Polaron Formation in the Three-Band Peierls-Hubbard Model for Cuprate Superconductors

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Exact diagonalization calculations show a continuous transition from delocalized to small polaron behavior as a function of intersite electron-lattice coupling. A transition, found previously at Hartree-Fock level [Yonemitsu et al., Phys. Rev. Lett. 69, 965 (1992)], between a magnetic and a non magnetic state does not subsist when fluctuations are included. Local phonon modes become softer close to the polaron and by comparison with optical measurements of doped cuprates we conclude that they are close to the transition region between polaronic and non-polaronic behavior. The barrier to adiabatically move a hole vanishes in that region suggesting large mobilities.

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The discovery of high Tc superconductors [1] has triggered a renewed interest in strongly correlated systems. More recently the interplay between strongly correlated carriers and lattice effects has produced a lot of experimental and theoretical attention [2]. Recent infrared (IR) absorption experiments show that added carriers produce substantial lattice relaxation around them showing up in phonon side bands and typical shake-up bands related to Cu-O stretching modes [3–5]. Similar effects were previously found in photodoped [6,7] experiments.

The nature of doping states coupled to the lattice has been studied in inhomogeneous Hartree-Fock (HF) with random phase approximation (RPA) fluctuations calculations [8–10]. This approach predict the experimentally observed doping induced phonon side bands as a consequence of polaron formation, however the competition between the self-trapping effects and the kinetic energy of the hole is absent. The same problem arises in a recently introduced LDA+U scheme [11].

In this work we have performed exact diagonalization and HF with RPA fluctuation calculations of the three-band-Peierls-Hubbard model describing the Cu-O planes. The exact calculations confirm the formation of a local-singlet-polaron (LSP) for large electron-lattice coupling strength (λ), analogous to the lattice polaron state found in HF and LDA+U. However the mean field picture is qualitative wrong for small λ. Contrary to the HF and LDA+U approaches a minimum electron-lattice coupling strength (λc) is necessary to produce the polaron in accordance with the situation in uncorrelated systems [12]. Furthermore by extending the previous HF results [8] and comparing with exact diagonalization we show that a previously found transition between a magnetic and a non magnetic state on Cu is a feature of the approximations involved and have no counterpart with the exact results. We show also that as the polaron is formed...
in hole doped materials local softening of the phonon modes occur. This explains the doping induced phonon side bands and by direct comparison with experiments we can estimate how far from $\lambda_c$ a real material is. Our result suggest that doped cuprates are close to the crossover region where polaron formation occurs. We find that in that region the barrier for adiabatic motion of a hole vanishes suggesting relatively large mobilities.

We consider a three-band-Peierls-Hubbard model\cite{8-10} in which for simplicity Cu atoms are kept fix and O ions are allowed to move with displacements $u_i$ in the direction of the Cu-O bond. Holes have an on-site interaction $U_d$ on Cu and $U_p$ on O, a Cu-O repulsion $U_{pd}$, on-site energies on Cu $E_d$, and on O $E_p$, and Cu-O hopping $t$ (O-O hopping is neglected here). When an O moves in the direction of one Cu with displacement $|u_i|$ the corresponding Cu-O hopping changes by $\alpha|u_i|$. Opposite signs apply when the O moves in the opposite direction. Each Cu-O bond has a spring with force constant $K$\cite{8-10}. An electron-lattice coupling constant is defined as $\lambda = \frac{\alpha^2 K}{\hbar}$.

Parameters are $E_p - E_d = 3, U_d = 8, U_p = 3, U_{pd} = 1, t_{pd} = 1, K = 32t_{pd} \text{Å}^{-2}$\cite{8-10,13}. Details of the method are presented in a preliminary report\cite{13}.

