FINITENESS OF THE HOPPING INDUCED ENERGY CORRECTIONS
IN CUPRATES

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Received March 2, 2009

The paper continues the rigorous investigations of the mean field Green
function solution of the effective two-dimensional two-band Hubbard model
[N. M. Plakida et al., Phys. Rev. B, 51, 16599 (1995)] of the superconducting phase
transitions in cuprates, started in [Gh. Adam, S. Adam, J. Phys. A: Math. Theor., 40,
11205 (2007)]. Discussion of the (δ, T) phase diagram of the model points to the
divergence of the energy spectrum in the limit of vanishing doping δ. Finite energy
spectra at all possible doping rates δ are obtained provided the hopping part of the
effective Hamiltonian is renormalized with an effective factor pointing to the site-
pairs availability for fermion hopping processes.

1. INTRODUCTION

More than two decades after the discovery of the high critical temperature
superconductivity in cuprates, a theoretical model able to describe consistently
the corresponding phase transition is still missing. An attractive candidate is the
effective two-dimensional two-band Hubbard model derived by Plakida et al. [1]
from the more cumbersome three-band p-d model [2, 3] by use of projection
techniques based on cell-cluster perturbation theories [4–6] which provide a
hierarchy of the various interaction terms.

The present paper is devoted to the scrutiny of the two-band Hubbard
model from the point of view of its consistency with a number of essential
features of the cuprates. The starting point of this investigation is provided by
the rigorous results reported [7] for the generalized mean field approximation
(GMFA) solution of the thermodynamic Green function (GF) matrix of the
model [8, 9]. We find that, in order to get consistent solutions everywhere within
a given cuprate family, including its reference stoichiometric structure, the
doping rate δ is to enter explicitly the model Hamiltonian as a renormalization
factor of the Hubbard 1-forms which define the fermion hopping conduction
neighbourhoods of the spin lattice sites.
The paper starts with the discussion of the cuprate features which are explicitly included into the basic model hypotheses, as well as with other features which have to be accommodated within the model solution to get a consistent description of the properties of the cuprates (section 2). The Hamiltonian of the model [1] is then rewritten in an algebraically equivalent form (section 3) which allows easy identification of the various contributions to the GMFA-GF solution. The rigorous solution of the GMFA-GF matrix of the model is rewritten in an alternative form which explicitly points to the energy spectrum divergence in the limit of vanishingly small doping rates $\delta$ (section 4). A way to secure spectrum finiteness over the cuprate families is discussed in section 5. The paper ends with conclusions in section 6.

2. ESSENTIAL FEATURES OF CUPRATES

2.1. CuO$_2$ PLANES EMBEDDED IN LAMELLAR STRUCTURES

Irrespective of the specific details of their chemical composition, the cuprates show lamellar perovskite structures in the $(a, b)$ plane, carrying as distinctive elements the CuO$_2$ planes, separated from each other along the $c$-axis by intermediate planes or other structures of various compositions. Some of these intermediate structures have the role to cement the crystal structure, while other (charge reservoir layers in some cuprates, chain layers in other cuprates [10]) provide means for the manipulation of the doping level inside the CuO$_2$ planes which are generally assumed to bring the overwhelming contribution to the superconductivity in cuprates.

Taking into account the weak connection with each other of the CuO$_2$ planes, the quasi-two-dimensional behaviour of the superconducting properties of the cuprates is simplified, within the effective two-dimensional two-band Hubbard model, to a single CuO$_2$ plane. Then the effects coming from the weak inter-planar interaction among the CuO$_2$ planes are incorporated via effective parameters into the model.

While Geballe and Koster [10] speculate about possible important contributions to the superconducting pairing coming from structures lying outside the CuO$_2$ planes, the correct estimate of their relative magnitude cannot be obtained unless the quantitative CuO$_2$ plane contributions are estimated.

2.2. EXISTENCE OF THE FERMI SURFACE

Fermi surface sheets in well prepared cuprate single crystals have been undoubtedly evidenced, first, by 2D-ACAR positron spectroscopy at the
beginning of the nineties [11–13] and then by ARPES and optical methods [14]. This result is of paramount importance for the detailed description of the superconducting phase transition. The existence of the Fermi surface selects from the energy band structure contributed by the outer $d$-electron levels of the Cu ions and the outer $p$-electron levels of the O ions entering the CuO$_2$ planes only those energy bands which lay nearest to the Fermi level of the cuprates.

2.3. THE CHARGE TRANSFER INSULATOR NATURE OF CUPRATES

The identification of the energy bands staying nearest to the Fermi surface follows from the hierarchy of the interactions resulting in energy level splittings and hybridizations inside these compounds.

The crystal field effects coming from the symmetries of the crystalline structure at the Cu and O sites inside the CuO$_2$ planes determine specific splittings of the Cu 3$d$ levels and O 2$p$ levels [14]. In the hole representation, where the vacuum state is defined by filled Cu 3$d^{10}$ and O 2$p^6$ states, the resulting copper one-hole $d_{x^2-y^2}$ state and the two oxygen one-hole $p_x(x)$ and $p_y(y)$ states inside a given elementary cell belong to a same irreducible representation of the point group symmetry of the cuprate. They will therefore hybridize among themselves resulting in characteristic energy band structures around the Fermi level.

The three parameters which determine the main features of this energy band structure ($U$ – the strength of the electrostatic repulsion among the electrons, $\Delta$ – the $p$-$d$ interband splitting, and $W$ – the band width) satisfy $U > \Delta > W$, which points to the charge transfer insulator nature [15] of the cuprates. Two important consequences follow.

