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FOR ADVANCED STUDIES

Polarons and Excitons in Charge-Transfer Systems

Thesis submitted for the degree of

"Magister Philosophiæ"

Condensed Matter Sector

CANDIDATE:

José Lorenzana

SUPERVISOR:

Prof. Yu Lu

Academic Year 1989/90

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Nadie acierta antes de errar,
y aunque la fama se juega,
el que por gusto navega
no ha de temerle a la mar.

J. Hernandez

Cosa e' un polarone?,
un orso polare grosso?

An outsider's question.

Acknowledgements

To put the Acknowledgements at the end of the thesis is to relegate the ones to be honoured into oblivion. If someone arrives at this page, he really deserves to be in the list. Let's then recall here the ones that helped me in this work.

I would like to express my cordial thanks to Prof. Erio Tosatti who provided me with the critical view which every scientific work needs. I appreciated fruitful discussions with Profs. Alberto Parola and Allan Bishop. I am very grateful to Prof. Yu Lu. He encouraged me and gave me support, with his enthusiasm for these ideas. His guide and critical reading of the manuscript was very valuable. Many ideas for this work originated from my work with Profs. B. Alascio, C. A. Balseiro and the group of Bariloche. I wish to express my gratitude to them for their encouragement and valuable discussions in the early stages of this work.

1 Introduction

In 1987 Bednorz and Müller[1] received the Nobel Prize for the remarkable discovery of ceramic materials superconducting at unexpected high temperatures for the time being. The general belief was that the following year's Nobel prize was going to be assigned to the theorist or theorists who could explain such phenomena. This proved to be too optimistic, for still there is no theory of the high-temperature superconductors (HTSC) allowing to rationalize the enormous amount of accumulated experimental data and, at the same time, having some predictive power. Many ideas[2] have been proposed. One of the strongest test for these ideas was the appearance of compounds that do not satisfy the initial assumptions. In this way the discovery of HTSC without Cu-O chains[3] with Tc of 115 K discarded the models based on one-dimensional structures and the discovery of non-magnetic BiO_3-based[4] compounds makes hard to support the theories based exclusively on magnetism, if one wants to obtain an unified view of these phenomena.

The charge transfer mechanism proposed for CuO_2-based HTSC by different groups[5]-[7] proved to be one of the most robust mechanisms against this kind of test. The same ideas have been shown to be applicable to BiO_3-based[8] compounds and electron-doped[9] Cu-O layers. In this sense, it is suggestive that a small value of the metal-to-O charge-transfer-energy seems to be what distinguishes high-temperature superconducting oxides from low temperature or even non-superconducting oxides[10,11]. In spite of the progress made up to date, there is still much to be done in order to turn this idea into a complete theory. This work is an attempt to make an advance in that sense.

The high-temperature superconductors (HTSC) are insulating compounds that become metallic upon doping. It is believed that the charge gap in the stoichiometric compounds is mainly of charge transfer

origin[12]. Charge transfer systems are also found in one-dimensional conductors [13].

In this work we show that the nearest-neighbour Coulomb repulsion of the p-d model (Sec. 2) treated in a site-dependent Hartree-Fock approximation (Bogoliubov-de Gennes Formalism) (Sec. 3) can generate charge transfer polaron and exciton states (Sec. 4). The importance of charge transfer excitations in HTSC has been stressed by theorists[5]-[7] and experimentalists[14]-[19]. Structure related to charge transfer excitations in the Cu-O planes has been identified in optical measurements[17]-[19]. Polaronic effects have been invoked[20]-[23] to explain experimental results like optical spectroscopy[24,25], photoinduced optical absorption[26,27] and transport[28], among others. For a complete review see Refs.[29,30]. The photoinduced optical absorption experiments by Kim et al.[27] and Taliani et al.[31] show the importance of localized states in the gap. The former tell us that such states do not appear in the isostructural compound La_2NiO_4, while the latter shows that they are common features in both Cu and non-magnetic Bi-based high temperature superconductors. Experiments supporting self trapping effects and importance of charge transfer excitations are reviewed in Sec. 6. In Sec. 7 we discuss our results in the context of HTSC and propose some routes for the future study.

2 The Model

A prototype hamiltonian to describe strongly correlated charge transfer systems is the p-d model of HTSC. This model has been proposed in the early times of the HTSC studies for the $La_{2-x}Sr_xCuO_4$, and applies to all the Cu-O based compounds. It has been later generalized to the three-dimensional Bi-O compounds[8]. In the case of the $La_{2-x}Sr_xCuO_4$ it takes into account the following:

- The compound is quasi-two-dimensional.
- The La valence states are far above the Fermi energy[32].
- The main states near the Fermi energy[32] are the $d_{x^2-y^2}$ orbitals of the Cu and the p_x,p_y of the O directed towards the Cu. Their energies are close to each other, producing a bonding and non-bonding bands. They are the ones that mix the most.
- On-site correlations are large[32].
- As suggested by many authors we include also the interatomic repulsion[5]-[7]. We expect it to be important because we know that the carrier density is small[33] and, as a consequence, the screening length is large. On the other hand, if the Cu-O bond were ionic, this term would not play any important role, but we know this is not the case.

Motivated by the HTSC applications we shall name the atoms Cu and O but we expect to find the same physics in similar one-dimensional strongly correlated systems. The hamiltonian reads as

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

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

For the sake of simplicity most of our results are in 1D but we expect similar physics in 2D.

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 [7],

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

By doing this we loose all the relevant information about the spin degrees of freedom (which are described by a Heisenberg model) but we gain simplicity on the charge degrees of freedom. We know that U_d is very large. Naively, one could expect the results to be insensitive to the value of U_p because double occupancy on O is rare. However we shall see later (Sec. 7) that this is not the case.

3 The Bogoliubov-de Gennes Formalism (site dependent Hartree-Fock approximation)

We start with the spinless hamiltonian Eq. (2). In the Hartree-Fock approximation the four-fermion terms $n_i n_{i+1}$ are decoupled by:

$$\begin{aligned} n_i n_{i+1} &= n_i < n_{i+1} > + n_{i+1} < n_i > - < n_i >< n_{i+1} > \\ &\quad + C_i^\dagger C_{i+1}\gamma_i + C_{i+1}^\dagger C_i \gamma_i - \gamma_i^2, \end{aligned} \tag{3}$$

where we have defined,

$$\gamma_i =< C_i C_{i+1}^\dagger > . \tag{4}$$

The first three terms are the diagonal or Hartree part and the last three terms are the exchange or Fock part. The Hamiltonian now reads as

$$H_{HF} = \sum_i [\tilde{E}_i C_i^\dagger C_i + \tilde{t}_i (C_i^\dagger C_{i+1} + C_{i+1}^\dagger C_i)] + \varepsilon \, , \tag{5}$$

where

$$\begin{aligned} \tilde{E}_i &= (-1)^i \Delta + U_{pd}(< n_{i+1} > + < n_{i-1} >) \, , \\ \tilde{t}_i &= t + U_{pd}\gamma_i \, , \\ \varepsilon &= -\sum_i U_{pd}(< n_i >< n_{i+1} > -\gamma_i^2) \, . \end{aligned} \tag{6}$$

We can define new operators

$$a_\nu^\dagger = \sum_i \alpha_i^\nu C_i^\dagger \tag{7}$$

that diagonalize H_{HF}. By solving

$$[H_{HF}, a_\nu^\dagger] = E_\nu a_\nu^\dagger \tag{8}$$

we obtain the Schrödinger like equations

$$(\tilde{E}_i - E_\nu)\alpha_i^\nu + \tilde{t}_i \alpha_{i+1}^\nu + \tilde{t}_{i-1}\alpha_{i-1}^\nu = 0 \, . \tag{9}$$

Now the ground state is given by

$$|\Psi >= \prod_{\nu<\nu_f} a_\nu^\dagger |0> \ . \tag{10}$$

So we get the self-consistency equations

$$< n_i >= \sum_{\nu<\nu_f} (\alpha_i^\nu)^2 \tag{11}$$

and from Eq. (4)

$$\gamma_i = - \sum_{\nu<\nu_f} \alpha_{i+1}^\nu \alpha_i^\nu, \tag{12}$$

where we assume that all the α_i^ν are real. In order to solve these equations, we just diagonalize Eq. (9) with some initial value for the α_i^ν and then recalculate the renormalized matrix elements Eq. (6). We return to Eq. (9) and reiterate until convergence. We check that the energy decreases monotonically in order to be stabilized at some equilibrium value.

4 Results

4.1 Uniform 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 Hartee-Fock ground state is unstable and, hence, something better should be tried.

There are several candidates such as phase separation, superconductivity or, as we shall 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 an heuristic argument in the strong coupling limit. The effective levels for a chain of Cu and O at half-filling vs. the site are schematically shown in Fig. 2(a). In the Hartree approximation the diagonal energies of the orbitals renormalize as:

$$\tilde{E}_d = E_d + 2n_O U_{pd}, \tag{13}$$

$$\tilde{E}_p = E_p + 2n_{Cu} U_{pd}. \tag{14}$$

At half-filling and for small t, $n_{Cu} \sim 1$ and $n_o \sim 0$, then

$$\tilde{E}_d \sim E_d, \tag{15}$$

and

$$\tilde{E}_p \sim E_p + 2U_{pd}. \tag{16}$$

When we add holes they go mainly to O sites raising the Cu level. These will increase the mixing of Cu and O and will imply a transfer of charge from Cu to O. The net effect will be that n_{Cu} decreases, and the O level

