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Charge-transfer polarons and excitons

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We show that polarons and excitons of charge-transfer origin arise quite naturally in the p-d model of high-temperature superconductors. We consider the limit in which on-site Coulomb repulsion on both Cu and O is taken to be infinite and treat the Cu-O repulsion U_{pd} in the Hartree-Fock approximation. We find that the uniform Hartree-Fock solution is unstable (the compressibility is negative) for small enough doping. Using an unrestricted Hartree-Fock scheme we find in one dimension (1D) that one particle added to the half-filled case forms a self-trapped polaron state of charge-transfer origin. We also find that there is no phase separation. Within the same formalism we subsequently study exciton states. In 2D we obtain similar compressibility results, suggesting that the ground state is also polaronic. Our results are also relevant for one-dimensional charge-transfer systems.

The high-temperature superconductors (HTSC) are insulating compounds that become metallic upon doping. The charge excitation gap in the stoichiometric compounds is believed to be mainly of charge-transfer origin.[1] Charge-transfer systems are also found in one-dimensional conductors.[2] In this work we show that the nearest-neighbor Coulomb repulsion treated in a site dependent Hartree-Fock approximation (Bogoliubov–de Gennes formalism) can give rise to polaron and exciton states of charge-transfer origin. The importance of charge-transfer excitations in HTSC has been stressed by both theorists[3–5] and experimentalists.[6–11] Structure related to charge-transfer excitations in the Cu-O planes has been identified in optical measurements.[9–11] Polaronic or self-trapping effects, due to the lattice or some more exotic origin, have been invoked[12–15] to explain experimental results like optical spectroscopy,[16,17] photoinduced optical absorption,[18–21] and transport,[22] among others (for a complete review see Refs. 23 and 24).

A prototype Hamiltonian to describe strongly correlated charge-transfer systems is the p-d model. Motivated by the HTSC applications, we will call the atoms Cu and O, but we expect the same physics to be found in other one-dimensional strongly correlated systems. The Hamiltonian reads as

$$H=\sum_{i,\sigma}\left(E_{i\sigma}C^{\dagger}_{i\sigma}C_{i\sigma}+\tfrac{1}{2}\sum_{j,\sigma'}U_{ij\sigma\sigma'}n_{i\sigma}n_{j\sigma'}\right)+\sum_{j\neq i,\sigma}E_{ij}C^{\dagger}_{i\sigma}C_{j\sigma}, \tag{1}$$

where $C^{\dagger}_{i\sigma}$ creates a hole on site i with spin σ. $E_{i\sigma}=E_d$ (E_p) and $U_{ii\sigma\bar{\sigma}}=U_d$ (U_p) for a Cu (O) site. Nearest-neighbor matrix elements are $E_{ij}=t$ and $U_{ij\sigma\sigma'}=U_{pd}$, and the direct O-O hopping is $E_{ij}=-t'$. We define $\Delta=(E_p-E_d)/2$.

For the sake of simplicity most of our results are given in one dimension (1D), but we expect similar physics in 2D. We work in such units that $t=1$. In 1D and in the limit $U_p, U_d \longrightarrow \infty$, charge and spin degrees of freedom decouple and the former are described by a spinless-fermion Hamiltonian,[25]

$$H=\sum_i[(-1)^i\Delta C^{\dagger}_i C_i+t(C^{\dagger}_i C_{i+1}+\text{H.c.})+U_{pd}n_i n_{i+1}]. \tag{2}$$

The spin degrees of freedom are described by the Heisenberg model. By doing this we gain simplicity in the charge degrees of freedom. We know that U_d is very big. Naively one may expect the results to be insensitive to the value of U_p because double occupancy on O is rare. However, as we will see later this is not the case.

In Fig. 1 we show the chemical potential as a function of doping in the uniform Hartree-Fock approximation for different values of U_{pd}/t. We see that the compressibility is negative for small enough doping. This means that the uniform Hartree-Fock ground state is unstable. There are various candidates as alternative ground states, such as phase separation, superconductivity, or, as we will see, a polaronic phase. Since we are in the unstable phase, no precise statement can be made. The instability can be traced back to the behavior of the renormalized Hartree-Fock diagonal energies. Let us give a heuristic argument in the strong-coupling limit. The effective levels for a chain of Cu and O at half filling are schematically shown in Fig. 2(a). In a Hartree approximation the diagonal energies of the orbitals renormalize as $\tilde{E}_d=E_d+2n_{\text{O}}U_{pd}$, $\tilde{E}_p=E_p+2n_{\text{Cu}}U_{pd}$. At half filling and for small t, $n_{\text{Cu}}\sim 1$ and $n_{\text{O}}\sim 0$; then $\tilde{E}_d\sim E_d$, and $\tilde{E}_p\sim E_p+2U_{pd}$. When we add holes they go mainly to O sites, raising the Cu energy level. This will increase the mixing of Cu and