First, the hybridization of the copper $d_{x^2-y^2}$ hole with the oxygen $p_x(x)$ and $p_y(y)$ holes results in two one-hole mixed (predominantly oxygen) $p$-$d$ states. This interaction inside the elementary cell of the cuprate singles out the characteristic Zhang-Rice (ZR) singlet [16], such that the two energy bands lying nearest to the Fermi level are the ZR band and the upper Hubbard (UH) band. Thus, the effective two-band model of the superconducting phase transition in cuprates retains from the complete set of $p$-$d$ bands inside the CuO$_2$ plane precisely the ZR and UH bands and incorporates the overall small effects coming from the other bands into the parameters of the model.

Second, since $\Delta \approx 2W$, the resulting model Hamiltonian corresponds to the strong correlation limit. This leads to considerable complications in the mathematical characterization of the system excitations originating in inelastic interactions since the kernel of the resulting integral representations of the corresponding Green functions is not separable.
2.4. ROLE OF THE DOPING: CUPRATE FAMILIES

A high critical temperature superconductor does not simply exist as a well defined stoichiometric structure. It belongs to a family of cuprates (e.g., LSCO, YBCO, etc.), characterized by the occurrence of a characteristic stoichiometric reference structure and its specific kind of doping (either with holes, giving rise to a hole doped cuprate family, or with electrons, giving rise to an electron doped cuprate family). Within each family, the modification of the doping rate δ results in drastic modifications of the physical properties.

The reference structure is an insulator characterized by a strong antiferromagnetic exchange interaction (the highest known values of the antiferromagnetic exchange parameters occur in cuprates [17]). While the antiferromagnetic ordering is preserved at doping rates \( \delta < \delta_{cr} \), a doping range exists, \( \delta_{cr} < \delta < \delta_{cr}^2 \), at which a superconducting phase transition occurs with a doping dependent measured onset critical temperatures, \( T_c = T_c(\delta) \). At some optimum doping rate, \( \delta = \delta_{opt} \in (\delta_{cr}, \delta_{cr}^2) \), the critical temperature \( T_c \) reaches a maximum which allows the characterization of the cuprate as a high critical temperature superconductor. As a consequence, a given cuprate family exhibits a characteristic \((\delta, T)\) phase diagram (see, e.g., [14, 18, 19]).

A consistent theoretical model has to give full account of the \((\delta, T)\) phase diagram, with correct reproduction of the antiferromagnetic ordering at zero and low doping rates, of the characteristic properties measured in the underdoped \((\delta < \delta_{opt})\) and the overdoped \((\delta > \delta_{opt})\) regimes respectively and, of course, to predict correctly the optimum doping rate \( \delta = \delta_{opt} \) at which the critical superconducting temperature reaches its maximum across the family.

2.5. THE EFFECTIVE SPIN LATTICE

The stoichiometric reference structure \((\delta = 0)\) of a cuprate family is an insulator characterized by a very large gap \((\Delta \sim 2 \text{ eV}) [19, 20]\) between the two subbands lying nearest to the Fermi level. As a consequence, its electron (hole) states are frozen at the nodes \(i\) of the two-dimensional regular lattice defined by the positions of the copper ions inside the CuO\(_2\) plane.

The essentials of the behaviour of the system are preserved if the actual CuO\(_2\) lattice is replaced by an effective two-dimensional spin lattice having the spins placed at the copper sites inside the CuO\(_2\) plane. Three consequences are immediate for the characterization of the effective spin lattice. First, the spin lattice constants, \(a_x\) and \(a_y\), are given by the lattice constants of the physical CuO\(_2\) plane. Second, since the reference physical structure shows antiferromagnetic
ordering, any pair of two first order neighbouring spins within the reference effective spin lattice have the spins ordered in opposite directions. Third, there are four such possible states at each lattice site \( i \) in the effective spin lattice: \( |0\rangle \) (vacuum), \( |\uparrow\rangle \) and \( |\downarrow\rangle \) (single particle spin states inside the hole subband), and \( |2\rangle = |\uparrow\downarrow\rangle \) (singlet state in the singlet subband).

The doping of the electron states within the physical CuO\(_2\) plane is equivalent to the creation of defects inside the spin lattice by means of either spin vacancies and/or singlet states. As a consequence of the occurrence of spin defects, the spin lattice ceases to be frozen: hopping conduction arises.

2.6. HUBBARD OPERATOR DESCRIPTION OF HOPPING

The fact that the single d electron states are tightly-bound at the sites of the copper ions within the CuO\(_2\) lattice accounts for the unusually low conduction rate in the doped cuprates. As a consequence, adequate description of the hopping processes between the effective lattice spin sites is got [1] in terms of the Hubbard operators (HOS) [21], \( X_i^{\alpha\beta} = |\alpha\rangle \langle \beta| \), where \( |\alpha\rangle \) and \( |\beta\rangle \) denote the initial, respectively final spin states at the spin lattice site \( i \).

At every spin lattice site \( i \) the Hubbard operator multiplication rule holds

\[
X_i^{\alpha\beta} X_i^{\gamma\eta} = \delta_{\beta\eta} X_i^{\alpha\gamma},
\]

together with the completeness relation which secures the rigorous fulfillment of the Pauli exclusion principle,

\[
X_i^{00} + X_i^{\sigma\sigma} + X_i^{\overline{\sigma}\overline{\sigma}} + X_i^{22} = 1.
\]

The single spin state creation/annihilation in a subband are described by fermionic HOs, while the singlet creation/annihilation, spin or charge densities, particle numbers, are described by bosonic HOs. Therefore, the Hubbard operator algebra is defined both in terms of anticommutation and commutation relations. For a pair of fermionic HOs, the anticommutator rule holds

\[
\{X_i^{\alpha\beta}, X_j^{\gamma\eta}\} = \delta_{ij} (\delta_{\beta\eta} X_i^{\alpha\gamma} + \delta_{\alpha\gamma} X_i^{\beta\eta}),
\]

whereas, if one or both HOs are bosonic, the commutation rule holds

\[
[X_i^{\alpha\beta}, X_j^{\gamma\eta}] = \delta_{ij} (\delta_{\beta\eta} X_i^{\alpha\gamma} - \delta_{\alpha\gamma} X_i^{\beta\eta}).
\]

Since there are two kinds of inhomogeneities (vacancies and singlets) introduced by the doping inside the spin lattice, two fundamentally different hopping conduction processes will happen: fermion hopping (of single spins to vacancies
inside the spin lattice or single spin interband transitions) and *boson hopping* (of singlet spin pairs to vacancies inside the spin lattice).