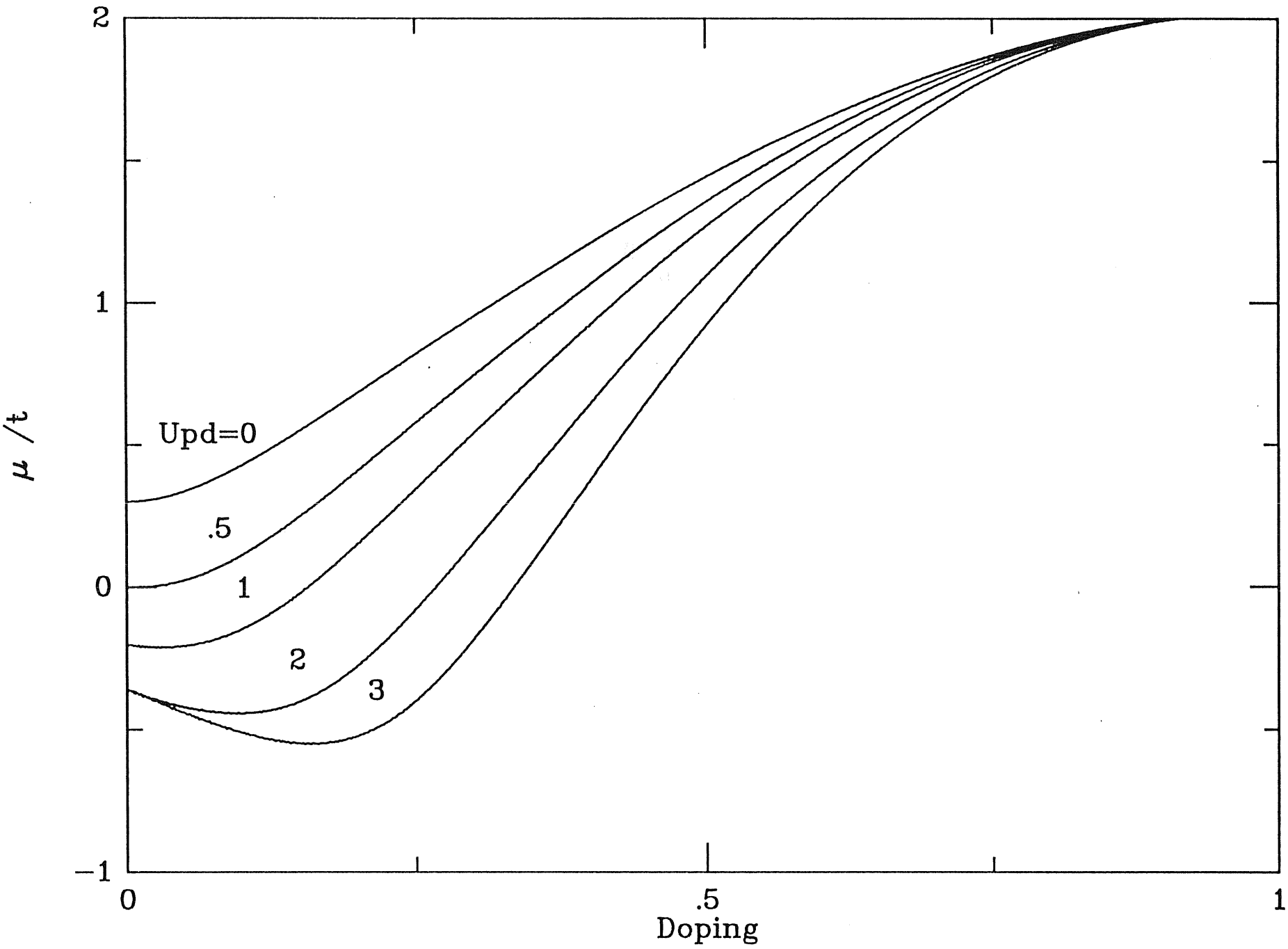

FIG. 1. Chemical potential as a function of doping in 1D for $\Delta = .3$. We subtracted the corresponding value of $2U_{pd}$ to each curve in order to make them all fall on the same scale.

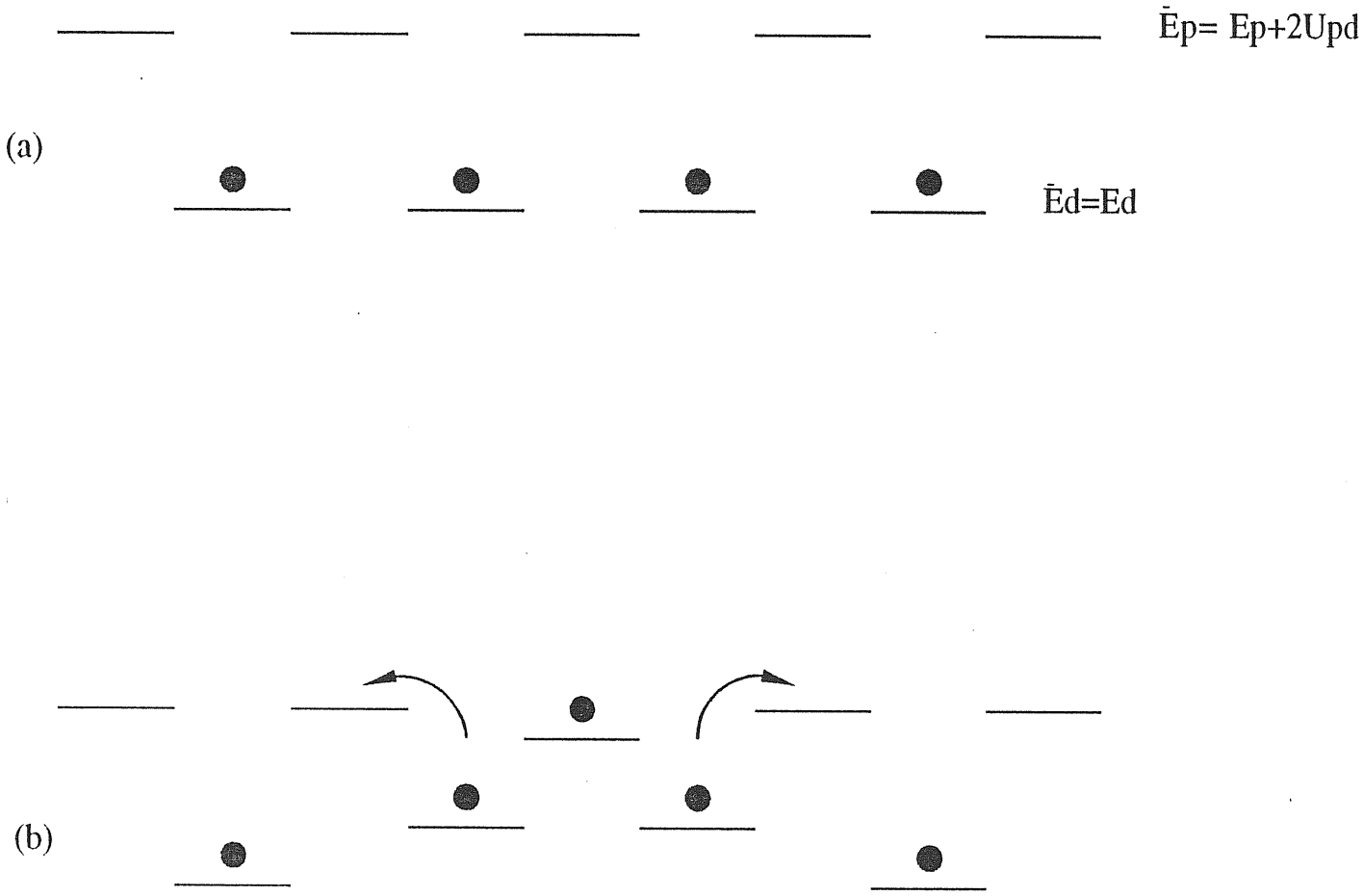

FIG. 2. Schematic plot of the renormalized energy levels in real space. A dot represents an occupied site. (a)Ground state at half filling, (b) One particle added. Arrows indicate increased charge transfer.

renormalizes to lower energies. This means that we are putting charge in a level whose energy is decreasing. Therefore, the chemical potential decreases with doping and the compressibility turns out to be negative.

4.2 Non-uniform case

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 neighbouring Cu will strongly renormalize and then, there will be charge transfer towards 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.

This effect can be studied in a wide region of parameter space performing the unrestricted Hartree-Fock approximation (Sec. 3).

In Fig. 3 we show the example of one hole added to the stoichiometric case.

In a simplified view, 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 (Eqs. (13),(14)). Therefore, 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 features of the bottom Bloch state of the O band. The amplitude is larger on O sites and it changes sign from one O site to the next. Note that the polaron forms an "impurity"-like state. In all cases we found that the self-trapped solution has lower energy than the uniform one.

Our problem presents a neat analogy with 1D problems studied in the past[34]. In this context a related problem has been studied by