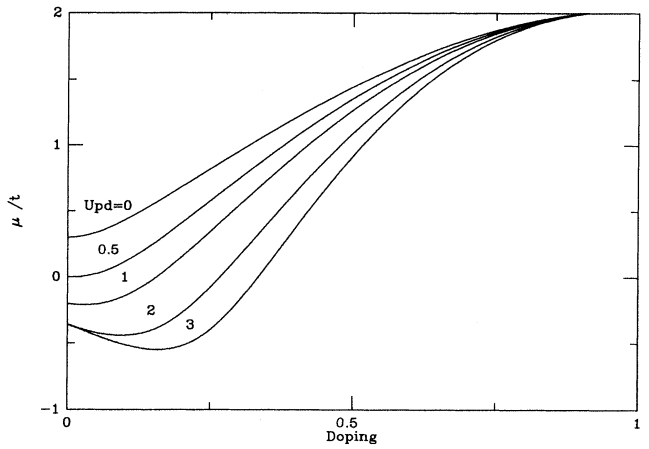

FIG. 1. Chemical potential as a function of doping in 1D for $\Delta = 0.3$. We have subtracted the corresponding value of $2U_{pd}$ to each curve in order to make them all fall within the same scale.

O and will imply a transfer of charge from Cu to O. The net effect will be that n_{Cu} diminishes and the O level renormalizes to lower energies. So we are putting charge in a level whose energy is decreasing. This means that the chemical potential is decreasing with the doping and that the compressibility is negative.

Let us now suppose that instead of putting the charge in a Bloch state we localize it on an O site [Fig. 2(b)]. The energies of the neighboring Cu atoms will strongly renormalize and then will transfer the Cu charge to the O. The net effect will be that the O level will locally renormalize to lower energies. This will create a potential in which the hole can be self-trapped.

The effect can be studied in a wide region of the parameter space by making an unrestricted Hartree-Fock approximation. We decouple the many-body term in Eq. (2) as

$$n_i n_{i+1} \tilde{=} n_i\langle n_{i+1}\rangle + \langle n_i\rangle n_{i+1} - \langle n_i\rangle\langle n_{i+1}\rangle + (C_i^{\dagger} C_{i+1}\gamma_i + \mathrm{H.c.}) - |\gamma_i|^2,$$
$$\gamma_i = \langle C_i C_{i+1}^{\dagger}\rangle. \tag{3}$$

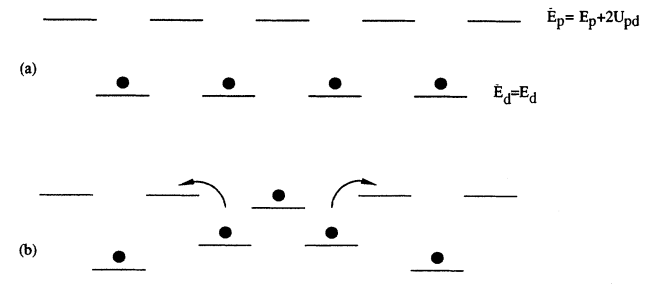

FIG. 2. Schematic plot of the renormalized energy levels in real space. A dot represents an occupied site. (a) Ground state at half filling and (b) one particle added. Arrows indicate increased charge transfer.

In Fig. 3 we show an example of one hole added to the stoichiometric case. Roughly speaking we can think of the particles of the O band as moving in a potential generated by the charge distribution on the Cu site and vice versa. So in Fig. 3 the plot of the charge distribution represents, in a different scale, the distribution of site energies in which the particles move. The depletion in the Cu charge pulls down a state from the O band, and the bump in the O charge pulls up states from the Cu band. The polaron wave function carries some characteristics of the bottom Bloch state of the O band. The amplitude is bigger on O sites and it changes sign from one O site to the next. Note that the polaron forms an "impurity-like" state. In this picture polarons will form a dispersive band that will grow with doping. This is fully consistent with many different experiments such as optical measurements,[16,26] photoinduced absorption,[18–21] photoemission spectroscopy,[27,28] and x-ray absorption.[28] Narrow, "heavy-electron-like" bands have recently been measured[29] by angle-resolved photoemission spectroscopy. Note also that the appearance of impurity-like states from the O band implies a strong reduction of the optical gap as seen in optical transmittance experiments.[26] In all these cases we found that the self-trapped solution has lower energy than the uniform one.