The formation of the lattice polaron can be understood by repeating Zhang and Rice’s (ZR) construction in the case in which the O ions are allowed to relax adiabatically in a symmetric breathing mode along the Cu-O bonds with displacements $|u_i| = u$. Following ZR consider first a single CuO$_4$ cluster with two holes. The energy of the local singlet state as a function of $u$ is $E(u) = \epsilon - \beta u + 4K_p u^2$, where $\epsilon = \Delta - 8t^2\left(\frac{1}{\Delta} + \frac{1}{U_d - \Delta}\right)$ is the energy of the local singlet in absence of lattice relaxation. $\beta = 16\alpha t\left(\frac{1}{\Delta} + \frac{1}{U_d - \Delta}\right)$ is a renormalized coupling with the lattice. $K_p = K - 2\alpha^2\left(\frac{1}{\Delta} + \frac{1}{U_d - \Delta}\right)$ is a renormalized spring-force-constant. The corresponding phonon frequency of the breathing mode $\omega_p^2 = 2K_p/M$, with $M$ the O mass, is smaller than the one for the “undoped case” (only one hole) $\omega_0^2 = 2K_0/M$, with $K_0 = K - \frac{\alpha^2}{\hbar^2}$. A renormalized electron-lattice coupling strength can be defined as $\lambda_p = \frac{\beta^2}{\hbar^2}$. Large $\lambda_p$ implies strong tendency for polaron formation. The expression for $\beta$ (note the large factor in front which comes from coherence effects), shows that the strong covalency of ZR wave function favors polaron formation and competes with $\Delta$ and $U_d$.

We can find equilibrium positions for the lattice displacements $u^0 = -\frac{\beta}{4K_p}$. The resulting state is a LSP showing local softening of the lattice breathing modes. Note that in the electron doped case (no holes) a hardening is obtained. We show below that IR active modes in the hole doped case behave in a similar manner in accordance with previous RPA results\cite{8}. When the ZR singlet is allowed to hop, a competition will arise between the self-trapping and the delocalization effects.

To further substantiate these findings we have performed a Lanczos diagonalization and HF plus RPA
study of the cluster in the inset of Fig. 1. The O ion mass was taken to be infinity (adiabatic approximation), the O displacements where determined by iterating self-consistent equations for unconstrained O’s displacements. As we show below this is particularly important close to $\lambda_c$. In Fig. 1 we show the O displacements as a function of $\lambda$ in the two approaches. The higher branch corresponds to an O neighbor to Cu$_1$ (see inset), so it represents the equilibrium displacement in the site of the polaron ($u^p_0$) and the lower branch correspond to an O neighbor to Cu$_4$ ($u^n_0$). For $\lambda < \lambda_c$ both branches coincide in the exact result and there is no polaron formation whereas for $\lambda > \lambda_c$ the particle self-traps around Cu$_1$ and the displacement there grows rapidly. The non zero lattice displacement for $\lambda < \lambda_c$ indicates a tendency to charge density wave formation (CDW) in which the O’s around Cu$_1$ and Cu$_4$ slightly contract and is discussed elsewhere [13]. Contrary to the exact results the HF calculation shows $\lambda_{c,HF} = 0$. This is a consequence of the fact that in this approach the particle is already self-trapped without coupling to the lattice [8–10,15] forming a magnetic polaron state reminiscent of a local singlet [14]. The same is true in LDA+U. Hence the competition between the self-trapping effects and the translational motion of the hole is absent in these mean field approaches. Note that for large $\lambda$, when the symmetry is broken in both approaches HF and the exact result are in good agreement. This is because the displacements are determined by the one body density matrix which is optimized in HF. In contrast, as we show below, two body correlations are badly reproduced.

It was found in HF [8] that as $\lambda$ approaches a cross-over value $\lambda^*$ a transition occurs to a non-magnetic state in Cu$_1$. This cross-over is signaled by an increase in the double occupancy of Cu$_1$ towards the non-magnetic limit ($\langle n_{\uparrow Cu_1} n_{\downarrow Cu_1} \rangle_{\text{nonmag}} = n^2_{Cu_1}/4$) with $n_{Cu_1} = \langle n_{\uparrow Cu_1} + n_{\downarrow Cu_1} \rangle$ as shown in Fig. 2 by the triangles. In our case $\lambda^* \sim 0.6$. We have calculated the evolution with $\lambda$ of the exact double occupancy at this Cu. The result is shown by the open squares in Fig. 2. For $\lambda < \lambda_c$ one should be aware that HF breaks translational symmetry in a different way to that of the exact result, so it is difficult to compare both solutions in detail. For $\lambda = 0$ this can be partially solved by averaging over the four possible locations of the mean field state [10,16] (large triangle in Fig. 2). The result overestimates the double occupancy. For $\lambda > \lambda_c$ both the exact and HF results break translational invariance in the same way. It is clear in that limit that the exact double occupancy is well below the non-magnetic limit. We note also that the sudden increase at $\lambda_c$ does not reflect in the total Cu double occupancy that remains constant and it is rather an effect due to the rearrangement of the charges. To identify the source of the discrepancy we add fluctuations to the HF double occupancy by calculating the RPA correlation energy and using the Hellmann-Feynman theorem. Remarkably we
find that RPA partially restores translational invariance so that, contrary to the HF case, there is little difference for $\lambda \sim 0$ and $\lambda \sim \lambda_c$ between the double occupancy in Cu$_1$ alone and the spatially averaged value (see Fig. 2). The intermediate region is discussed below. In the polaronic region we show the result at Cu$_1$ whereas in the delocalized region the spatial average is used (small circles). We also show the result at Cu$_1$ for $\lambda = 0$ (big circle). As $\lambda^*$ is approached fluctuations become too big and the RPA breaks down. This is obvious in Fig. 2 where at $\lambda^*$ the RPA overestimate the correction and a non-physical zero value of the double occupancy is obtained. If it is calculated on Cu$_1$ alone it becomes negative. In the polaronic region the correction is overestimated but it is clear from both approaches that the Cu remains magnetic.