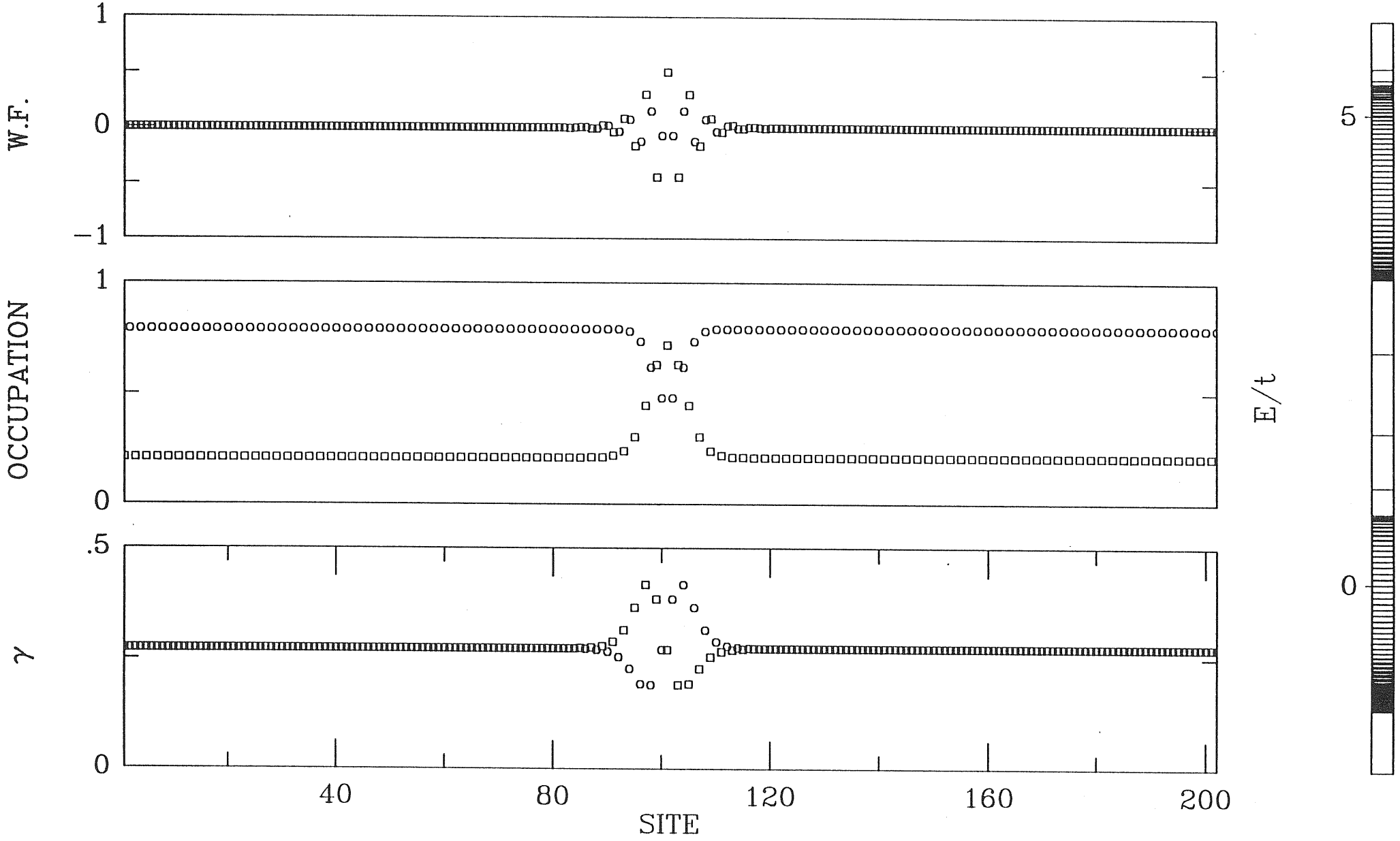

FIG. 3. One particle added to the half filling case for $\Delta = .1$, $U_{pd} = 2$. We show the one particle wave function (W.F.) of the polaron state, the site occupation, and the γ as a function of the site. Circles correspond to Cu and squares to O except for γ in which they differentiate even and odd bonds. The plot on the right is the one particle energy levels; note the states in the gap.

Hubbard[13]. He showed that for the case $\Delta = 0$ and $t << U_{pd}$ (strong coupling), one hole added to the system dissociates into a soliton (kink-like) 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 located "in the wrong place". In our case we can think of the polaron as a bound state of the pair. For $\Delta = 0$ the ground state is degenerate. Similar to Hubbard's[13] results we found kink-like solutions. In a kink-like solution half of the chain has the charge displaced towards the Cu sites, and the other half vice versa. Furthermore, in the next section we show that in the continuum limit the unrestricted Hartree-Fock equations can be mapped into a problem closely related to that of the polyacetylene[34]. In this limit the polaron solution dissociates as a free soliton pair. Fig. 4 shows the weak coupling version of Hubbard's strong coupling result. We see that the localized wave function has equal weight on Cu and O sites as required from symmetry considerations. It has similar oscillating behavior to the polaron case. It is interesting to note the behavior of γ. There is a constant part and a oscillating part. The later is clearly dominated by the localized states. That is in Eq. (12) the sum over the extended states has a smooth behavior and the sum over the localized states provides the oscillating part.

We can now consider the problem of phase separation. If there is a phase separation one would expect that for more than one particle added, the system will nucleate a hole-rich phase. Due to the short-range character of the interactions it is enough to consider the two-polaron case. We generated a configuration with two particles close to each other and iterated up until convergence. We found that the energy decreases monotonically and the system converges to a situation in which the polarons are well far apart (Fig. 5). Hence, in our formalism there is no phase separation.

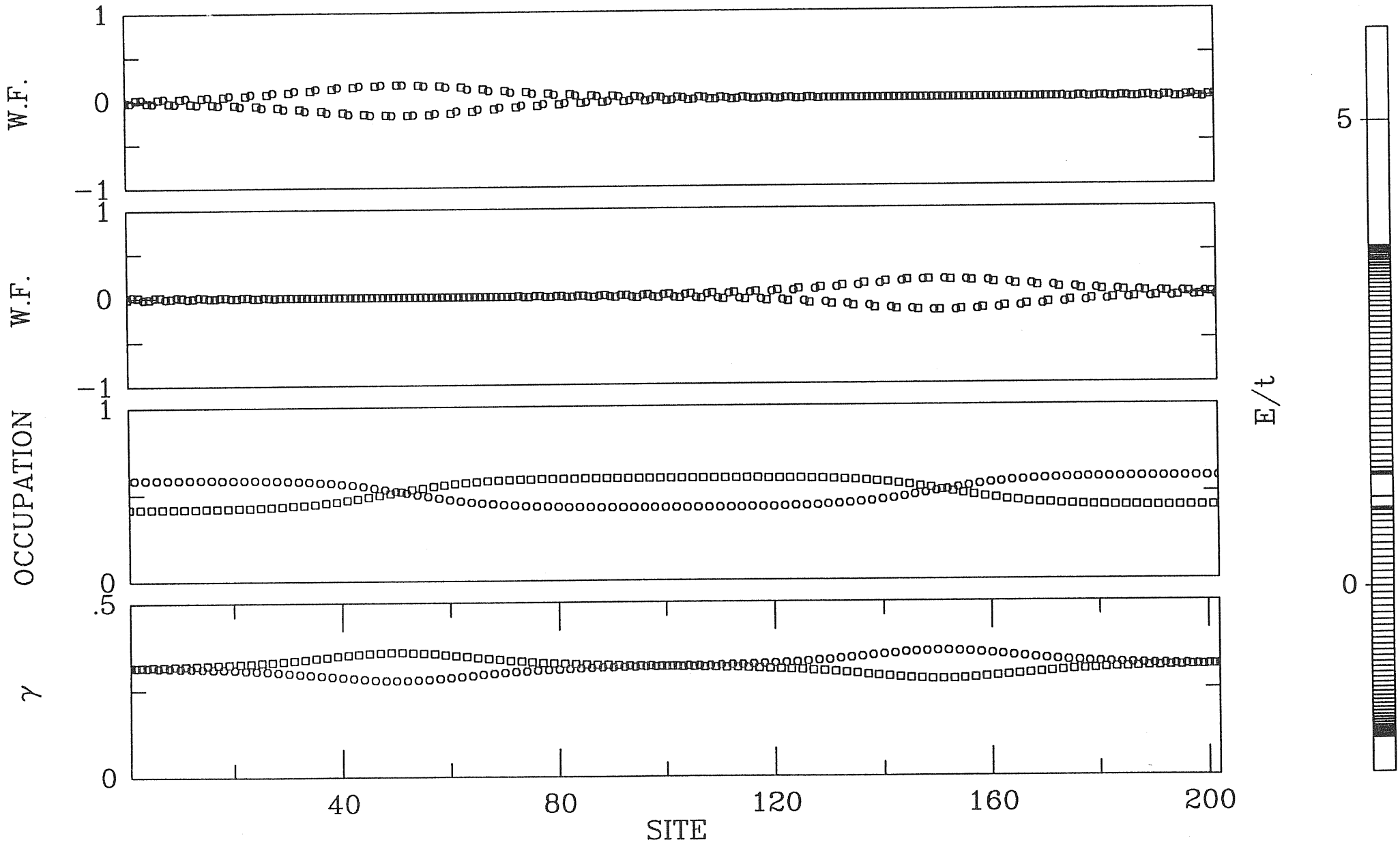

FIG. 4. One particle added to the half filling case for $\Delta = 0$, $U_{pd} = 1$. We show the one particle wave function (W.F.) of the two kink states, the site occupation, and the γ as a function of the site. Circles correspond to Cu and squares to O except for γ in which they differentiate even and odd bonds. The plot on the right is the one particle energy levels; note the states in the gap.

