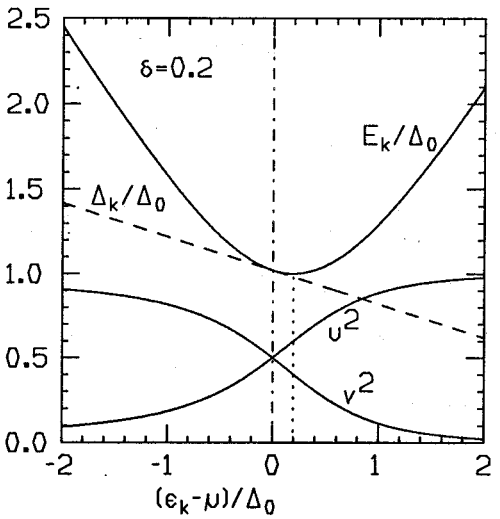


FIG. 4. Quasiparticle energy, gap function and coherence factors versus hole band energy for gap slope $\delta = \Delta_m/(D/2) = 0.2$. The vertical dot-dashed and dotted lines indicate the positions of the chemical potential $\mu$ and of the quasiparticle energy minimum $\mu + \nu$.

## IV. BOSE DECONDENSATION VERSUS PAIR UNBINDING

In electron-hole symmetric bipolaron models of superconductivity, the transition to the normal state generally occurs through Bose decondensation, and bound pairs still exist above $T_c$.[22] More generally, it is assumed that such a scenario always occurs when the pair coherence length is short.[23] However, this is not so in the models considered here. Qualitatively, the coherence length is given approximately by

$$\xi \sim \frac{t_2}{\epsilon_b} \tag{19}$$

with $\epsilon_b$ the pair binding energy and $t_2$ the single particle hopping amplitude. The Bose condensation temperature is in the range where center of mass excitations of the pairs start to play a significant role and is proportional to the pair hopping amplitude

$$T_c^{Bose} \sim t_p \tag{20}$$

while the BCS pair unbinding transition is proportional to the pair binding energy

$$T_c^{BCS} \sim \epsilon_b \tag{21}$$

Thus even in the regime of short coherence length ($\xi < 1$) one may have

$$T_c^{BCS} << T_c^{Bose} \tag{22}$$

provided that the pair hopping amplitude is larger than the single particle amplitude

$$t_p >> t_2 \tag{23}$$

While Eq.(23) cannot happen for electron-hole symmetric polarons (in fact, the opposite occurs) it is an essential feature of the models considered here. In particular, in the strong coupling regime ($t_2 << \Delta t$) the pair binding energy and pair hopping amplitude are given by[19]

$$\epsilon_b = 2zt_p - V \tag{24a}$$

$$t_p = \frac{2\Delta t^2}{U - V} \tag{24b}$$

so that the pair binding energy can be arbitrarily small for a finite value of the pair hopping amplitude.

In other words, in the models discussed here in the regime of low hole concentration the pairs are of small spatial extent and yet highly mobile and weakly bound. When the temperature is raised, they will dissociate well before the temperature range where center of mass excitations of the pairs would have started to play a role (cf Eq. (22)). This scenario is rather different from what occurs in electron-hole symmetric polaron models and should be evident experimentally, e.g. by a sharp break in the Knight shift as the temperature is raised across the critical temperature. Only at an extremely low hole concentration does a cross-over to a Bose-condensation description occur in the models considered here.[24]

## V. MODELS FOR ELECTRON-HOLE ASYMMETRIC POLARONS

Because electron-hole is not an exact symmetry of solids, any microscopic model for the description of physical reality should, in principle, contain electron-hole symmetry-breaking terms, which should only be discarded after establishing that they are irrelevant for the physics of interest. Here we discuss how electron-hole symmetry-breaking terms arise in small polaron models in a natural way.