Our problem presents a clear analogy with one-dimensional problems studied in the past.[30] In this context a related problem has been studied by Hubbard.[2] He showed that for the case $\Delta = 0$ and $t \ll U_{pd}$ (strong coupling) one hole added to the system dissociates into a soliton (kinklike) pair, each one with charge $e/2$. When $\Delta \neq 0$, the free soliton pair is not stable because the charge between the two solitons is "in the wrong place." For our case we can think of the polaron as a bound state

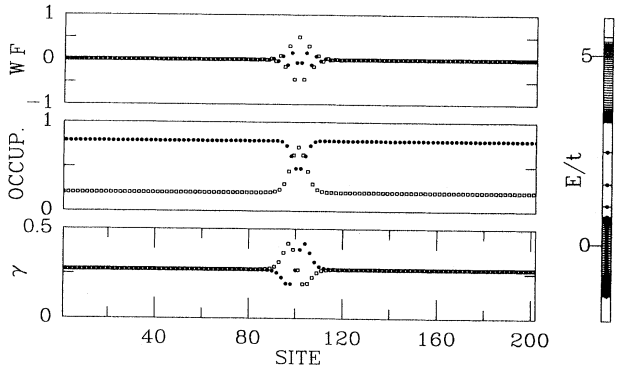

FIG. 3. One particle added to the half-filling case for $\Delta = 0.1$ and $U_{pd} = 2$. We show the one-particle wave function (WF) of the polaron state, the site occupation, and the γ as a function of the site. Solid circles correspond to Cu and squares correspond to O except for γ in which they differentiate even and odd bonds. The plot on the right-hand side is the single-particle energy level; note the states in the gap. A dot represents an occupied level.

of the soliton pair.

Furthermore, we found that in the continuous limit the unrestricted Hartree-Fock equations can be mapped into a problem similar to the polyacetylene one. The difference is that there is no spin degeneracy in our case.

Now we can consider the problem of phase separation. If there is phase separation one expects that, for more than one particle added, the system will nucleate a hole-rich phase. Due to the short-range character of the interactions considered here it is enough to consider a two-polaron case (we do not expect that the long-range part of the Coulomb interaction will modify this result). We generated a configuration with two particles overlapping and iterate up to convergence. We found that the energy decreases monotonically and the system converges to a situation in which the polarons are far apart (Fig. 4), so within our formalism there is no phase separation.

We can also study excitonic states. In an excitonic state we take the stoichiometric case and move one particle from the top of the lower band to the bottom of the upper band. In Fig. 5 we show an example.

We note that the charge excitation gap is smaller than the uniform Hartree-Fock gap.[31] The exciton is more localized than the polaron because the self-trapping potential is deeper. This can be understood by comparing the distribution of charge in the Cu for the two cases. For the polaron case the self-trapped potential is generated by a relatively small lack of charge on the Cu that has been transferred to the O (see Fig. 3) while for the exciton there is one particle missing that generates the self-trapped potential. For the same reason the exciton spectrum is symmetric.

The polarons and excitons considered here are not due to the atomic displacements, so we did not include these degrees of freedom. Even so one expects that subsequent to the formation of the self-trapped state the lattice will relax around it as is seen in the experiments.[19,20]

For 2D the problem is more difficult because there is no exact mapping to the spinless model. Nevertheless we expect a spinless Hamiltonian to be a good approximation for the charge degrees of freedom, and such an approximation has been used in the past.[5] In Fig. 6 we show the chemical potential in the two-dimensional case in the uniform Hartree-Fock approximation. Since the same instability appears we also expect important polaron effects to be present. It is clear that the strong-coupling argument leading to the formation of a potential well in Fig. 2(b) is independent of the dimensionality providing that there is self-trapping. On the other hand, self-trapping itself depends critically on the dimensionality,[32] so it is not clear in which parameter range polaron formation will occur in 2D. This problem is addressed in a paper planned for future publication.[33]

Within a different formalism Grilli *et al.*[34] found the same instability in the compressibility in 2D, but they