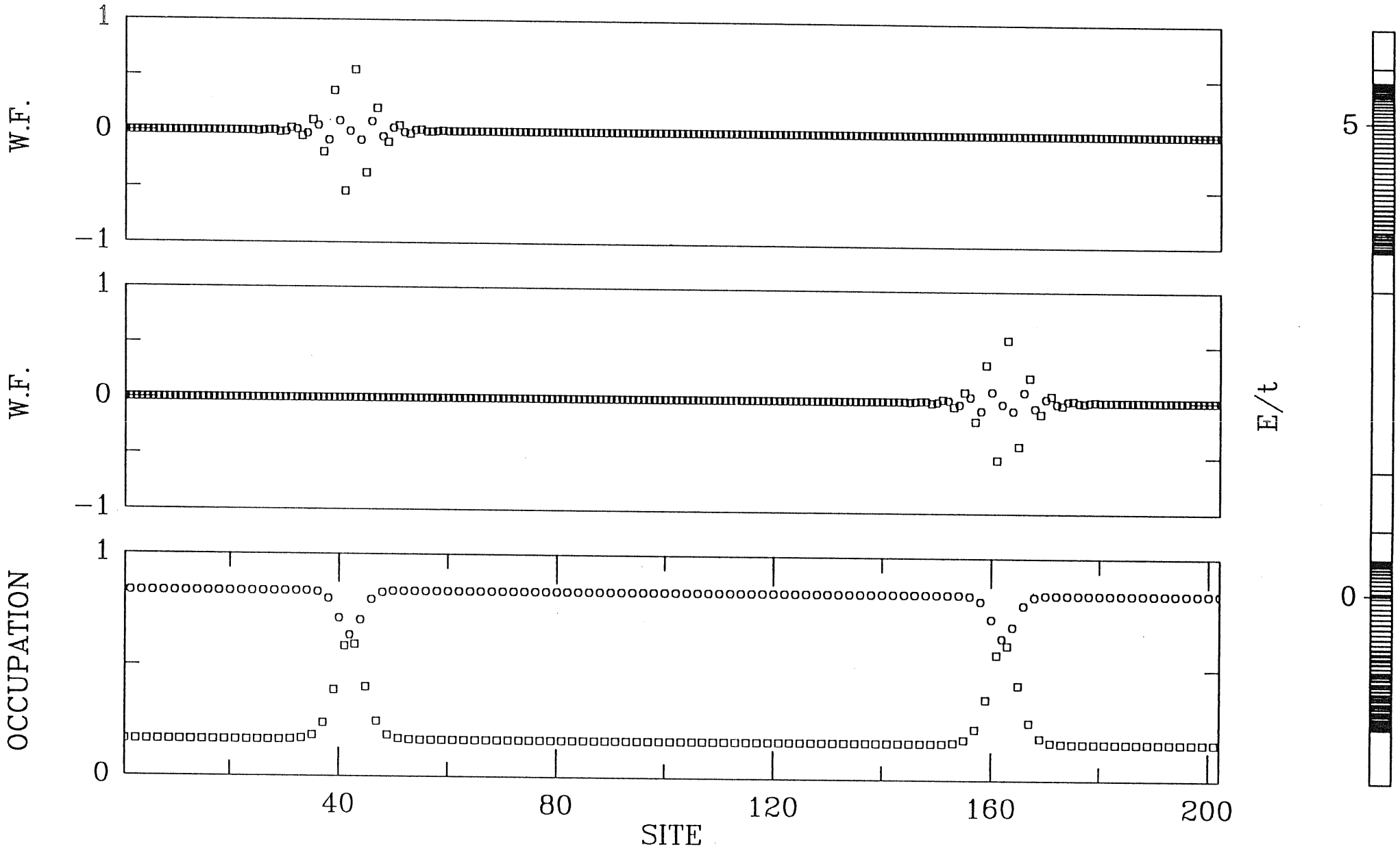

FIG. 5. Two particles added to the half filling case for $\Delta = .3$, $U_{pd} = 2$. We show the one particle wave function (W.F.) of the two-polaron state and the site occupation Circles correspond to Cu and squares to O. The plot on the right is the one particle energy levels; note the states in the gap.

We can also study excitonic states. In such state we consider the stoichiometric case leaving the top state of the lower band empty, and the bottom state of the upper band full. In Fig. 6 we show an example.

We note that the charge gap for these excitations is smaller than the uniform Hartree-Fock gap. For equal parameters 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-trapping potential is generated by a relatively small lack of charge on the Cu, which has been transferred to the O (see Fig. 3), while for the exciton case, there is a whole particle missing which generates the self-trapping potential. For the same reason the exciton spectrum is symmetric.

In the limit $\Delta = 0$ the exciton solution dissociates into a free kink-antikink pair.

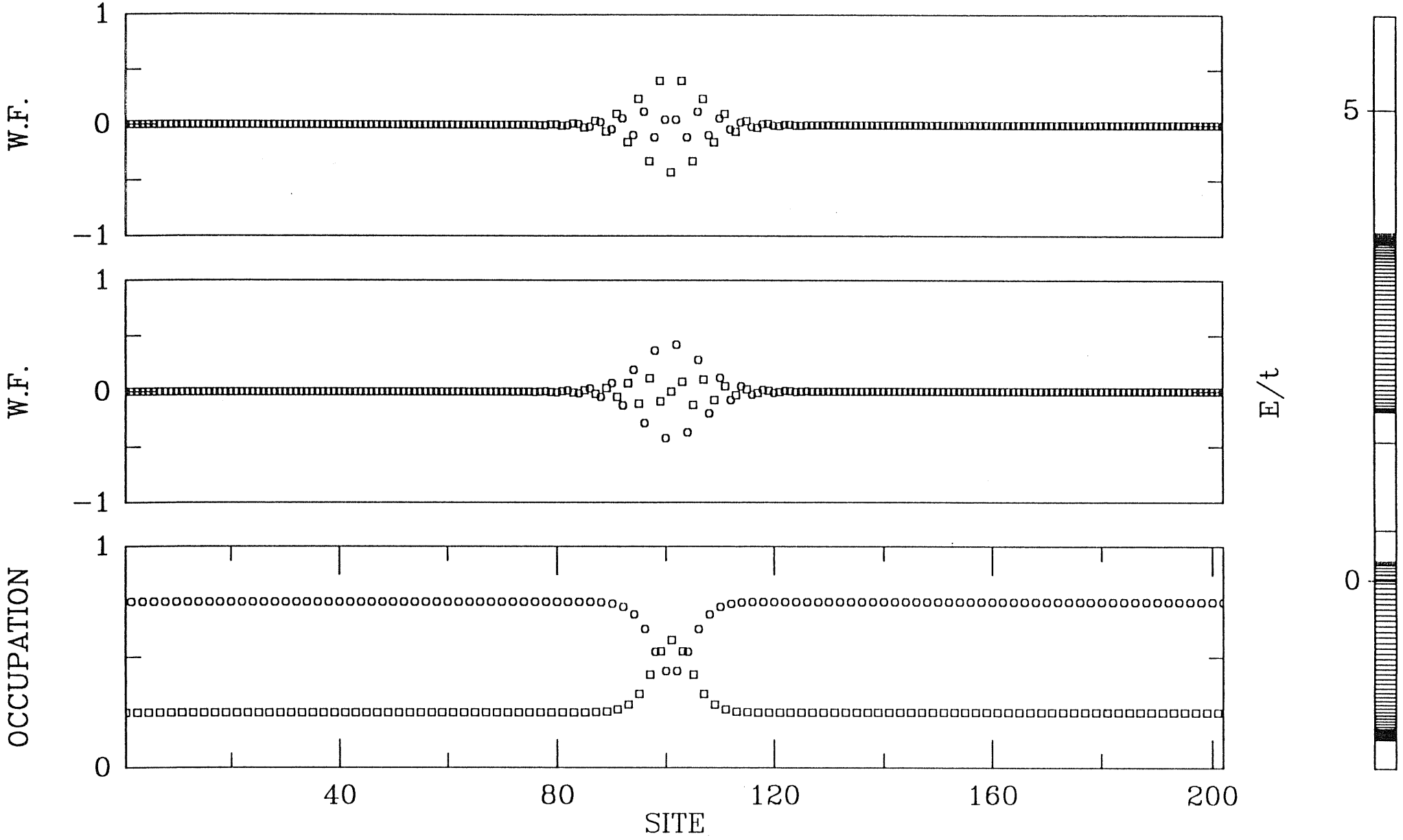

FIG. 6. Exciton state for $\Delta = .3$, $U_{pd} = 1$. We show the one particle wave function (W.F.) of the two localized states and the site occupation. Circles correspond to Cu and squares to O. The plot on the right are the one particle energy levels.

4.3 Two-dimensional case

In 2D the problem is more difficult because there is no exact mapping into the spinless case. Anyway, we expect a spinless hamiltonian to be a good approximation for the charge degrees of freedom and, indeed, such an approximation has been used in the past[7]. In Fig.7 we show the chemical potential in the 2D case. In addition to the $d-p$ hopping we introduce here also the direct O-O hopping t'. Since the same instability appears we also expect important polaronic effects to be present.

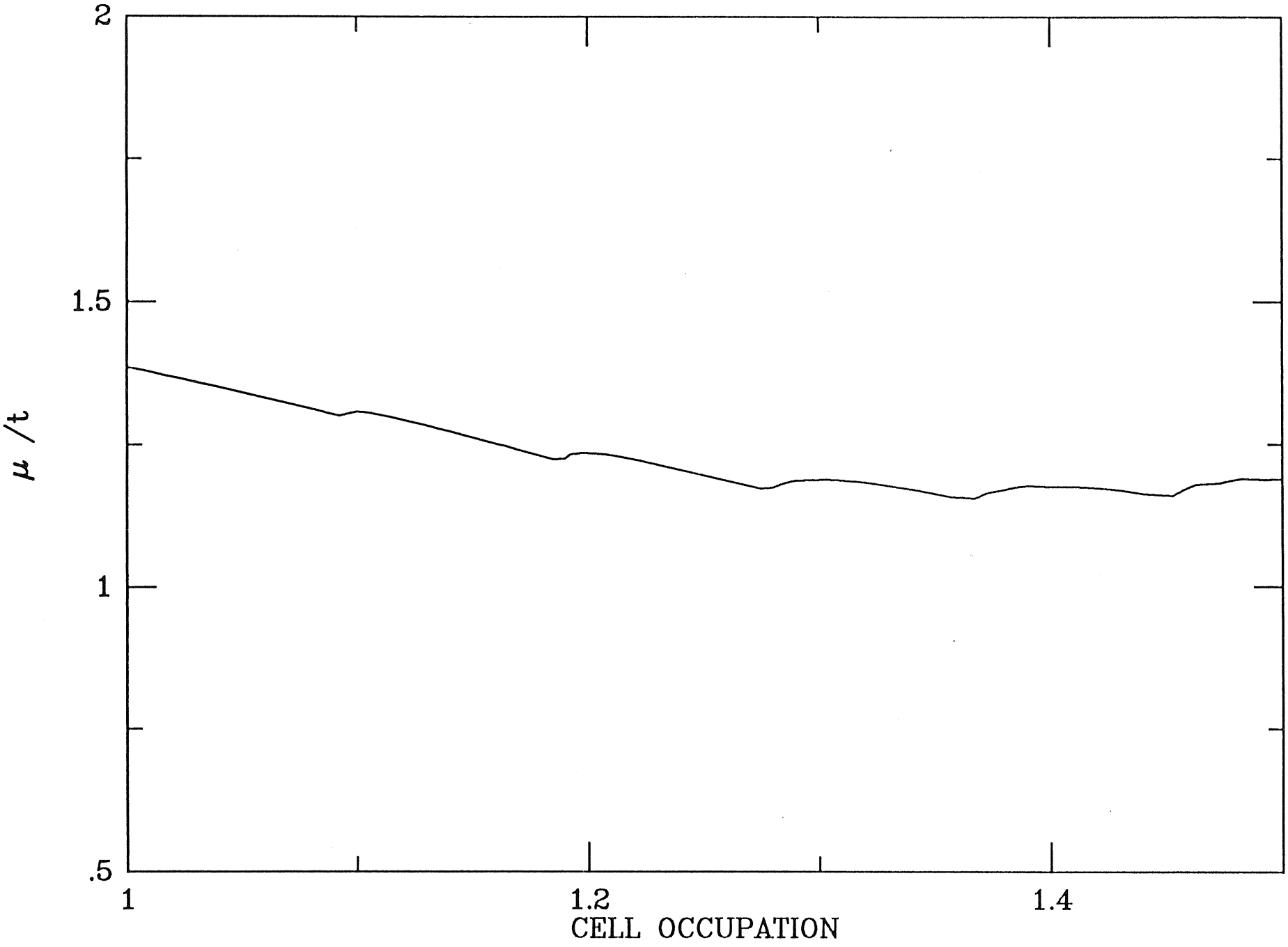

FIG. 7. Chemical potential as a function of cell occupation for 2D, $\Delta = .25$, $t' = .2$, $U_{pd} = 1$. The ripple is due to the discreetness of the mesh.