2.7. HOPPING CONDUCTION NEIGHBOURHOOD OF A SPIN LATTICE SITE

Projection techniques based on cell-cluster perturbation theory [4–6] showed that the relative intensity of the hopping process relating the sites \( i \) and \( m \) of the spin lattice is determined by the non-vanishing Wannier coefficient \( \nu_{im} \) following from the overlap of the wave functions of the \( d \)-copper and \( p \)-oxygen states. The coefficients \( \nu_{im} \) show (non-exponential) decrease with the distance \( r_{im} = |\mathbf{r}_m - \mathbf{r}_i| \) inbetween the sites \( i \) and \( m \). Significantly different from zero are the Wannier coefficients within the first three coordination spheres around a given reference site \( i \). An instance of typical values is [1, 22]: for the nearest neighbouring (nn) \( m \)-sites (the first coordination sphere), \( \nu_{im} \sim \nu_1 = 0.14 \); for the next nearest neighbouring (nnn) \( m \)-sites (the second coordination sphere), \( \nu_{im} \sim \nu_2 = -0.13 \nu_1 \), while for the \( m \)-sites located at the third coordination sphere, \( \nu_{im} \sim \nu_3 = 0.16 \nu_1 \).

The scrutiny of the hopping part of the Hamiltonian of the effective two-band Hubbard model [1] showed [7] (see also [23]) that a hopping conduction neighbourhood of a given spin lattice site \( i \) can be defined in terms of the Hubbard 1-form of labels \( (\alpha\beta, \gamma\eta) \),

\[
\tau^{\alpha\beta;\gamma\eta}_{ij} = \sum_{m,n} \nu_{nm} X^{\alpha\beta}_{im} X^{\gamma\eta}_{mj}, \quad (\tau^{\alpha\beta;\gamma\eta}_{ij})^\dagger = -\tau^{\beta\alpha;\eta\gamma}_{ij}. \tag{5}
\]

The actual labels \( (\alpha\beta, \gamma\eta) \) are defined by the available in-band or inter-band transitions within the effective spin lattice.

2.8. FINITE HOPPING INDUCED ENERGY CORRECTION EFFECTS

The creation of defects inside the spin lattice by doping has two kinds of consequences on the normal state of a cuprate. First, the emergence of hopping processes result in the occurrence of hopping conductivity. Second, since the hopping causes finite modifications of a small fraction of the electron states in the neighbourhoud of the Fermi surface, the correlations stemming from hopping induce *finite* corrections to the energy spectrum of the compound. The fulfillment of this condition by the mean field energy spectrum which follows from the effective two-band Hubbard model will be shown in section 5 to ask for a non-trivial modification of the hopping part of its Hamiltonian.
2.9. UNCONVENTIONAL ANOMALOUS PAIRING IN CUPRATES

Experimental measurements resulting in inferences on the pairing mechanism in cuprates concern the charge and the spin of the superconducting current carriers, as well as the phase of the energy gap $\Delta(k)$. Until the discovery of the cuprates, it was known that the anomalous pairing yielding zero spin and charge $2e$ Cooper pairs in the superconducting phase stems from the lattice phonon mediated interaction between conduction electron pairs in metallic samples. This $s$-wave pairing mechanism, which results in a gap function $\Delta(k)$ that preserves the symmetry of the Fermi surface of the compound, was initially assumed in many papers to work in the cuprates as well.

Flux quanta measurements in cuprates at temperatures lower than $T_c$ evidenced that the superconducting current is carried by electron pairs having the charge $2e$ [24], while the small but significant drop off of the Cu Knight shift below $T_c$ [25] pointed to singlet pairing in cuprates.

Soon after the discovery of the cuprates, P. W. Anderson [26] assumed that the pairing mechanism should be unconventional. For the time being, there are several classes of models the starting hypotheses of which predict the occurrence of a $d_{x^2-y^2}$-pairing mechanism. The two-dimensional two-band Hubbard model results in a static $d_{x^2-y^2}$-pairing exchange mechanism (see [9] and [7]). The inelastic correlation effects beyond the GMFA solution add a $d_{x^2-y^2}$-pairing spin fluctuation mechanism as well [9].

This $d$-pairing mechanism results in a gap function $\Delta(k)$ the symmetry of which is lower than that of the Fermi surface. Phase-sensitive experiments, measuring the phase shifts in a dc SQUID involving a corner Josephson junction [27], or detecting half-flux quanta in a frustrated geometry [28], revealed that the occurrence of a robust $d_{x^2-y^2}$-pairing is a common feature of both the hole-doped and electron-doped cuprates. In hole-doped cuprates like YBCO, showing a small orthorhombic distortion from the tetragonal reference lattice in the CuO$_2$ plane, a small additional $s$-wave component was also evidenced.

The phase-sensitive Andreev–Saint-James spectroscopy data [29] confirmed these findings.

2.10. SUPERCONDUCTING PHASE KINETIC ENERGY MINIMIZATION

The occurrence of the superconducting phase below some critical temperature $T_c$ happens as a result of the minimization of the total energy of the system by the correlated spin configuration of Cooper pairs to a value which is lower as compared to that of the normal Fermi-liquid state.
In the conventional superconductors, the electron-phonon interaction mechanism, which yields, below $T_c$, ordered Cooper pairs within a manifold of the electron states lying near the Fermi level, results in significant minimization of the potential energy of the system.