### A. Generalized Holstein Models

The site Hamiltonian for a conventional Holstein model is given by[15]

$$H_i = \frac{p_i^2}{2M} + \frac{1}{2}Kq_i^2 + \alpha q_i n_i + U n_{i\uparrow} n_{i\downarrow} \tag{25}$$

with $(p_i, q)$ canonical coordinates of a vibrational degree of freedom of mass $M$ and force constant $K$. This model is electron-hole symmetric; however, various modifications of it to include physical effects that occur in nature will turn it electron-hole asymmetric,[25] namely:

(i) Allow for a variation of the electron-phonon coupling constant $\alpha$ with site occupation.[26] A possible parametrization is

$$\alpha \rightarrow \alpha + \frac{\alpha'}{2}(n_i - 1). \tag{26}$$

This is equivalent to allowing for dependence of the on-site repulsion $U$ on the phonon coordinate $q_i$.

(ii) Allow for a variation of the stiffness $K$ with site occupation

$$K \rightarrow K(n_i) \tag{27}$$

(iii) Allow for a variation of the electronic mass with site occupation, $M \rightarrow M(n_i)$. (This effect is likely to be small). Both this as well as the effect (ii) imply a variation of the vibration frequency $\omega_0 = \sqrt{K/M}$ with site occupation.

(iv) Anharmonic effects:[27,28] the potential energy is modified to

$$\frac{1}{2}Kq^2 \rightarrow \frac{1}{2}Kq^2 + \beta q^4 \tag{28}$$

($\beta > 0$).

The overlap matrix element of the oscillator ground state wave function with $n$ and $n'$ carriers at the site is given by

$$< n|n' >= \left[\frac{2(a_n a_{n'})^{\frac{1}{2}}}{a_n + a_{n'}}\right]^{\frac{1}{2}} e^{-\frac{a_n a_{n'}}{2(a_n + a_{n'})}(q_n - q_{n'})^2} \tag{29}$$

with

$$q_n = -\frac{\alpha(n)}{K(n)}n + \frac{4\beta\alpha(n)^3}{K(n)^4}n^3 \tag{30a}$$

$$a_n = \frac{\sqrt{K(n)M(n)}}{\hbar} \tag{30b}$$

If any of the above-listed situations occurs,

$$< 0|1 > \neq < 1|2 > \tag{31}$$

and electron-hole asymmetry results. Consideration of the physical nature of each of these effects leads to the conclusion[25] that the *sign* of the symmetry breaking is always such that, in the electron representation, $< 0|1 >> < 1|2 >$, as assumed in the previous sections. Furthermore, the *magnitude* of the symmetry breaking effects needed to satisfy the condition for superconductivity Eq. (12) is estimated to be rather modest: of order 10% for cases (i) or (ii), and less than 1% for case (iv), when these effects are considered separately. (In reality, they are likely to act together.) The magnitude of polaronic band narrowing in the regime where the criterion for superconductivity is satisfied is much smaller than in the conventional electron-hole symmetric Holstein model.[22]

For the particular case (i), the usual Lang-Firsov canonical transformation[29] is easily generalized. New boson creation and annihilation operators and new fermion operators are introduced through the relations

$$\bar{a}_i = a_i + g(n_i + \frac{\alpha'}{\alpha}n_{i\uparrow}n_{i\downarrow}) \tag{32a}$$

$$\bar{c}_{i\sigma} = X_{i\sigma}c_{i\sigma} \tag{32b}$$

with

$$X_{i\sigma} = e^{g(1+\frac{\alpha'}{\alpha}n_{i,-\sigma})(a_i^\dagger - a_i)} \tag{33a}$$

$$g = (\frac{\epsilon_b}{\hbar\omega_0})^{1/2} \tag{33b}$$

$$\epsilon_b = \frac{\alpha^2}{2K} \tag{33c}$$

Here, $\bar{a}_i$ is the new phonon destruction operator, $\bar{c}_{i\sigma}$ the new fermion destruction operator and $\epsilon_b$ the polaron binding energy. The site Hamiltonian is diagonal in terms of the new operators:

$$H_i = \hbar\omega_0(\bar{a}_i^\dagger\bar{a}_i + \frac{1}{2}) + U_{eff}\bar{n}_{i\uparrow}\bar{n}_{i\downarrow} - \epsilon_b\bar{n}_i \tag{34}$$