5 Continuum Limit

In the previous section we have seen that for reasonable values of the parameters the localized solutions extend to several lattice sites. It is natural, then, to try to consider the problem in the continuum limit in a manner analogous to the problem of solitons and polarons in conducting polymers[35]. We begin with the spinless fermion hamiltonian Eq. (2). We write it in a different notation to emphasize the fact that there are two non-equivalent sites in the unit cell,

$$\begin{aligned} p_l &= C_{2l} \,, \\ d_l &= C_{2l+1} \,, \end{aligned} \tag{17}$$

where l now labels the cell. The hamiltonian reads as

$$H = T + V + V_i \,, \tag{18}$$

where

$$T = \sum_l t(p_l^\dagger d_l + p_l^\dagger d_{l-1} + h.c.) \,, \tag{19}$$

$$V = \sum_l \Delta(n_l^p - n_l^d) \,, \tag{20}$$

$$V_i = \sum_l U_{pd}(n_l^p n_l^d + n_l^p n_{l-1}^d) \,. \tag{21}$$

Let us first take the continuum limit for the kinetic energy T. We Fourier transform the operators

$$
\begin{aligned}
p_k &= \frac{1}{N^{1/2}} \sum_l e^{-ikl} p_l \ , \\
d_k &= \frac{1}{N^{1/2}} \sum_l e^{-ikl} d_l \ .
\end{aligned}
\tag{22}
$$

We have taken the lattice spacing $a = 1$, but we shall restore it when needed for the sake of clarity.

The kinetic energy is given by

$$
T = \sum_k 2t \cos(k/2)(p_k^\dagger d_k e^{-ik/2} + h.c.) \ . \tag{23}
$$

This can be easily diagonalized. The dispersion relation has two branches $E_k = \pm 2t \cos(k/2)$. They are linear close to $k = \pi$. We can shift the Brillouin zone in order to have the linear features appearing at the origin. Defining

$$
q = k - \pi \ , \tag{24}
$$

we have $E_q = \pm 2t \sin(q/2)$. We are interested in low energy phenomena close to the Fermi energy. For the half-filling case the Fermi momentum is $q = 0$ ($k = \pi$). The physics does not depend on the precise form of the dispersion relation far from the Fermi energy. Therefore, we can linearize the Hamiltonian about $q = 0$ and introduce a cutoff W equal to the band width.

$$
\begin{aligned}
T &= \sum_q 2t \sin(q/2)(p_q^\dagger d_q e^{-i(\frac{\pi}{2}+\frac{q}{2})} + h.c.) \sim \\
&\sim \sum_q tq(p_q^\dagger d_q e^{-i\frac{\pi}{2}} + h.c.) \ .
\end{aligned}
\tag{25}
$$

This is diagonalized by

$$
\begin{aligned}
\Psi_{1q} &= \frac{1}{2^{1/2}}(p_q + i d_q) \ , \\
\Psi_{2q} &= \frac{1}{2^{1/2}}(p_q - i d_q) \ ,
\end{aligned}
\tag{26}
$$

with energy $\mp tqa$. Ψ_{1q} (Ψ_{2q}) describes left (right) going fermions. Close to this momentum the field operator will have a fast spatial variation ($e^{i\pi l}$) modulated by a slow spatial variation (e^{iql}). We are interested in the slowly varying part which is related to the low energy phenomena. Returning to real space,

$$\Psi_{1,2l} = \frac{1}{N^{1/2}} \sum_q e^{i\pi l} e^{iql} \Psi_{1,2q} \ . \tag{27}$$

This can be written in terms of the original site creation and annihilation operators,

$$\begin{aligned} \Psi_{1l} &= \frac{1}{2^{1/2}} e^{-i\pi l}(p_l + i d_l) \ , \\ \Psi_{2l} &= \frac{1}{2^{1/2}} e^{-i\pi l}(p_l - i d_l) \ . \end{aligned} \tag{28}$$

We can now take the continuum limit putting these expressions into the original kinetic energy Eq. (19), and transforming sums into integrals and finite differences into derivatives. Second derivatives must be dropped because they are of higher order. We get then

$$T = it \int_0^L dx [\Psi_1^\dagger(x) \frac{\partial}{\partial x} \Psi_1(x) - \Psi_2^\dagger(x) \frac{\partial}{\partial x} \Psi_2(x)] \ , \tag{29}$$

where $L = Na$ is the chain length. In the same way the site energy is written as

$$V = \frac{\Delta}{a} \int_0^L dx [\Psi_1^\dagger(x) \Psi_2(x) + \Psi_2^\dagger(x) \Psi_1(x)] \ . \tag{30}$$

We want now to write the continuum limit for the interaction part V_i. For the sake of simplicity we first perform the Hartree-Fock approximation Eq. (3). The expectation values like $< n_l^d >, \gamma_l$ will be smooth functions of l. Then, we can replace $< n_{l+1}^d >, \gamma_{l+1}$ with $< n_l^d >, \gamma_l$. We define,

$$\delta_l = < n_l^d > - < n_l^p > \ ,$$

(31)

$$n_l \;=\; < n_l^d > + < n_l^p > \;.$$

The cell charge n_l must not be confused with the atomic charge $< n_i >$ of Sec. 3. With these definitions, the interaction term can be written as

$$V_{iHF} = U_{pd} \sum_l \; [\; n_l^p(n_l + \delta_l) + n_l^d(n_l - \delta_l) + (p_l^\dagger d_l \gamma_l + p_l^\dagger d_{l-1}\gamma_l + h.c.) - \frac{n_l^2 - \delta_l^2}{2} + 2\gamma_l] \tag{32}$$

which in the continuum limit becomes

$$\begin{aligned} V_{iHF} \;=\; & \frac{U_{pd}}{a}\int_0^L dx\delta(x)[\Psi_1^\dagger(x)\Psi_2(x) + \Psi_2^\dagger(x)\Psi_1(x)] \\ & + \frac{U_{pd}}{a}\int_0^L dx n(x)[\Psi_1^\dagger(x)\Psi_1(x) + \Psi_2^\dagger(x)\Psi_2(x)] \\ & + iU_{pd}\int_0^L dx\gamma(x)[\Psi_1^\dagger(x)\frac{\partial}{\partial x}\Psi_1(x) - \Psi_2^\dagger(x)\frac{\partial}{\partial x}\Psi_2(x)] \\ & + \frac{U_{pd}}{a}\int_0^L dx[-\frac{n^2(x) - \delta^2(x)}{2} + 2\gamma(x)] \;. \end{aligned} \tag{33}$$

We can obtain a more compact expression by using the Pauli spin matrices and the identity,

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{34}$$

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{35}$$

Defining a pseudospinor

$$\Psi(x) = \begin{pmatrix} \Psi_1(x) \\ \Psi_2(x) \end{pmatrix}, \tag{36}$$

the renormalized parameters

$$\tilde{t}(x) \;=\; t + U_{pd}\gamma(x) \;, \tag{37}$$

$$\tilde{\Delta}(x) \;=\; \Delta + U_{pd}\delta(x) \;, \tag{38}$$

and putting all together, the hamiltonian reads as

$$H_{HF} = \int_0^L dx \Psi(x)^\dagger [i\tilde{t}(x)\sigma_3 \frac{\partial}{\partial x} + \frac{\tilde{\Delta}(x)}{a}\sigma_1 + \frac{U_{pd}n(x)}{a} I]\Psi + \int_0^L dx \frac{U_{pd}}{a}[\frac{n(x)^2 - \delta(x)^2}{2} + 2\gamma(x)^2] \, . \quad (39)$$

We can obtain the self-consistent Hartree-Fock equation minimizing the energy,

$$\begin{aligned} \frac{\partial < H_{HF} >}{\partial n(x)} &= \frac{U_{pd}}{a} < \Psi(x)^\dagger I \Psi(x) > + \frac{U_{pd}}{a} n(x) = 0 \, , \\ \frac{\partial < H_{HF} >}{\partial \delta(x)} &= \frac{U_{pd}}{a} < \Psi(x)^\dagger \sigma_1 \Psi(x) > + \frac{U_{pd}}{a} \delta(x) = 0 \, , \\ \frac{\partial < H_{HF} >}{\partial \gamma(x)} &= iU_{pd} < \Psi(x)^\dagger \sigma_3 \frac{\partial}{\partial x} \Psi(x) > + 4\frac{U_{pd}}{a}\gamma(x) = 0 \, . \end{aligned} \quad (40)$$

To solve these equations we can express the field in terms of the operators that annihilate particles in the self-consistent single-particle states of H_{HF}, i.e.,

$$\Psi(x) = \sum_\nu \varphi_\nu(x) c_\nu, \quad (41)$$

where

$$\varphi_\nu(x) = \begin{pmatrix} u_\nu(x) \\ v_\nu(x) \end{pmatrix} . \quad (42)$$

The ground state is written as

$$|\Psi> = \prod_\nu{}' c_\nu^\dagger |0> \, , \quad (43)$$

where the prime indicates that the index ν runs only over occupied states. The φ_ν are found by varying $< H_{HF} >$ with respect to φ_ν^* and using the Lagrange multiplier ε_ν to guarantee the normalization.

$$[i\tilde{t}(x)\sigma_3 \frac{\partial}{\partial x} + \frac{\tilde{\Delta}(x)}{a}\sigma_1 + \frac{U_{pd}n(x)}{a} I]\varphi_\nu = \varepsilon_\nu \varphi_\nu \, . \quad (44)$$