Experimental data concerning the energy distribution of the superconducting phase in cuprates [30, 31] have shown that this associates the minimization of the kinetic energy of tightly bound pairs of electron states. Therefore, the anomalous pairing within a model consistent with these data is to involve essentially the kinetic energy (i.e., hopping), while vanishing or small correction contributions coming from the potential energy terms.

The anomalous pairing within the two-dimensional two-band Hubbard model stems mainly from the hopping part of the model Hamiltonian [9, 7], hence it is of kinetic origin.

2.11. SPIN-CHARGE SEPARATION

The spin-charge separation in cuprates, was shown by P. W. Anderson [19] to provide natural understanding of the anomalous cuprate behaviour occurring in all the four distinct phases of a $(\delta, T)$ phase diagram: the normal metallic phase, the pseudogap state separated from the previous one by the temperature $T^* = T^*(\delta)$, the $d$-wave superconducting phase, and the antiferromagnetically ordered phase which occurs at vanishing doping or in the underdoped regime.

As recently discussed in [23, 33], the spin-charge separation is recovered in the GMFA rigorous solution of the two-band Hubbard model [7] as a consequence of the fact that the spin-charge correlation matrix elements vanish exactly.

3. STANDARD MODEL HAMILTONIAN

Using (5), the Hamiltonian of the effective two-band Hubbard model [1] can be rewritten in the locally manifest Hermitian form

$$H = H_0 + H_h,$$

with the single particle contribution

$$H_0 = \sum_i h_{0,i}, \quad h_{0,i}^\dagger = h_{0,i},$$

$$h_{0ij} = E_1 \sum_\sigma X_1^{\sigma\sigma} + E_2 X_2^{22},$$

and the hopping contribution
The hopping induced energy corrections in cuprates

\[ H_h = \sum_i h_{h,i}, \quad h_{h,i}^\dagger = h_{h,i}, \]

\[ h_{h,i} = \frac{K_{11}}{2} \sum_\sigma (\tau_{1,0,0,0,0}^{\sigma} - \tau_{1,0,0,0,0}^{\sigma}), + \frac{K_{22}}{2} \sum_\sigma (\tau_{1,0,\sigma,2,0}^{2,\sigma} - \tau_{1,0,\sigma,2,0}^{2,\sigma}) + \frac{K_{21}}{2} \sum_\sigma 2\sigma \left[ (\tau_{1,0,0,0,0}^{\sigma} - \tau_{1,0,0,0,0}^{\sigma}) + (\tau_{1,0,0,0,0}^{\sigma} - \tau_{1,0,0,0,0}^{\sigma}) \right]. \]  

(8)

In these equations the summation label \( i \) runs over the sites of an infinite two-dimensional lattice with the lattice constants \( a_x \) and \( a_y \) respectively defined by the crystal structure of the cuprate. The spin projection values in the sums over \( \sigma \) are \( \sigma = \pm 1/2, \quad \bar{\sigma} = -\sigma \).

In (6), \( E_1 = \tilde{\epsilon}_d - \mu \) denotes the hole subband energy for the renormalized energy \( \tilde{\epsilon}_d \) of a \( d \)-hole and the chemical potential \( \mu \). The energy parameter of the singlet subband is \( E_2 = 2E_1 + \Delta \), where \( \Delta \approx \Delta_{pd} = e_p - e_d = 2 \text{ eV} \) is an effective Coulomb energy \( U_{\text{eff}} \) corresponding to the difference between the two energy levels of the model. The hopping energy parameters \( K_{ab} = 2t_{pd}K_{pd} \) depend on \( t_{pd} \), the hopping \( p-d \) integral, and on energy band dependent form factors \( K_{ab} \). The label 1 points to the hole subband, while 2 to the singlet subband. Inband (\( K_{11} = K_{22} \)) and interband (\( K_{21} = K_{12} \)) processes are present.

The quasi-particle spectrum and the superconducting pairing within the Hamiltonian (6) are obtained [8, 9] by the equation of motion technique for the retarded and advanced two-time \( 4 \times 4 \) GF matrices in the \( (r, t) \)-representation, which represent a single matrix in the \( (q, \omega) \)-representation. The GMFA solution of this matrix is summarized in the next section.

4. MEAN-FIELD APPROXIMATION

The Green function matrices of the model define space-time correlations for the four-component Nambu column operator [8, 9]

\[ \hat{X}_{ij} = (X_i^{\sigma,0} X_j^{\Omega,0} X_i^{\sigma,0} X_j^{\Omega,0}) \]  

(9)

and its adjoint operator \( X_j^{\dagger} = (X_j^{\sigma,0} X_j^{\Omega,0} X_j^{\sigma,0} X_j^{\Omega,0}) \). In (9), the superscript \( \top \) denotes the transposition.

The retarded GF matrix is written, in Zubarev notation [32], as follows

\[ \tilde{G}_{ij}^{(r)}(t-t') = \left\langle \left\langle \hat{X}_{ij}(t) \right| \hat{X}_{ij}^{\dagger}(t') \right\rangle = -i\theta(t-t') \langle \langle \hat{X}_{ij}(t), \hat{X}_{ij}^{\dagger}(t') \rangle \rangle \]  

10

where \( \langle \cdots \rangle \) denotes statistical average over Gibbs grand canonical ensemble.
The advanced GF matrix replaces in (10) the temporal factor by $i\theta(t' - t)$.

The GF matrix in the $(r, \omega)$-representation is related to the GF matrix in the
$(r, t)$-representation by the non-unitary Fourier transform,

$$
\tilde{G}_{ij\sigma}(t - t') = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{G}_{ij\sigma}(\omega) e^{-i\omega(t - t')} d\omega,
$$

where the superscripts $(r)$ and $(a)$ have been omitted.

The analytic continuations of the retarded and advanced Green functions in
the complex energy $\omega$-plane define a single complex function, denoted $\tilde{G}_{ij\sigma}(\omega)$,
with cuts (jumps) along the real energy axis.