One should note that whereas HF shows a transition between a magnetic and a non-magnetic state in Cu$_1$ the two solutions in HF plus RPA above and below $\lambda^*$ represent the same physical situation in two different ways. Since the effect of increasing $\lambda$ is to relax the O towards the Cu we can use $\lambda$ as a measure of the local covalency in the polaron. Consider the CuO$_4$ cluster with two holes as before. In the limit in which covalency dominates ($\lambda > \lambda^*$) the HF wave function has the form $|HF\rangle = \prod_{\sigma}(\phi_p p_{\sigma}^+ + \phi_d d_{\sigma}^+)|0\rangle$ where $p_{\sigma}^+ = \frac{1}{2} \sum_{j=1}^4 p_{j\sigma}^+$ and the sum runs over the four O. $p_{j\sigma}^+$ creates a hole on O (Cu). This wave function has spin zero but large double occupancy on Cu given by $\phi_d^2$. For an occupancy on Cu of order one this correspond to $\sim 1/4$ as is the case in Fig. 2 for large $\lambda$. RPA introduces correlations and this reduces double occupancy as is clear in Fig. 2 for large $\lambda$. The net result is a singlet with small double occupancy which looks very much like the ZR wave function. On the other extreme when covalency is not so dominant [$\lambda < \lambda^*$] the HF wave function has broken symmetry and the single particle orbitals depend on spin, that is $|HF\rangle = \prod_{\sigma}(\phi_{p,\sigma} p_{\sigma}^+ + \phi_{d,\sigma} d_{\sigma}^+)|0\rangle$. This describes a magnetic state on Cu, say with up spin, and on O with opposite spin when $\phi_{d,\downarrow}^2 < \phi_{d,\uparrow}^2$ and $\phi_{p,\downarrow}^2 < \phi_{p,\uparrow}^2$. The HF wave function is not a singlet now but RPA corrects for that through terms of the form $J_{Cu-O}\frac{1}{2}(S_d^+ S_p^- + S_d^- S_p^+)$ present in the residual interaction. Here $J_{Cu-O}$ is the Cu-O exchange. RPA also reduces further the double occupancy and the net result is, as before, similar to a ZR wave function. Now is evident that the transition between these two HF solutions has no physical meaning but is a consequence of how HF plus RPA reproduce the physics in two different situations. An analogy can be made with the problem of a magnetic impurity in a metal. Anderson's classical treatment \cite{7} shows also a magnetic and a non-magnetic solution at HF level which can be associated with the magnetic and non-magnetic state of the Cu. Note the similarity between Fig. 5 in Ref. \cite{7} and Fig. 1(b) in Ref. \cite{8}. Our result shows the danger of using mean field alone as a criteria to distin-
guish between magnetic and non-magnetic states.

To study how the LSP moves through the lattice we had parametrized the lattice displacement which interpolates between the LSP in Cu$_1$ and in Cu$_4$. Note that the transition between nearest neighbors Cu is not allowed in a Néel ordered infinite lattice without producing excitations [18]. In Fig. 3 we show the total energy as a function of a collective coordinate ($\delta$). The displacement are set as $u_i = \frac{1}{2}(u_0^p + u_0^\omega) \pm \delta$ and the signs are chosen in such a way that for $\lambda > \lambda_c$ and $\delta = \frac{1}{2}(u_0^p - u_0^\omega)$ the configuration of the polaron sitting in Cu$_1$ is obtained. For $\lambda < \lambda_c$ there is a single minimum which corresponds to no polaron formation whereas for $\lambda > \lambda_c$ there are two minima which correspond to the LSP sitting in Cu$_1$ or in Cu$_4$. Note that at the transition point the barrier vanishes. Is essential for this result to consider a full relaxation of all O in the cluster. If only the O around Cu$_1$ are relaxed, the barrier never vanishes and the transition becomes first order like [13]. This is qualitatively different from a previous Holstein-Hubbard study [18]. There coupling with O c-axis displacements was considered and the transition between the polaronic and non-polaronic state was found to be always first order like.