The self-consistent Hartree-Fock equations Eq. (40) now read as

$$\begin{aligned} \delta(x) &= -\sum_{\nu}{}' \varphi_{\nu}^{*}(x)\sigma_1\varphi_{\nu}(x) , \\ \gamma(x) &= -i\frac{a}{4}\sum_{\nu}{}' \varphi_{\nu}^{*}(x)\sigma_3\frac{\partial}{\partial x}\varphi_{\nu}(x) , \\ n(x) &= \sum_{\nu}{}' \varphi_{\nu}^{*}(x) I \varphi_{\nu}(x) . \end{aligned} \tag{45}$$

This is a system of coupled nonlinear equations, and in principle it is very difficult to solve. However, some analytical progress can be done in some special cases. First we neglect the spatial variation of $\tilde{t}$. We take it as a constant and measure all the energies in units of $\tilde{t}$ (we restore it for clarity when convenient). We look now for solutions with n =const. With this simplification our equations become,

$$\begin{aligned} -i\frac{\partial u_{\nu}}{\partial x} + \tilde{\Delta}(x)v_{\nu} &= E_{\nu}u_{\nu} , \\ \tilde{\Delta}(x)u_{\nu} + i\frac{\partial v_{\nu}}{\partial x} &= E_{\nu}u_{\nu} , \end{aligned} \tag{46}$$

and the self-consistency equation is

$$\tilde{\Delta}(x) = \Delta - U_{pd}\sum_{\nu}{}' [u_{\nu}^{*}(x)v_{\nu}(x) + v_{\nu}^{*}(x)u_{\nu}(x)] , \tag{47}$$

where

$$E_{\nu} = \varepsilon_{\nu} - U_{pd}n . \tag{48}$$

Similar equations[36] are used in the theory of inhomogeneous superconductors where they are known as the Bogoliubov-de Gennes equations. They are also used in the theory of one dimensional conducting polymers[34]. In analogy with the polyacetylene problem in the limit $\Delta = 0$ they are equivalent to the one component Gross-Neveu model[37].

5.1 Uniform case

The simplest solution is the homogeneous case where

$$\begin{aligned} u(x) &= u_o e^{iqx}, \\ v(x) &= v_o e^{iqx}. \end{aligned} \tag{49}$$

We use the upper index (u, l) to label the upper and lower bands, respectively.

$$\begin{aligned} u_o^{u,l} &= \frac{\tilde{\Delta}}{\sqrt{L[\tilde{\Delta}^2 + (E^{u,l} - q)^2]}}, \\ v_o^{u,l} &= \frac{E^{u,l} - q}{\sqrt{L[\tilde{\Delta}^2 + (E^{u,l} - q)^2]}}. \end{aligned} \tag{50}$$

The band energy is

$$E_q^{u,l} = \pm\sqrt{\tilde{\Delta}^2 + q^2}\,. \tag{51}$$

We can substitute Eqs. (49)-(51) into Eq. (47) in order to determine the self-consistent value of $\tilde{\Delta}$. Transforming the sum into an integral we obtain

$$\tilde{\Delta} = \Delta + \frac{U_{pd}}{\pi}\int_O^{W/2} d\omega \frac{\tilde{\Delta}}{\sqrt{\tilde{\Delta}^2 + \omega^2}}\,. \tag{52}$$

In the limit we are interested in, $\tilde{\Delta} << W$ and Eq. (52) can be written as

$$\tilde{\Delta} = W e^{-\frac{\pi}{U_{pd}}(1-\frac{\Delta}{\tilde{\Delta}})}\,. \tag{53}$$

5.2 Non-uniform case

In the general case Eq. (46) can be decoupled by changing the variables as follows,

$$f_\nu^{\pm} = u_\nu \pm i v_\nu\,, \tag{54}$$

obtaining the Schröedringer-like equation,

$$(-\frac{\partial^2}{\partial x^2} + V^{\pm})f^{\pm} = E^2 f^{\pm} \,, \tag{55}$$

$$V^{\pm} = \tilde{\Delta}^2 \pm \frac{\partial \tilde{\Delta}}{\partial x} \,. \tag{56}$$

The solutions of this equations are well know[34]. For $\Delta = 0$ one has kink-like solutions, and for any Δ polaron-like solutions. Unfortunately, in general they do not satisfy the condition n =const. However, one can argue that qualitatively similar solutions can be found.

There is one special case for which the condition n =const. is satisfied, and it is the exciton solution. The gap function is,

$$\Delta(x) = \Delta_0 - k_0(t^+ - t^-) \,, \tag{57}$$

where Δ_0 is the gap parameter far away from the exciton and, therefore, is determined by Eq. (52),

$$t^{\pm} = \tanh[k_0(x \pm x_0)], \tag{58}$$

x_0 is determined by,

$$\tanh(k_0 x_0) = \frac{k_0}{(\Delta_0 + \omega_0)} \,, \tag{59}$$

ω_0 is defined by,

$$\omega_0^2 = \Delta_0^2 - k_0^2 \,. \tag{60}$$

The only parameter that remains free is k_0. It will be determined by the self-consistency condition Eq. (47).

The one-particle states are the same corresponding to a polaron solution. There are two localized states in the gap. One with energy ω_0,

$$\begin{aligned} f_u^+ &= \sqrt{\frac{k_0}{2}} s^-, \\ f_u^- &= -i\sqrt{\frac{k_0}{2}} s^+, \end{aligned} \tag{61}$$

and the other with energy $-\omega_0$,

$$\begin{aligned} f_l^+ &= \sqrt{\frac{k_0}{2}} s^- , \\ f_l^- &= i\sqrt{\frac{k_0}{2}} s^+ , \end{aligned} \tag{62}$$

where

$$s^{\pm} = \mathrm{sech}[k_0(x \pm x_0)] \, , \tag{63}$$

The extended states are

$$\begin{aligned} f_{u,l}^+ &= \frac{e^{ikx}(k + ik_0 t^-)}{\sqrt{L(k_0^2 + k^2)}} \, , \\ f_{u,l}^- &= \frac{(k - i\Delta_0)}{E_k^{u,l}} \frac{e^{ikx}(k + ik_0 t^+)}{\sqrt{L(k_0^2 + k^2)}} \, . \end{aligned} \tag{64}$$

The boundary condition is,

$$f_k^{\pm}(L/2) = f_k^{\pm}(-L/2) \, , \tag{65}$$

which in the limit $L >> x_0$ gives,

$$kL + 2\arctan(k_0/k) = 2\pi n \, , \tag{66}$$

with n integer. In order to test the self-consistency we have to insert Eq. (57),(61),(64) in Eq. (47). The occupied states are all the extended states of the lower band and the upper localized state. Using the fact that Δ_0 satisfies Eq. (52) we obtain,

$$k_0 = \frac{U_{pd}}{L} \sum_k{}' k_0 \frac{\sqrt{k^2 + \Delta_0^2}}{k^2 + k_0^2} - \frac{1}{2}\omega_0 U_{pd} \, , \tag{67}$$

which determines k_0.

There is one conceptual conclusion from this section. Up to now we considered only static solutions. In the limit considered here the

translational symmetry is a continuous symmetry. The localized solutions spontaneously break this symmetry. From the Goldstone theorem one expects that the fluctuation spectrum about the mean field solution has a zero energy mode that recovers the translational symmetry of the problem. This is a mode in which the Hartree-Fock solution rigidly translates with infinitesimal velocity.

6 Review of some experiments supporting self trapping and importance of charge transfer excitations

6.1 Polaronic effects

We have shown that the p-d model gives rise to polaronic or self-trapped states of charge transfer origin in a natural way. This should manifest in spectroscopic data as states in the gap and in transport properties as the enhancement of the effective mass of the carriers. Once a self-trapped state is formed, one expects that the lattice will relax around it creating localized or resonant phonon states. This should be seen in a spectroscopic experiment as states that split of from the phonon bands, or as shifts of the phonon bands. Effects of this kind have been reported by many experimentalists. Here we give some examples.

Many theorists[20]-[23] have invoked polaronic effects due to the lattice, or some more exotic origin to explain experimental results like optical spectroscopy[24,25], photoinduced infrared absorption[26,27], transport[28] among others. For a complete review see Refs.[29,30].

The strongest evidence of self-trapped states comes from optical properties. In photoinduced optical absorption the semiconducting compound is optically doped by promoving electrons from the valence band to the conduction band with a laser. The optical absorption of the sample is measured as a function of the photon energy.

Ginder et al.[38] performed such measurements in La_2CuO_4. They found a gap of 2eV and two photoinduced absorption peaks at .5eV and 1.4eV. They interpret them as long lived defect states and make reference to the case of one dimensional polymers where "electrons photoexcited across the band gap and holes that remain in the valence band eventually form long-lived defect states such as solitons, polarons, and

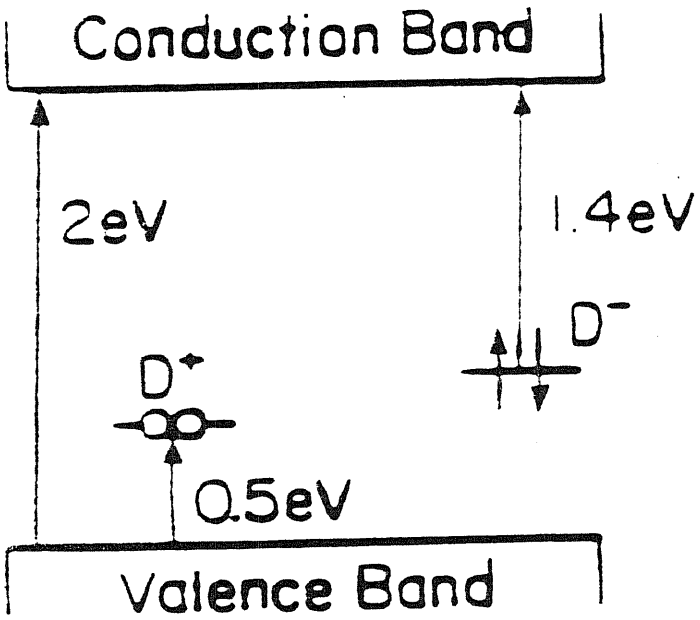

FIG. 8. Possible energy-level diagram for photoinduced defect states in the energy gap of La_2CuO_4. Reproduced from Ref. 38.

bipolarons." We show in Fig. 8 their schematic illustration of the defect levels. The studies of Kim et al.[27] and Taliani et al.[31] demonstrate that the lattice relaxes around these localized states. They measure the variation of reflectivity with the laser on and off. By comparing vibrational lines with the corresponding Raman lines they can see shifts of the phonon bands due to distortion of the lattice. The common temperature and intensity dependence of the corresponding spectral features allow them to associate the lattice distortion with the localized electronic state. For $YBa_2Cu_3O_{6.25}$ the bound energy of the "hole state" (D^+ in Fig. 8) is .14eV suggesting a less localized state in the higher T_c system[27].