The energy spectrum of the Hamiltonian (6) is solved in the reciprocal
space. The GF matrix in this $(q, \omega)$-representation is related to the GF matrix in
$(r, \omega)$-representation by the non-unitary discrete Fourier transform

$$
\tilde{G}_{ij\sigma}(\omega) = \frac{1}{N} \sum_{q} e^{-i\mathbf{q} \cdot \mathbf{r}_{j} - i\mathbf{q} \cdot \mathbf{r}_{i}} \tilde{G}_{\sigma}(q, \omega).
$$

For an elemental Green function of labels $(\alpha\beta, \gamma\eta)$, we use the notation
\( \langle X_i^{\alpha\beta}(t) \middle| X_j^{\gamma\eta}(t') \rangle \)
in the $(r, t)$-representation and, similarly, \( \langle X_i^{\alpha\beta} \middle| X_j^{\gamma\eta} \rangle \)
(assuming Hubbard operators at $t = 0$), in the $(r, \omega)$-representation. In the
$(q, \omega)$-representation, it is convenient to use the notation $G^{\alpha\beta, \gamma\eta}(q, \omega)$.

We shall consider henceforth the GMFA-GF, $\tilde{G}_{0}(q, \omega)$ in the form [7],

$$
\tilde{G}_{\alpha}(q, \omega) = \tilde{\chi} \left( \tilde{\chi}_{\alpha} - \tilde{A}_{\alpha}(q) \right)^{-1} \tilde{\chi}; \quad \tilde{\chi} = \left\{ \tilde{X}_{i\alpha}, \tilde{X}_{i\alpha}^{\dagger} \right\};
$$

$\tilde{A}_{\alpha}(q) = \sum_{j} e^{i\mathbf{q} \cdot \mathbf{r}_{j}} \tilde{A}_{ij\alpha}; \quad \mathbf{r}_{j} = \mathbf{r}_{j} - \mathbf{r}_{i}; \quad \tilde{A}_{ij\alpha} = \left\{ \left[ \tilde{X}_{ij\alpha}, H \right], \tilde{X}_{ij\alpha}^{\dagger} \right\}.
$$

Two kinds of particle number operators, related to the singlet subband,

$$
n_{i\alpha} = X_{i}^{\sigma\sigma} + X_{i}^{22}, \quad n_{\sigma} = X_{i}^{\sigma\sigma} + X_{i}^{22}, \quad N_{i} = n_{i\alpha} + n_{i\bar{\alpha}},
$$

and to the hole subband respectively,

$$
n_{i\bar{\alpha}} = X_{i}^{\bar{\sigma}\bar{\sigma}} + X_{i}^{00}, \quad n_{\bar{\sigma}} = X_{i}^{\bar{\sigma}\bar{\sigma}} + X_{i}^{00}, \quad N_{i}^{h} = n_{i\bar{\alpha}} + n_{i\bar{\bar{\alpha}}},
$$

can be defined. The completeness relation implies $n_{i\alpha} + n_{i\bar{\alpha}} = n_{\sigma} + n_{\bar{\sigma}} = 1$.

The $\tilde{\chi}$ matrix in (13) is diagonal,
\[ \tilde{\chi} = \begin{pmatrix} \tilde{\chi} & 0 \\ 0 & \tilde{\chi} \end{pmatrix}, \quad \tilde{\chi} = \begin{pmatrix} \chi_2 & 0 \\ 0 & \chi_1 \end{pmatrix}, \quad \tilde{\rho} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}, \]

(17)

where \( \chi_2 \) and \( \chi_1 \) denote spin and site independent averages,

\[ \chi_2 = \langle n_{\alpha \sigma} \rangle = \langle n_{\sigma \alpha} \rangle; \quad \chi_1 = \langle n_{\alpha \sigma}^h \rangle = \langle n_{\sigma \alpha}^h \rangle = 1 - \chi_2. \]

(18)

In terms of the doping rate \( \delta \), it results that in the hole-doped cuprates,

\[ \chi_2 = \delta, \quad \chi_1 = 1 - \delta, \]

(19)

while in the electron-doped cuprates,

\[ \chi_1 = \delta, \quad \chi_2 = 1 - \delta. \]

(20)

To understand the consequences following for the energy spectrum, we rewrite the GMFA-GF (13) in the algebraically equivalent form

\[ \tilde{G}_0^\sigma(q, \omega) = \tilde{\chi}^{1/2} \left[ I \omega - \tilde{\varepsilon}_\sigma(q) \right]^{-1} \tilde{\chi}^{-1/2}, \]

(21)

where \( I \) denotes the \( 4 \times 4 \) unit matrix, while \( \tilde{\varepsilon}_\sigma(q) \) is the Hermitian matrix

\[ \tilde{\varepsilon}_\sigma(q) = \tilde{\chi}^{-1/2} \tilde{A}_\sigma(q) \tilde{\chi}^{-1/2}. \]

(22)

The GMFA spectrum of the model Hamiltonian (6) is therefore given by the eigenvalues of \( \tilde{\varepsilon}_\sigma(q) \). Using the results reported in [7], we get

\[ \tilde{\varepsilon}_\sigma(q) = \begin{pmatrix} \tilde{E}_\sigma(q) & \tilde{\phi}_\sigma(q) \\ (\tilde{\phi}_\sigma(q))^\dagger & -(\tilde{E}_\sigma(q))^\dagger \end{pmatrix}. \]

(23)

The normal correlations contribute the \( 2 \times 2 \) matrices,

\[ \tilde{E}_\sigma(q) = \begin{pmatrix} C_{22} & 2\sigma C_{21} \\ 2\sigma C_{21}^* & C_{11} \end{pmatrix}, \quad -(\tilde{E}_\sigma(q))^\dagger = \begin{pmatrix} -C_{22} & 2\sigma C_{21}^* \\ 2\sigma C_{21} & -C_{11} \end{pmatrix}, \]