with[30]

$$U_{eff} = U - \frac{1}{K}(\alpha^2 + 2\alpha\alpha' + \frac{\alpha'^2}{2}) \tag{35}$$

the effective on-site interaction. The inter-site hopping operator

$$H_t = -t\sum_{\substack{<ij>\\ \sigma}}(c_{i\sigma}^\dagger c_{j\sigma} + h.c.) \tag{36}$$

is rewritten in terms of the new operators as

$$H_t = -t\sum_{\substack{<ij>\\ \sigma}}(\bar{X}_{i\sigma}^\dagger\bar{X}_{j\sigma}\bar{c}_{i\sigma}^\dagger\bar{c}_{j\sigma} + h.c.) \tag{37a}$$

$$\bar{X}_{i\sigma} = e^{g(1+\frac{\alpha'}{\alpha}\bar{n}_{i,-\sigma})(\bar{a}_i - \bar{a}_i^\dagger)} \tag{37b}$$

and the Hamiltonian

$$H = \sum_i H_i + H_t \tag{38}$$

describes the full dynamics of the problem in terms of the new "polaron operators" $\bar{c}_{i\sigma}$ and the new phonon operators that refer to vibrations around the equilibrium position for given electronic occupation of the site

$$\bar{q}_i = q_i + \frac{1}{K}(\alpha n_i + \alpha' n_{i\uparrow}n_{i\downarrow}). \tag{39}$$

The situation here is somewhat more complicated than in the usual case because the "dressing operators" Eq. (37b) depend on fermion in addition to boson operators. The coherent hopping amplitude resulting from the zero-phonon processes is obtained by taking the expectation value of Eq. (37b) in the zero-phonon states, yielding the matrix elements Eq. (29) which for this case are

$$< \bar{X}_{i\sigma} >_0 (\bar{n}_{i,-\sigma} = 0) = < 0|1 > = e^{-\frac{\alpha^2}{4K\hbar\omega_0}} \tag{40a}$$

$$< \bar{X}_{i\sigma} >_0 (\bar{n}_{i,-\sigma} = 1) = < 1|2 > = e^{-\frac{(\alpha+\alpha')^2}{4K\hbar\omega_0}} \tag{40b}$$

In the zero-phonon subspace the Hamiltonian Eq. (38) takes the form Eq. (11), without the $V$ term. Nearest neighbor interaction will arise from direct Coulomb interaction as well as from virtual hopping processes.[31]

### B. Electronic tight binding models

In the derivation of a tight binding model from first principles, a variation of the hopping amplitude with site occupation arises from the following two effects:

(i) An off-diagonal matrix element of the Couloub interaction between Wannier orbitals at nearest neighbor sites.[32,33]

(ii) The "orbital expansion" that occurs when a second electron is adeed to an orbital that already has an electron, arising due to the strong on-site Coulomb repulsion.[34,10,35] In other words, higher energy atomic orbitals become partially occupied. Because of this the

hopping amplitudes to or from such a doubly occupied site will be different from that of a singly occupied site.

The second effect in particular is a polaronic effect: when an electron leaves a doubly occupied site the second electron relaxes to a new orbital configuration, and an overlap matrix element modulates the hopping amplitude of the first electron. A simple way to describe this physics is using a tight binding model with two orbitals per site.[36]

First principles calculations bear out these qualitative considerations and yield estimates of the variation of hopping amplitude with occupation.[35,36] It is found that whenever the hopping amplitudes show substantial variation with site occupation, it is the hole hopping amplitude that is smaller.

### C. Spin-fermion Hamiltonian

A Hamiltonian describing the interaction of electrons with local spin 1/2 degrees of freedom:

$$H_i = (Vn_i - \omega_0)\sigma_z + \Delta\sigma_x^i + Un_{i\uparrow}n_{i\downarrow} \qquad (41)$$

has been used in a variety of contexts: to describe excitonic superconductivity,[37] to describe coupling to anharmonic apex oxygen motion in high $T_c$ oxides,[27] and to describe conduction of holes through anions[10] to list just a few. This Hamiltonian gives rise to small polarons similarly as the Holstein model, and except for the special case $V = \omega_0$, is electron-hole asymmetric. For the cases where this Hamiltonian has been used, there is no physical reason that would determine that $V = \omega_0$.