Due to the fact that these photoinduced absorption features are not observed in the isostructural compound La_2NiO_4, Kim et al. conclude that polaron or bipolaron formation plays an important role in the HTSC. It is interesting to note that similar features[31] with a localized electronic state at .5eV are present in the non-magnetic $BaBiO_3$

ruling out an exclusively magnetic (spin-bag-like) polaron.

M. Suzuki[39] measured the optical transmittance and reflectance together with the Hall coefficient in single crystal thin films of $La_{2-x}Sr_xCuO_4$ for different values of x. In the transmittance for x=0 he found an absorption edge corresponding to a band gap of 2eV. The edge splits due to Sr doping. As the concentration of Sr is increased, the lower edge shifts towards lower energies giving rise to an absorption peak. This absorption is considered to reflect the modified density of states near the top of the valence band. This also means that the 2ev gap measured by Ginder et al.[38] does not collapse during doping.

In the reflection spectra, he found another peak centered at 1.8eV. He interprets that as due to the enhanced density of states near the top of the valence band in agreement with optical transmission.

He interprets the behaviour of the absorption coefficient in the following terms. "E_F shifts to lower energies from the band edge by doping, forming a band of about 1eV in width. At the same time, the band gap, which was originally 2eV, decreases to about 1.2eV." He reports agreement of this results with electron energy-loss spectroscopy (EELS) measurements by Nüker et al.[40] who also found defect states growing with doping. As a possible explanation Suzuki invokes the spin-bag mechanism of Schrieffer et al.[41]. In this framework the local suppression of the spin-density wave (SDW) gap by the introduced holes "may be reflected in the optical absorption spectrum as the reduction of the optical gap, as just observed in the present (his) study. Indeed the optical density at this reduced energy, which may be proportional to the number of spin-bags, increases nearly proportional to the hole concentration." An analogous explanation replacing SDW gap by charge transfer gap and spin-bag by charge transfer polarons obviously applies.

Other evidence of polaron formation comes from the studies of Bo-

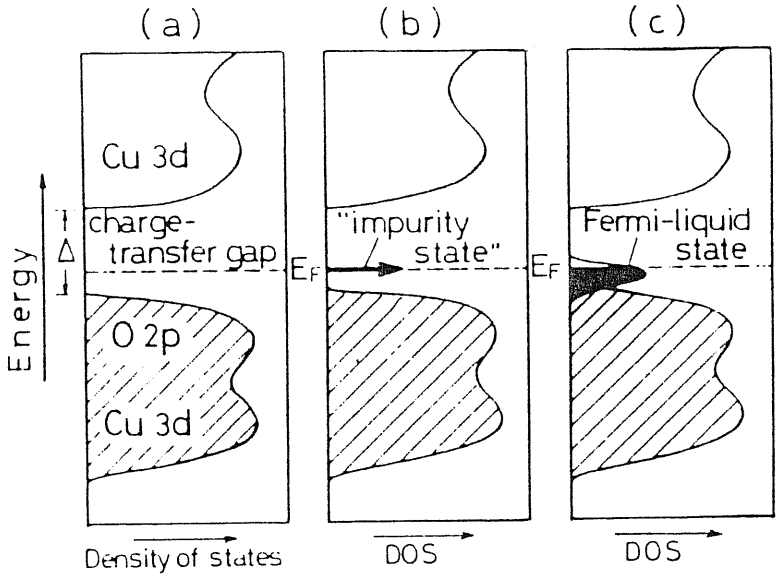

FIG. 9. Schematic diagram of the electronic structure and formation of Fermi-liquid states in high-Tc superconductor. (a) charge transfer semiconductor; (b) "impurity states" are created at the Fermi level by hole-doping; (c) Fermi-liquid states are formed by overlapping of the "impurity states". Reproduced from Ref. 43.

zovic [24,25]. He claims to be able to explain the "frequency, temperature, and carrier concentration of the optical conductivity without any fitting" by assuming intermediate polarons of diameter $\sim 6\dot{A}$ and mass $m_{ab} = 2 - 5\ m_e$.

States in the gap have also been detected in photoemission spectroscopy[42,43] and X-ray absorption[43]. In Fig. 9 we show the schematic picture of Matsuyama et. al. Angle resolved photoemission spectra have revealed that these states form narrow dispersive-like bands crossing the Fermi level[44]. Similar impurity-like states have been observed[45] in X-ray-absorption in the electron doped case.

Of course these experiments do not tell us the nature of this states. A possible interpretation is that they are Kondo-like resonances[46] however this is ruled out[43] because they are mainly of O character, whereas a Kondo-like state should have a dominant Cu $3d$ nature. We belive that charge-transfer polarons are good candidates.

Once the self trapped-state is formed, other effects like distortion

of the magnetic background or phonons can contribute to the binding energy.

6.2 Charge transfer excitations

Charge transfer excitations in which holes from the Cu band are excited across the gap to form exciton states should be also seen in spectroscopies. Traditionally in conventional semiconductors the pressure variation of possible candidate structures has been used to identify their origin.

Early optical measures in thin films of $YBa_2Cu_3O_{7-\delta}$ by Bozovic et al. showed a lack of evidence for excitons[47] in contradiction with previous results in sintered samples[15,48]. Incidentally they interpreted their results as due to polarons. Later studies[49] with thicker films on oriented $YBa_2Cu_3O_{7-\delta}$ found excitonic-like features. This was confirmed in many subsequent works[16]-[19],[50,51]. Kelly et al.[50] made a careful optical study in sinterized and single-crystal samples of $YBa_2Cu_3O_x$. In Fig. 10 we show their measured imaginary part of the dielectric function for different O contents. There are two sharp excitations, one at 1.7eV, and the other at 4.1 eV whose intensities decrease as the system becomes metallic. There is another weaker structure at 2.6-2.7 eV. Venkateswaran et al.[17] made a study of the optical properties as a function of pressure and identified the 1.75eV and 2.6eV features as charge-transfer excitations involving Cu(d) and O(p) states in the Cu-O planes. Kelly et al.[19] made an extensive study of the 1.7eV and 4.1eV features and showed that the former is present in many different families of the Cu-O including Nd_2CuO_4, a parent compound of a n-type superconductor. They confirm that the former are related to charge transfer excitations in the planes and the later is related to charge transfer excitations in the Cu-O chains. For $La_{2-x}Sr_xCuO_4$ the 1.7eV

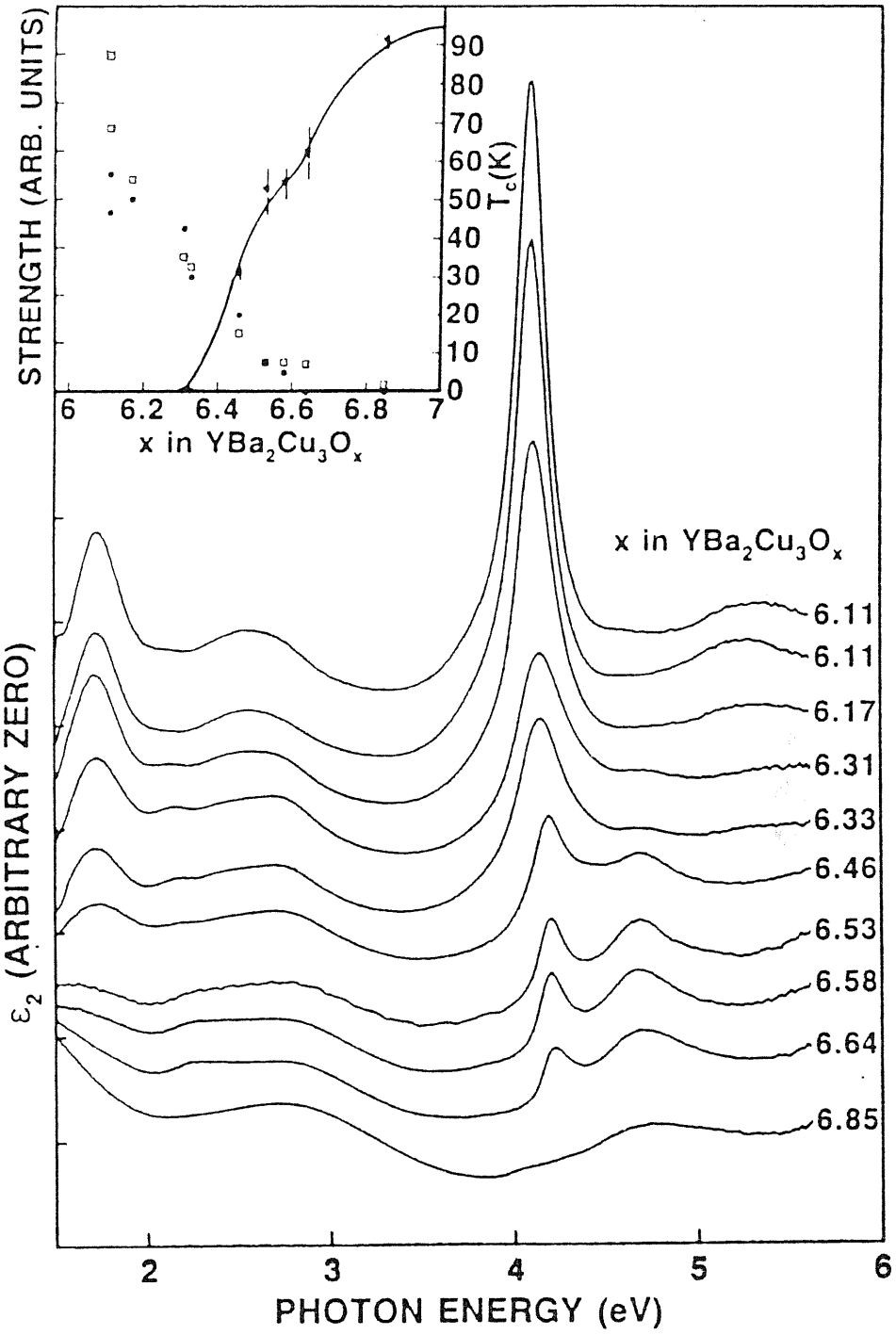

FIG. 10. Measured imaginary part of the dielectric function of $YBa_2Cu_3O_x$ as a function of O content. A constant vertical scale is used and the curves are offset uniformly. The inset shows peak intensities as determined from Lorentzian line-shapes fits. Open boxes correspond to the 4.1-eV peak and closed circles to the 1.7-eV peak. Critical temperatures and transition widths were determined by ac susceptibility. Reproduced from Ref. 50.

feature shifts to 2.1 eV. Similar structures were found[51] by electron energy-loss spectroscopy (EELS).