(24)

with the distinct matrix elements

\[ C_{22} \equiv C_{22}(q) = (E_i + \Delta) + [a_{22} + d_{22}(q)]/\chi_2 \]

(25)

\[ C_{11} \equiv C_{11}(q) = E_i + [a_{22} + d_{11}(q)]/\chi_1 \]

(26)

\[ C_{21} \equiv C_{21}(q) = [a_{21} + d_{21}(q)]/\sqrt{\chi_1 \chi_2} \]

(27)

Here \( a_{mn} \) and \( d_{mn}(q) \) denote respectively the one-site and two-site contributions to the matrix \( \tilde{A}_\sigma(q) \) coming from the hopping Hamiltonian (8):
\[ a_{22} = k_{11} \left\langle \tau_{1}^{0|\sigma, \sigma^0} \right\rangle - k_{22} \left\langle \tau_{1}^{0|\sigma^2, 2\sigma} \right\rangle, \]

(28)

\[ a_{21} = (k_{11} - k_{22}) \cdot 2 \sigma \left\langle \tau_{1}^{0|\sigma, \sigma^0} \right\rangle + k_{21} \left( \left\langle \tau_{1}^{0|\sigma^2, 2\sigma} \right\rangle - \left\langle \tau_{1}^{0|\sigma^2, 2\sigma} \right\rangle \right), \]

(29)

\[ d_{mn}(q) = k_{mn} \sum_{a=1}^{3} v \alpha \gamma \alpha (q) [\chi_{\alpha}^\delta + (-1)^{m+n} \chi_{m+n}] + \frac{1}{2} J_{mn} \chi_{s-h}(q). \]

(30)

Here and in what follows, \( \left\langle \tau_{1}^{\lambda|\mu, \nu|\varphi} \right\rangle \) denotes the site-independent average of the Hubbard 1-form (5),

\[ \left\langle \tau_{1}^{\lambda|\mu, \nu|\varphi} \right\rangle = \sum_{a=1}^{3} v \alpha \cdot \frac{1}{N} \sum_{q} \left\langle X_{\lambda|\mu, \nu|\varphi} \right\rangle q \gamma \alpha (q) \]

(31)

for all the label sets \( (\lambda, \mu, \nu, \varphi) \) of interest. Further,

\[ \left\langle X_{\lambda|\mu, \nu|\varphi} \right\rangle q = \frac{i}{2\pi} \int_{-\infty}^{+\infty} \frac{d \omega}{1 + e^{-\beta \omega}} [G_{\lambda|\mu, \nu|\varphi}(q, \omega + i\epsilon) - G_{\lambda|\mu, \nu|\varphi}(q, \omega - i\epsilon)], \]

(32)

while the quantities \( \gamma \alpha (q) \) denote the nn \( (\alpha = 1) \), nnn \( (\alpha = 2) \), and third neighbour \( (\alpha = 3) \) geometrical form factors, \( \gamma_{1}(q) = 2[\cos(q_{x}a_{x}) + \cos(q_{y}a_{y})] \), \( \gamma_{2}(q) = 4 \cos(q_{x}a_{x}) \cos(q_{y}a_{y}) \), \( \gamma_{3}(q) = 2[\cos(2q_{x}a_{x}) + \cos(2q_{y}a_{y})] \).

In equation (33), \( \chi_{\alpha}^\delta [\alpha = 1, 2, 3] \) denote the nn, nnn, and third coordination sphere parameters respectively coming from the phenomenological representation of the spin-spin correlation function \( \left\langle S_{i} S_{j} \right\rangle \).

The exchange energy parameters are given by

\[ J_{mn} = 4 k_{mn} k_{21}/\Delta, \quad \{mn\} \in \{22, 11, 21\}. \]

(33)

Finally, the singlet hopping contribution \( \chi_{s-h}(q) \) is given by

\[ \chi_{s-h}(q) = \sum_{\alpha=1}^{3} v \alpha^2 \cdot \frac{1}{N} \sum_{k} \Xi_{k} \gamma \alpha (q - k) \]

(34)

where \( \Xi_{k} = 2 \sigma \left\langle X_{\alpha}^{0|\sigma, \sigma^0} \right\rangle k \), while \( \Xi_{k} = 2 \sigma \left\langle X_{\alpha}^{0|\sigma^2, 2\sigma} \right\rangle k \) for hole-doped and electron-doped cuprates respectively, with averages defined by (32).

The anomalous correlations contribute to (23) the \( 2 \times 2 \) matrices,
The hopping induced energy corrections in cuprates

\[
\hat{\phi}_\alpha(q) = \begin{pmatrix}
-2\sigma T_2 & T_{21} \\
-T_{21} & 2\sigma T_1
\end{pmatrix}; \quad \left(\hat{\phi}_\alpha(q)\right)^\dagger = \begin{pmatrix}
-2\sigma T_2^* & -T_{21}^* \\
T_{21}^* & 2\sigma T_1^*
\end{pmatrix}
\] (35)

where

\[
T_2 = T_2(q) = [K_{22}b_1 + (1-\delta)\xi_2 b_2(q) + \delta \tilde{\xi}_2 b_3(q)]/\chi_2
\] (36)

\[
T_1 = T_1(q) = [K_{11}b_1 + (1-\delta)\tilde{\xi}_1 b_2(q) + \delta \xi_1 b_3(q)]/\chi_1
\] (37)

\[
T_{21} = T_{21}(q) = [K_{21}b_1 + (1-\delta)\xi_2 b_2(q) + \delta \tilde{\xi}_2 b_3(q)]/\sqrt{\chi_1 \chi_2}
\] (38)

with the two-site exchange energies \(\xi_1 = J_{21}\) and \(\xi_2 = (J_{11} + J_{22})/2\).