Many experiments show local softening of IR modes upon hole doping [3,6,7] or hardening for electron doping [4]. To study this effect we had made a frozen phonon calculation by moving in phase the two O at the right and left of Cu$_1$ and computed the corresponding phonon frequency ($\omega_p$) and compared with the result in the undoped case ($\omega_0$) ( inset of Fig. 3). The local softening effect is particularly well resolved in photodoped La$_2$CuO$_4$ where the 708 cm$^{-1}$ Cu-O stretching mode gets bleached and a new band grows at 640 cm$^{-1}$. This corresponds to $\omega_0^2/\omega_p^2 \sim 1.22$) and a $\lambda \sim 10\%$ higher than $\lambda_c$ [21]. This result, and the fact that effective masses in real materials are not very large, point to a situation where the real $\lambda$ in the cuprates is close to $\lambda_c$. The physics close to that point is highly non-trivial for a finite value of the ion mass [12,22]. The transition is not any more sharp but is washed out by quantum fluctuations and $\lambda_c$ becomes a cross over value. The renormalization of the effective mass of quasiparticles is moderate and not exponentially large like in the large $\lambda$ limit. An appealing scenario is that for small doping polarons are formed with $\lambda$ close to $\lambda_c$. This will result in a small activation energy for thermal diffusion of the hole as is observed in lightly doped cuprates [1,4]. For higher doping, polaron formation is inhibited due to phase space restrictions and a more complicated object occurs sharing characteristics of the self-trapped and non-self-trapped state and hence more metallic behavior.

Very recently an infrared band at .1 eV in both hole [5] and electron hole [4] doped compounds has been identified as arising from shake-up process of a polaron phonon cloud. In the electron doped case [4] it was possible
to separate the phonon contribution which appears as higher harmonics of the Cu-O stretching modes considered here, indicating the relevance of these modes in forming the polaron. Similar structures are present in the hole doped data \[22,23\].

We believe that these effects can be generic to a wide class of materials and provide a framework for classification. For example low mobilities in compounds like \(\text{La}_{2-x}\text{Sr}_x\text{NiO}_4+\delta\) \[24,25,11\] can be understood as arising from a value of \(\lambda \gg \lambda_c\). In the former the self trapping probably inhibits the softening of the MIR band \[24\] observed in superconducting compounds \[27\] for which a physical picture was recently presented \[11,12\]. On the other hand we suggest that for \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) probably \(\lambda \sim \lambda_c\) where interesting physics can arise.

In summary, we have found a continuous transition between a LSP polaron and a delocalized state in a three-band-Peierls-Hubbard model. We showed that there is no quenching of magnetic moments as found in previous approaches and by comparison with optical measurements we suggest that cuprates are close to the transition region between polaronic and non-polaronic behavior. This leads to a rich phenomenology where lattice anharmonicities coexist with presumably high carrier mobilities.

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FIG. 1. Equilibrium positions for one oxygen ion surrounding Cu$_1$ (higer branches) and for another surrounding Cu$_4$ (lower branches) versus $\lambda$. The triangles (squares) are the HF (exact) result. The inset shows schematically the cluster studied in the presence of a polaron in Cu$_1$.

FIG. 2. Double occupancy versus $\lambda$. Full small (big) triangles are the HF result on Cu$_1$ alone (averaged over the four O), open triangles are the unpolarized limit on Cu$_1$, open squares are the exact result on Cu$_1$ and full circles the HF plus RPA result averaged on the four Cu’s ($\lambda < \lambda_c$) and on Cu$_1$ alone ($\lambda > \lambda_c$). We also show the averaged result for $\lambda = 0$ (full big circle).

FIG. 3. Total energy as a function of the collective coordinate $\delta$ for $\lambda = .7$ (diamonds), 1.05 (crosses) and 1.4 (circles). The inset shows the ratio $\omega_p^2/\omega_0^2$ versus $\lambda$. 

7