To illustrate the enlargement of the region in parameter space where superconductivity can occur in the presence of electron-hole asymmetry we plot in Fig. 5 for the Holstein model the effective mass enhancement

$$\frac{m^*}{m} = \frac{1}{< 1|2 >^2} = e^{-\frac{\alpha^2}{2K\hbar\omega_0}} \qquad (42)$$

versus effective interaction

$$U_{eff} = U - \frac{\alpha^2}{K} \qquad (43)$$

for various values of the oscillator frequency $\omega_0$. For the electron-hole symmetric case the condition for superconductivity is $U_{eff} < 0$; as the frequency decreases the effective mass enhancement that exists when the condition for superconductivity is met (intersection of straight lines with left vertical axis) becomes very large. For the electron-hole asymmetric case instead the condition for superconductivity Eq. (12) becomes (for $V = 0$)

$$\frac{m^*}{m} = \frac{1}{< 0|1 >^2 - \frac{U}{2zt}\frac{U_{eff}}{U}} \qquad (44)$$

The dashed lines show the condition Eq. (44) for various values of the overlap $< 0|1 >$ between the ground states of the oscillator with one and two holes, assuming for definiteness $U/2zt = 1$. Above a given dashed line superconductivity can occur for that value of $< 0|1 >$. It can be seen that as $< 0|1 >$ increases the region in parameter space where superconductivity occurs is greatly enlarged, and in particular the mass enhancement required for given $\hbar\omega_0/U$ is much smaller than in the electron-hole symmetric case. The optimal situation occurs for $< 0|1 >= 1$, where adding a second hole does not change the equilibrium position of the oscillator with respect to that when it had one hole. For example, for that particular case if the oscillator frequency is $\hbar\omega_0/U = 0.05$ superconductivity occurs for $m^*/m \sim 6$ while in the electron-hole symmetric case it occurs only for $m^*/m \sim 22,000$.

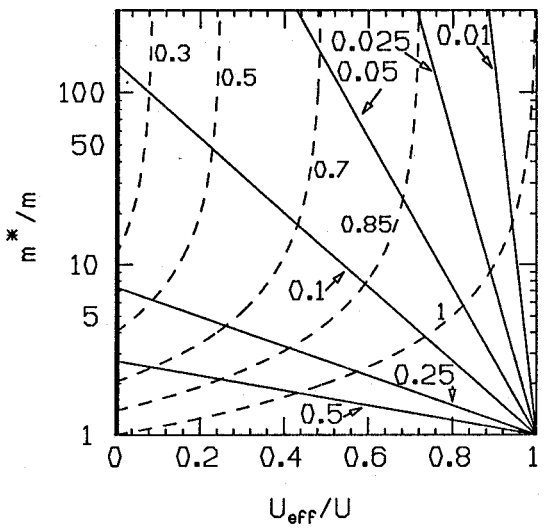


FIG. 5. Parameter range where superconductivity can occur in Holstein model. The straight solid lines give the values of the effective mass enhancement as function of the effective on-site repulsion (Eq. (43)) for various values of the oscillator frequency divided by the on-site repulsion: $\hbar\omega_0/U = 05$, 0.25, 0.1, 0.05, 0.025 and 0.01 (numbers next to the solid lines). In the electron-hole symmetric case the superconducting boundary is $U_{eff}/U = 0$ (thick vertical line); superconductivity occurs to the left of that line. The dashed lines give the criteria for superconductivity in the asymmetric case, for various values of the overlap $< 0|1 >$ (numbers next to dashed lines); superconductivity occurs in the region above a given dashed line for that value of $< 0|1 >$.