The anomalous one-site pairing matrix elements are given by Hubbard 1-form averages (31),

\[
b_1 = \sum_\sigma 2\sigma \langle \tau_1^{\sigma_1,\sigma_2} \rangle = \sum_\sigma 2\sigma \langle \tau_1^{0\sigma,0\sigma} \rangle,
\] (39)

where the first expression is to be used for hole-doped cuprates, while the second one for electron-doped cuprates.

The anomalous two-site pairing matrix elements following from the reduction to localized Cooper pairs [7] are

\[
b_2(q) = \sum_{\alpha=1}^3 v_\alpha \cdot \frac{1}{N} \sum_k \Pi_k \gamma_\alpha(q - k)
\] (40)

where \(\Pi_k = 2\sigma \langle X^{\alpha_1} X^{\alpha_2} \rangle_k\), while \(\Pi_k = 2\sigma \langle X^{0\alpha_1} X^{0\alpha_2} \rangle_k\) for hole-doped and electron-doped cuprates respectively, with averages defined in (32).

The anomalous three-site pairing matrix elements following from the reduction to localized Cooper pairs [7] and the splitting of the three-site terms as done in [33] are

\[
b_3(q) = \Pi_k^{(3)} \sum_{\alpha=1}^3 v_\alpha \cdot \gamma_\alpha(q)
\] (41)

where \(\Pi_k^{(3)} = 2\sigma \langle \tau_1^{\sigma_1,\sigma_2} \rangle_k\), while \(\Pi_k^{(3)} = 2\sigma \langle \tau_1^{0\sigma,0\sigma} \rangle_k\) for hole-doped and electron-doped cuprates respectively, with averages defined in (31).

5. MODIFIED HOPPING HAMILTONIAN

The results derived in the previous section provide the rigorous GMFA-GF solution for the energy matrix \(\tilde{\mathcal{E}}_\alpha(q)\) of the effective Hamiltonian (6). These
results have been derived assuming as starting hypotheses of the model six out of the eleven features discussed in section 2, namely those listed in the subsections 2.1–2.3 and 2.5–2.7.

The features discussed in subsections 2.9 and 2.10 are immediate consequences of the results reported in [9, 7] and in the previous section. The spin-charge separation (subsection 2.11) was shown in [23, 33] to be a straightforward consequence of the exact vanishing of the spin-charge correlation functions within the model.

The features mentioned in subsections 2.4 and 2.8 ask for the finiteness of all the terms of the matrix $\hat{E}_\sigma(q)$ at any value of the doping $\delta$, in particular at vanishing doping, $\delta = 0$.

From the equations (28)–(34) and (39)–(41), it results that both the normal and anomalous matrix elements coming from the hopping Hamiltonian (8) are finite in the limit of vanishing doping $\delta \to 0$.

Corroborating this result with the values (19) and (20) of the $\chi_1$ and $\chi_2$ parameters, from the equations (25)–(27) and (36)–(38) it results that, in the hole-doped cuprates, the normal terms $C_{22}(q)$ and $C_{21}(q)$, as well as the anomalous terms $T_2(q)$ and $T_{21}(q)$ become infinite in the limit $\delta \to 0$ due to the vanishing denominator $\chi_2$. Similarly, in the electron-doped cuprates, the normal terms $C_{11}(q)$ and $C_{21}(q)$, as well as the anomalous terms $T_1(q)$ and $T_{21}(q)$ become infinite in the same limit due to the vanishing denominator $\chi_1$.

A simple remedy to this inconsistency of the standard Hamiltonian of the model can be proposed from the scrutiny of the reduction process resulting in the effective Hamiltonian (6). The derivation of the hopping parameters was done under the hypothesis of occupied $d$-copper and $p$-oxygen states of interest. However, under doping, part of these orbitals is empty and this fact is to be reflected in the occurrence of an explicit doping rate dependence of the effective hopping parameters.

The simplest way is to assume the renormalization, with a convenient factor $\rho$, of the hopping Hamiltonian (8) as a whole. There are three possibilities to implement such a renormalization.

The first is to assume $\rho = \delta$. Such a hypothesis would induce, however, unphysical infinities in the theoretical limit $\delta \to 1$.

The second possibility is to assume $\rho = \min\{\chi_1, \chi_2\}$, which would cure both the limits $\delta \to 0$ and $\delta \to 1$, while inducing, however, some peculiarities (turning points at $\delta = 0.5$) in the doping dependence of both the normal and anomalous matrix elements entering $\hat{E}_\sigma(q)$.

The third possibility, which results in smooth dependence of the matrix elements of $\hat{E}_\sigma(q)$ on the doping rate $\delta \in [0, 1]$ is to define $\rho = \chi_1\chi_2$, which can
be understood as simply assuming the site-pairs availability for fermion hopping processes.

Under this hypothesis, the normal matrix elements (25)–(27) change to

\[ C_{22} = C_{22}(\mathbf{q}) = (E_1 + \Delta) + [a_{22} + d_{22}(\mathbf{q})] \cdot \chi_1 \]  
(42)

\[ C_{11} = C_{11}(\mathbf{q}) = E_1 + [a_{22} + d_{11}(\mathbf{q})] \cdot \chi_2 \]  
(43)

\[ C_{21} = C_{21}(\mathbf{q}) = [a_{21} + d_{21}(\mathbf{q})] \cdot \sqrt{\chi_1 \chi_2} \, , \]  
(44)

with the singlet hopping matrix element (34) replaced by

\[ \chi^{s-h}(\mathbf{q}) = \chi_1 \chi_2 \sum_{\alpha=1}^{3} v_{\alpha}^2 \cdot \frac{1}{N} \sum_{\mathbf{k}} \Xi_k \gamma_\alpha(\mathbf{q} - \mathbf{k}) \]  
(45)