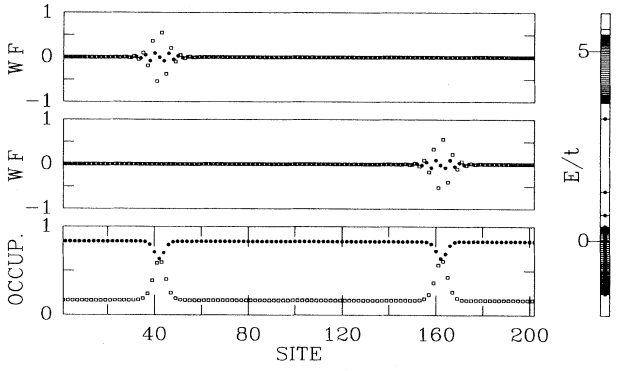

FIG. 4. Two particles added to the half-filling case for $\Delta = 0.3$ and $U_{pd} = 2$. We show the one-particle wave function (WF) of the two-polaron state and the site occupation. Solid circles correspond to Cu and squares correspond to O. The plot on the right-hand side is the single-particle energy level. A dot represents an occupied level.

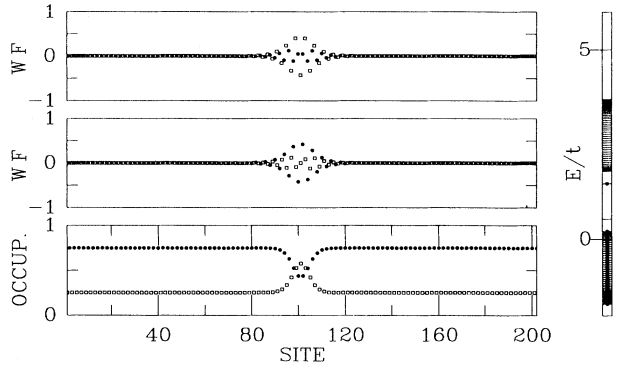

FIG. 5. Exciton state for $\Delta = 0.3$ and $U_{pd} = 1$. We show the one-particle wave function (WF) of the two localized states and the site occupation. Solid circles correspond to Cu and squares correspond to O. The plot on the right-hand side is the single-particle energy level. A dot represents an occupied level.

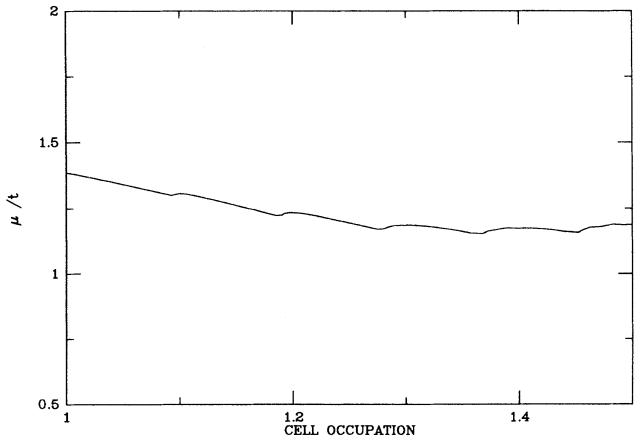

FIG. 6. Chemical potential as a function of cell occupation for 2D, $\Delta = 0.25$, $t' = 0.2$, and $U_{pd} = 1$. The ripple is due to the discreteness of the mesh.

interpreted it as phase separation. The difference is that they set the repulsion on the O atom equal to zero, while we set it equal to infinity. Because the polaron states are mainly due to O character, we expect the result of Fig. 4 to be different in their case, so, in principle, our results are not contradictory to each other, but further investigations must be done in order to clarify this point.

The p-d model has been studied in 2D and 3D in the limit $t \ll \Delta$ by perturbation theory to describe the hopping in connection with hole-doped CuO- and BiO-based HTSC,[35] and electron-doped CuO layers.[36] It has been shown that one particle added to the half-filling case produces charge-transfer excitations around it in a manner that resembles our results. When two particles are put close to each other, low-energy charge fluctuations are allowed that lower the energy and produce pairing. The same mechanism does not work in 1D, but we expect that within a suitable mean-field approach, bipolaron states, relevant for the superconductivity, can be found in 2D.[33]

In conclusion, we have shown that polaron and excitons of charge-transfer origin arise quite naturally in the *p-d* model for HTSC and give a qualitative explanation for various experiments. We expect that these nonlinear excitations play an important role in the physics of HTSC.

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