In summary, a variety of models of small polarons are naturally extended to describe electron-hole asymmetric polarons. These and other models can be used to describe polaronic effects arising from various physical processes such as electron-phonon, electron-electron or electron-spin interactions (even the Holstein model can be used to describe electronic effects if the excitation energy $\omega_0$ is an electronic energy scale). Superconductivity is much easier to achieve if electron-hole asymmetry is present. The essential point is that the electron-hole symmetric special cases of these models that are commonly studied

represent approximations that are questionable in light of the fact that electron-hole symmetry breaking terms do occur in nature and significantly modify the physics of these models.

## VI. COUPLING OF LOW AND HIGH ENERGY PHYSICS

The conductivity sum rule for a system governed by the tight binding Hamiltonian Eq. (11) yields[38]

$$\int_0^{\omega_m} \sigma_1^{\delta\delta}(\omega) = \frac{\pi e^2 a^2}{2\hbar^2} < -T_\delta > \tag{45}$$

Here, $\delta$ denotes a principal direction in the crystal lattice (assumed hypercubic). $a_\delta$ is the lattice spacing, and $\omega_m$ is a high frequency cutoff. $T_\delta$ is the kinetic energy in direction $\delta$:

$$T_\delta = -\sum_{i,\sigma} t^\sigma_{i,i+\delta}(c^\dagger_{i+\delta,\sigma} c_{i\sigma} + h.c.) \tag{46}$$

with the hopping amplitude given by Eq. (10). The expectation value of $T_\delta$ is

$$\begin{aligned} < T_\delta > &= -t(n)\sum_{i\sigma} < c^\dagger_{i+\delta,\sigma} c_{i\sigma} + h.c. > \\ &- 2\Delta t \sum_{i\sigma} \left[ < c^\dagger_{i\sigma} c^\dagger_{i,-\sigma} >< c_{i,-\sigma} c_{i+\delta,\sigma} > + h.c. \right] \\ &\equiv < T^t_\delta > + < T^{\Delta t}_\delta > \end{aligned} \tag{47}$$

As the system becomes superconducting, the anomalous expectation values in the second term of Eq. (47) become non-zero and the kinetic energy decreases (the first term in Eq. (47) is essentially unchanged when $T$ is lowered below $T_c$). Thus, the integrated optical absorption Eq. (45) increases. Quantitative examples are given in Ref. 39. This extra spectral weight goes into the $\delta$-function response at zero frequency that determines the London penetration depth, together with the spectral weight coming from the decrease in optical absorption at frequencies below the superconducting gap.[40]

Where is this extra spectral weight coming from? It does not come from any energy scale associated with the Hamiltonian Eq. (11). However we should remember that Eq. (11) is a low-energy effective Hamiltonian that only accounts for the diagonal transitions in the background degrees of freedom. The conductivity sum rule reminds us that there is also the possibility of high energy non-diagonal transitions in the background states, and a decrease in the weight of those transitions should account for the extra spectral weight that appears at low energies. The situation is schematically shown in Fig. 6. The extra spectral weight is given by

$$\delta A_h = \frac{\pi e^2 a^2_\delta}{2\hbar^2} < -T^{\Delta t}_\delta > \tag{48}$$

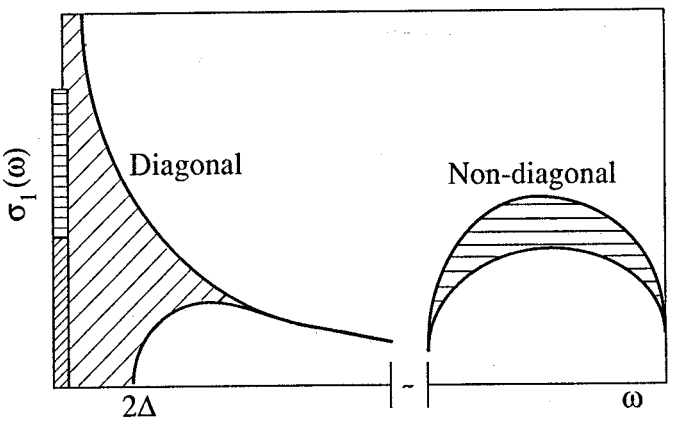


FIG. 6. Schematic depiction of spectral weight redistribution in the frequency-dependent conductivity as the system goes superconducting. Both the "missing areas" arising from intra-band (diagonal) transitions (diagonally hatched) and from non-diagonal transitions (horizontally hatched) contribute to the $\delta$-function at zero frequency that determines the London penetration depth.