The anomalous matrix elements (36)–(38) change now to

\[ T_2 = T_2(\mathbf{q}) = [\mathcal{K}_{22} b_1 + (1 - \delta) \xi_1 b_2(\mathbf{q}) + \delta \xi_1 b_3(\mathbf{q})] \cdot \chi_1 \]  
(46)

\[ T_1 = T_1(\mathbf{q}) = [\mathcal{K}_{11} b_1 + (1 - \delta) \xi_1 b_2(\mathbf{q}) + \delta \xi_1 b_3(\mathbf{q})] \cdot \chi_2 \]  
(47)

\[ T_{21} = T_{21}(\mathbf{q}) = [\mathcal{K}_{21} b_1 + (1 - \delta) \xi_2 b_2(\mathbf{q}) + \delta \xi_2 b_3(\mathbf{q})] \cdot \sqrt{\chi_1 \chi_2} \, , \]  
(48)

with the isotropic one-site pairing matrix element \(b_1\), Eq. (39), left unchanged, the two-site Cooper pair term (40) replaced by

\[ b_2(\mathbf{q}) = \chi_1 \chi_2 \sum_{\alpha=1}^{3} v_{\alpha}^2 \cdot \frac{1}{N} \sum_{\mathbf{k}} \Pi_k \gamma_\alpha(\mathbf{q} - \mathbf{k}) \]  
(49)

and the effective three-site term contribution (41) replaced by

\[ b_3(\mathbf{q}) = \chi_1 \chi_2 \cdot \Pi_{\mathbf{k}}^{(3)} \sum_{\alpha=1}^{3} v_{\alpha} \cdot \gamma_\alpha(\mathbf{q}) \]  
(50)

It is worthwhile to note that the crystallographic symmetry of the CuO\(_2\) lattice results in sizeable consequences on the relationships among the anomalous pairing matrix elements \(b_1, b_2(\mathbf{q}),\) and \(b_3(\mathbf{q})\).

In square CuO\(_2\) lattices, where \(a_x = a_y\) (e.g. for Bi-22(n-1)n, Tl-22(n-1)n, Hg-12(n-1)n, and Tl-12(n-1)n cuprate families with \(n = 1, 2, 3\)), due to the existence of the \(C_4\) rotation axis symmetry, the anomalous averages \(\langle \tau_{1}^{\sigma_2, \sigma_2} \rangle\) and \(\langle \tau_{1}^{0\sigma, \sigma} \rangle\) vanish identically. Therefore the isotropic anomalous one-site term \(b_1\), Eq. (39), and the three-site term \(b_3(\mathbf{q})\), Eq. (50), obtained after the splitting [23, 33] of the three-site higher order correlation terms ([7], section 6), equate to
zero, such that the anomalous contributions (46)–(48) to the energy matrix (23) essentially reduce to the two-site terms retained in [7].

The rectangular CuO$_2$ lattices (e.g., for the cuprate family YBCO), are very slightly different from square ones ($|a_x - a_y| \ll \min\{a_s, a_y\}$). Thus, after use of the $C_4$ rotation, small non-vanishing values of the anomalous averages $\langle \tau_1^{\sigma_2, \sigma_2} \rangle$ and $\langle \tau_1^{0\sigma_0, 0\sigma_0} \rangle$ arise. Then the terms $b_1$ and $b_2(\mathbf{q})$ in (46)–(48) are small almost everywhere inside the first Brillouin zone as compared to $b_2(\mathbf{q})$. Since the isotropic $b_1$ term points to the existence of an $s$-type contribution to the anomalous pairing, qualitative agreement exist with the experimental findings summarized in subsection 2.9. The three percent weight of the $s$-type pairing inferred from experiments in YBCO [34] might then be used as a constraint for tuning the values of the phenomenological hopping energy parameters of the model.

6. CONCLUSIONS

The scrutiny of the rigorous GMFA-GF solution of the Hamiltonian of the two-dimensional two-band Hubbard model of the superconducting phase transitions in cuprates [1] unveiled the occurrence of infinite quantities, stemming from hopping, in the matrix elements of the energy matrix $\hat{\mathcal{E}}_\sigma(\mathbf{q})$, Eq. (22), in the limit of the vanishing doping rates $\delta \to 0$.

An analysis of the essential features of the cuprates which follow both from experimental data and general theoretical representations shows that the abovementioned infinities originate in the procedure of deriving the Hamiltonian of the model, where the doping induced absence of part of the electron orbitals in the CuO$_2$ plane was ignored. A phenomenological approach to the inclusion of this feature into the model resulted in the modification of the effective hopping contribution to the Hamiltonian (6), namely,

$$H'_h = \chi_1 \chi_2 H_h,$$

with $H_h$ given by (8). Technically, this result may be viewed as a renormalization of the Wannier coefficients entering the Hubbard 1-forms (5) with the factor $\chi_1 \chi_2$ which expresses the availability of the spin states for fermion hopping transitions inside the hopping conduction neighbourhood of the reference spin lattice site $i$.

This leads, in the ($r, t$)-representation, to expressions of the hopping terms of the energy matrix $\hat{\mathcal{E}}_{ij\sigma}$ which simply multiply by a factor $\chi_1 \chi_2$ the corresponding quantities which have been obtained from $H_h$, Eq. (8).
The rigorous reduction of the order of correlation of the boson-boson statistical averages involving singlet hopping (normal hopping and anomalous charge-charge hopping correlations) brings supplementary $\chi_1\chi_2$ factors in the resulting expressions.

As a consequence, the normal correlation terms (23) as well as the anomalous correlation terms (35) remain finite at any doping rates $\delta$ both for the hole-doped and the electron-doped cuprates.

The detailed investigation of the consequences of this modification of the Hamiltonian of the two-dimensional two-band Hubbard model will be discussed elsewhere.

Acknowledgments. Partial financial support was secured by Romanian Authority for Scientific Research (Project 7/2006 SIMFAP).

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