A very interesting work by Rao et al.[14] has shown the importance of the charge transfer excitation energy. They made measurements of the Cu $2p$ core-level-photoelectron spectra in different compounds. In these experiments the kinetic energy distribution of the photoemitted electrons carries information of the dynamic response of the states near the Fermi energy. In the sudden approximation the wave function of the initial state is decomposed into the eigenstates of the final hamiltonian. It is assumed that the velocity of the photoelectron is so large that the rest of the system does not have time to respond to it. The initial state is a mixture of $|\mathrm{Cu}3d^9>$ and $|\mathrm{Cu}3d^{10}\underline{\mathrm{L}}>$. The later denotes a state in which a hole has been transfer from the Cu to a linear combination of the nearest neighbour O orbitals. The initial hamiltonian can be represented by a 2×2 matrix with a Δ difference in diagonal energies and t_{pd} off-diagonal elements. These are not the same parameters defined in the previous sections but are closely related. In the final state the $|\mathrm{Cu}3d^9>$ becomes $|\mathrm{Cu}2\underline{\mathrm{p}}3d^9>$, where $2\underline{\mathrm{p}}$ denotes the core hole, and is push up in energy (in a hole picture) due to the Coulomb repulsion with the core hole. Due to that, the hole, which was mainly on the Cu is transferred to the O ($|\mathrm{Cu}2\underline{\mathrm{p}}3d^{10}\underline{\mathrm{L}}>$ plus a small component of $|\mathrm{Cu}2\underline{\mathrm{p}}3d^9>$ final state). This gives rise to the main line. The possible transition to the mainly $|\mathrm{Cu}2\underline{\mathrm{p}}3d^9>$ state gives a satellite line. The relative intensity of the two features ($\mathrm{I}_s/\mathrm{I}_M$) is determined by Δ, t_{pd} and U_{dc}, the core-hole-d-hole repulsion. They showed that in all cases the $\mathrm{I}_s/\mathrm{I}_M$ ratio decreases as T_c increases. They suggest that the common factor determining the variation of T_c and $\mathrm{I}_s/\mathrm{I}_M$ is the Cu-O charge transfer energy. In order to substantiate this finding, they calculated the variation of the $\mathrm{I}_s/\mathrm{I}_M$ as a function of Δ. Finally they showed

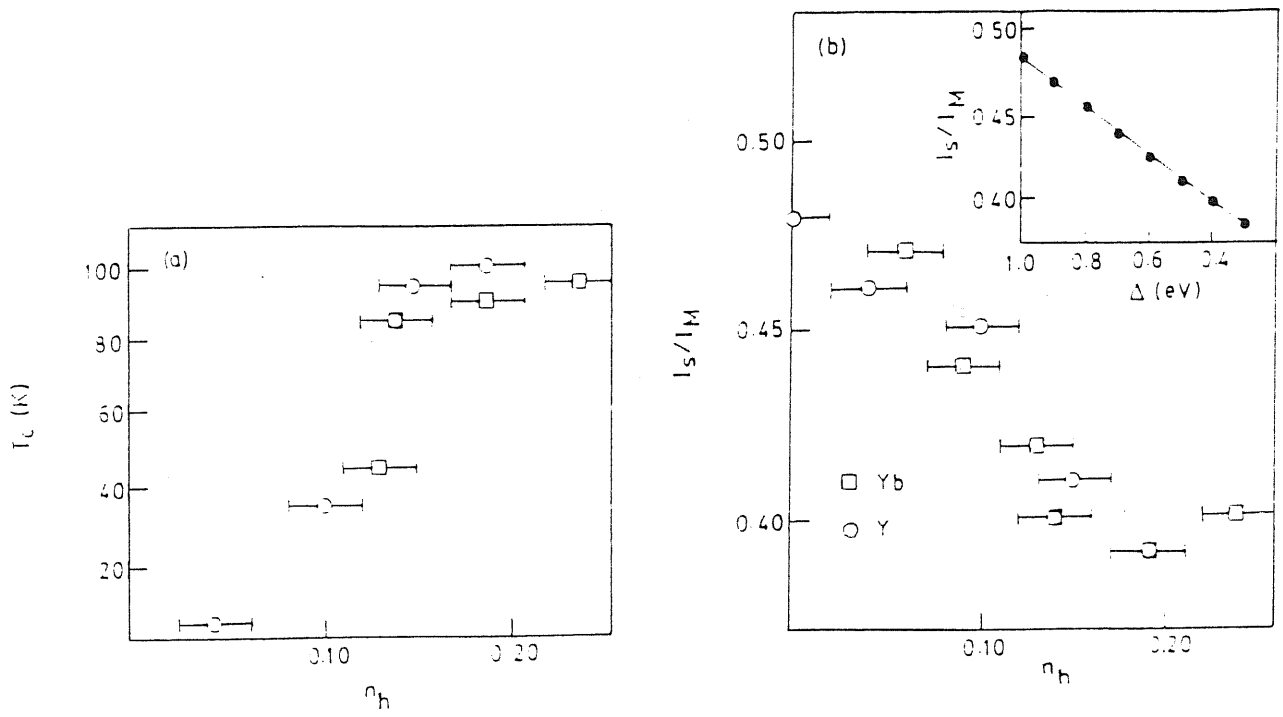

FIG. 11. (a) Variation of T_c with the number of moles of holes per formula weight n_h in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$ (R=rare earth); (b) variation of the I_s/I_M ratio with n_h in $Bi_2Ca_{1-x}R_xSr_2Cu_2O_{8+\delta}$. Inset shows the dependence of I_s/I_M on the charge-transfer energy, found from calculations. Reproduced from Ref. 14.

that Δ correlates with the carrier concentration. This gives a common interpretation with the experiments of Tranquada[52] et al. who showed that T_c correlates with the O hole concentration. In Fig. 11 we show the measured dependence of I_s/I_M as a function of hole concentration and its correlation with T_c. The decrease of Δ with increased carrier concentration is natural if one assumes the Δ to be renormalized by the U_{pd} (See Eq. (13),(14)). They estimate $U_{pd} \sim 2.7$, a value which is not entirely unreasonable if one takes into account that band structure and other effects have been neglected. These experiments encourage further studies on the role of charge-transfer excitations in connection with superconductivity.

7 Conclusions

The problem of which is the simplest model, one or two bands, that can capture the essential physics of the HTSC has been a subject of considerable controversy[53]-[58]. There is consensus that the p-d model describes the Cu-O layers[53,59], so the question is the degree to which the one-band model reproduces the physics of the two-band model. The question is not trivial because by simple arguments[53] one could draw the conclusion that it is possible, in some limit, to map the p-d model into a one-band model. However, one must be sure that no important piece of physics was lost in the process. This is not an easy task because, firstly, one has to be sure to understand the p-d model. Here we have shown that the p-d model gives rise quite naturally to self-trapping effects that cannot be captured by one-band models.

We see that one particle added to the half-filling case distorts the charge balance between Cu and O around it and forms a polaron of charge transfer origin. In this picture polarons will form a dispersive band growing with doping. As we could see in the previous section this is fully consistent with many different experiments like optical measurements[24,39], photoinduced absorption[38,27,31], photoemission spectroscopy[42,43] and X-Ray absorption[43].

Using a different formalism, Grilli[60] et al. found the same instability in the compressibility but they interpreted it as a phase separation. The difference is that they set the repulsion on the O equal to zero, while we set it equal to infinity. Since the polaron states are mainly due to O character, we expect the result of Fig. 5 to be different in their case, so in principle the results are not contradictory to each other. However, further investigations must be done in order to clarify this point.

The p-d model has been studied in higher dimensions in the limit $t << \Delta << U_p, U_d$ by perturbation theory in the hopping, in connec-

tion with hole-doped CuO and BiO based HTSC[8], and electron doped CuO layers[9]. It has been shown that one particle added to the half-filling case produces charge transfer excitations around it in a way which resembles our results. When two particles are put close together low energy charge fluctuations are allowed which 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.

There are other obvious routes for the future. One is to understand the dynamics of these excitations. An intuitive approach is to try to solve the time dependent Schröedinger equation in the Hartree-Fock approximation. In this way one can look for a solution in which the polaron with its self-trapping potential moves self-consistently. But a time dependent Hartree-Fock is nothing more than the RPA approximation. In other words, one has to look for the linear modes or the one loop corrections around the localized solution. One of them is the Goldstone mode discussed in Sec. 5. A similar problem has been faced for the polyacetylene[34]. Other interesting problems are the understanding of the effects of phonons, and the relationship with magnetism.

In conclusion, we have shown that polarons and excitons of charge transfer origin arise quite naturally in the p-d model for HTSC and could provide a qualitative explanation for several experiments. We believe that these nonlinear excitations play an important role in the physics of HTSC.

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