The frequency-dependent conductivity can be written in a spectral representation (at zero temperature) as

$$\sigma_1^{\delta\delta}(\omega) = \pi \sum_M \frac{|< 0|J_\delta|M >|^2}{E_M - E_0} \delta(\omega - \frac{E_M - E_0}{\hbar}) \tag{49}$$

where $E_M$ is the energy of the m-th excited state and $J_\delta$ is the current operator in the tight binding model. We denote by $|n_i^m >$ the m-th excited state of the background degree of freedom at site $i$ when there are $n_i$ electrons at the site. For an optical transition where an electron hops from site $i$ to site $j$ the matrix elements involving the background degrees of freedom are

$$R_{ij}^{mm'} =< n_i|n_i'^m >< n_j|n_j'^{m'} > \tag{50}$$

where $n_i$ and $n_i'$ are site occupation numbers before and after the transition, and we assume that initially the background degrees of freedom are in their ground state ($|n_i >= |n_i^0 >$). The optical absorption will be proportional to the square of these matrix elements. The "diagonal" transition that contributes to the intra-band spectral weight is $R_{ij}^{00}$. By completeness we have

$$\sum_{mm'} |R_{ij}^{mm'}|^2 = 1 \tag{51}$$

Now for a single hole hopping between two sites

$$R_{ij}^{mm'}(0) =< 1|2^m >< 2|1^{m'} > \tag{52}$$

while for a hole hopping when there is another hole present at one of the two sites

$$R_{ij}^{mm'}(1) =< 1|2^m >< 1|0^{m'} > \tag{53}$$

By our assumption Eq. (5) we have then

$$R_{ij}^{00}(0) < R_{ij}^{00}(1) \tag{54}$$

so that by completeness

$$\sum_{(m,m')\neq(0,0)} |R_{ij}^{mm'}(0)|^2 > \sum_{(m,m')\neq(0,0)} |R_{ij}^{mm'}(1)|^2 \tag{55}$$

Eq. (55) implies that the contribution from the hopping of one hole to the high frequency optical absorption (non-diagonal transitions) is larger when it is isolated than when it is in the presence of another hole, while the converse occurs for the low-frequency intraband absorption (diagonal transition) (Eq. (54)). The physics involved is simply the Franck-Condon principle that explains the distribution in intensity in absorption bands in molecules,[41] and is schematically depicted in Fig. 7. Thus as holes pair or as the hole concentration increases through doping a transfer of spectral weight from high frequencies to low frequencies occurs.

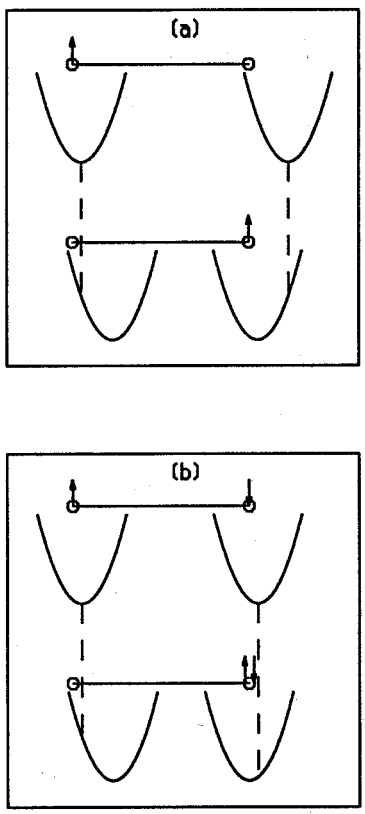


FIG. 7. Initial and final states for a hole undergoing an optical transition to a neighboring site in the absence (a) and in the presence (b) of another hole. The relative position of the potential curves for the background degrees of freedom are shown. Vertical transitions in the background degree of freedom, that carry large spectral weight, are shown as dashed lines; note that they occur at a lower total energy for the case of paired holes than for isolated holes.

In particular for the generalized Holstein models the matrix elements are given by

$$< n|n'^m > \equiv G_{0m}(g_{nn'}) = \frac{(2g_{nn'})^{m/2}e^{-g_{nn'}}}{(m!)^{1/2}} \tag{56a}$$

$$g_{nn'} = ln\frac{1}{< n|n' >} \tag{56b}$$

For a transition where the final states at sites $i$ and $j$ are $m$ and $m'$ we can sum over all possible contributions with $m+m'=M$ so that the total energy of the background final states is $\hbar\omega_0 M$:

$$\sum_{m+m'=M} |R_{ij}^{mm'}|^2 = \sum_{m+m'=M} G_{0m}^2(g_{n_i n_i'})G_{0m'}^2(g_{n_j n_j'}) = G_{0M}^2(g_{n_i n_i'} + g_{n_j n_j'}) \tag{57}$$

Thus for a single hole hopping between sites $i$ and $j$ the contribution to the optical absorption at frequency $\hbar\omega_0 M$ is $G_{0M}^2(2g_{12})$, when another hole is present it is $G_{0M}^2(g_{01}+g_{12})$ and when two other holes are present it is $G_{0M}^2(2g_{01})$. Figure 8 shows these probabilities for one case. The effect of both doping and pairing is to decrease the number of transitions where a single hole is present at the two sites involved relative to transitions where two holes are present. Thus the total spectral weight gets increasing contribution from Fig. (8b) relative to Fig. (8a). To calculate the relative contributions of the variouos hole configurations in the superconducting state the probability of two holes being at the same or nearest neighbor sites can be obtained from the superconducting pair wave function.[19]

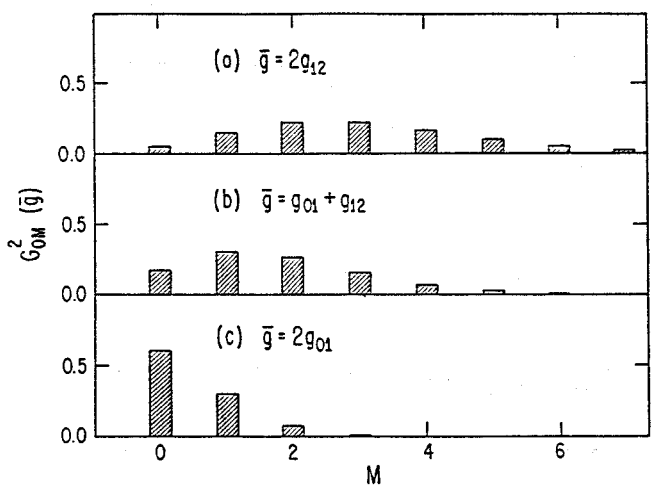


FIG. 8. Matrix elements for transition probabilities in generalized Holstein model, $G_{0M}^2(\bar{g})$, versus $M$. $\hbar\omega_0 M$ is the energy of the final state, with $\omega_0$ the oscillator frequency. Cases (a), (b) and (c) correspond to an isolated hole, and a hole in the presence of one and two other holes respectively. Note the shift in spectral weight towards lower frequencies as the hole concentration increases, and in particular the increase in the ground-state to ground-state (diagonal) transition probability at $M=0$. $g_{nn'}$ is given by Eq. (56b), and for this example $< 0|1 >= 0.88$, $< 1|2 >= 0.47$.

Note also that in addition to the $M=0$ peak (intraband contribution) other low-frequency peaks also grow

in going from (a) to (b) to (c). This may relate to the growth of the mid-infrared feature in high $T_c$ oxides seen under doping.[12,13] While the simple Holstein model should not be expected to reproduce the details of the optical spectra observed in high $T_c$ oxides we believe that it may capture the qualitative features, with the excitation energy $\omega_0$ being of electronic origin and of magnitude a fraction of an $eV$.

We have also performed explicit calculations of the various contributions to the optical absorption in the spin-fermion model Eq. (41).[42] While the shift in the relative weight of the various contributions upon pairing is clearly illustrated by these results it was not possible to establish quantitatively the equivalence of the extra spectral weight at low frequencies as given by Eq. (48) and the part of the optical absorption arising from non-diagonal transitions in Eq. (49). The reason is that that model, and tight binding models in general (including the Holstein model), do not conserve total oscillator strength.

## VII. DISCUSSION

Within the renormalization group theory of critical phenomena[43] a perturbation is "relevant" if it changes qualitatively the physics of the system, even if the magnitude of the perturbation is small. We have tried to argue here that electron-hole symmetry breaking perturbations are "relevant", in that sense, for the physics of polaronic systems. Because there is no underlying symmetry reason that would exclude such perturbations in real systems it is necessary to consider them, in particular with respect to the physics of superconductivity.

Superconductivity arises in electron-hole asymmetric polaronic systems due to the lowering of kinetic energy that occurs when carriers pair. The resulting superconductor exhibits a number of characteristic features associated with its low energy physics: isotropic $s$-wave state, strong dependence of the critical temperature on carrier concentration, energy-dependent BCS gap function, branch imbalance, positive pressure dependence of $T_c$, sensitivity to non-magnetic disorder, tunneling asymmetry, crossover from strong to weak coupling as the carrier concentration increases, etc. The transition from the superconducting to the normal state occurs through pair unbinding rather than Bose decondensation even in the regime where the coherence length is short. Many of these characteristic features have been seen in high $T_c$ oxide superconductors.

The most characteristic feature of these systems however is the remarkable coupling between low and high energy physics. When the superconducting gap opens up, a low energy phenomenon, changes in the optical absorption are predicted to occur at high frequencies, unrelated to the energy scale of the superconducting gap. This signature of the underlying physics has been seen experimentally.[44,45] The detailed temperature and carrier concentration dependence of the effect predicted[39] however has not yet been experimentally tested. Furthermore the related experimental prediction[20] that the observed London penetration depth should be shorter than expected from the normal state effective mass and from the low-frequency missing area in the conductivity remains open to experimental verification.

The model does not yield a precise first-principles prediction of the high frequency range where changes in the conductivity should occur, because the microscopic physics of the underlying polaronic processes have not yet been entirely clarified. However the phenomenology predicted by the model is unambiguous: the frequency range where changes in the optical conductivity should occur when the system goes superconducting is the same range where changes in the normal state conductivity upon doping should occur. Experiments then indicate that the main range in high $T_c$ oxides where a decrease in absorption should be seen upon pairing is in the visible (1 to 3 eV). Additionally, shift of spectral weight to lower frequencies should also be seen from the mid- and near infrared region. For a given frequency in that range however this could result in either an increase or decrease in intensity depending on the doping level.

Experiments in high $T_c$ oxides also show a variation of optical absorption at high frequencies with temperature in the normal state.[44,45] Within the class of models considered here we have found that a variation of the number of carriers with temperature in the normal state is likely to occur in the high $T_c$ oxide structures,[46] which may account for this as well as other anomalous normal state properties. Other observations in high $T_c$ oxides such as variations in the gap magnitude may be accounted for by generalizing the models discussed here to describe more than one band[47] and by existence of disorder.[48]

In summary, superconductivity in electron-hole asymmetric polaron systems is driven by the "undressing" of the heavily dressed polaronic carriers that occurs upon pairing. It parallels the same phenomenon occuring in the normal state as the carrier concentration is increased. Dilute carriers become increasingly "free" as the local carrier concentration increases, and are happy to pay the price of extra Coulomb repulsion that arises when they pair in order to achieve this "freer" state. However, if they are sufficiently "free" in the unpaired state (normal state at higher carrier concentration) the incentive to develop pairing correlations disappears. The same basic physics would apply to any Fermi liquid system where the quasiparticle dressing is a strong function of the local carrier concentration, even if the carriers are not strictly speaking "polaronic" in the conventional sense. If this is indeed the essential physics underlying the phenomenon of superconductivity in high $T_c$ oxides the possibility that it plays an essential role in other superconductors as well should not be excluded.

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