

# Aspects of electronic structure of high $T_c$ cuprate superconductors

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## Abstract

In this paper, we explore some aspects of electronic structure calculations of high  $T_c$  superconducting cuprates. We begin with a look at the composition, structure and generic phase diagram of the cuprate superconductors. We then introduce the simplest and most commonly used models in the literature. We then go on to comment on whether calculations based on these models explain some experimental observations.

## 1 Introduction

The success of the BCS (Bardeen,Cooper,Schrieffer) theory was an important landmark in the microscopic understanding of superconductivity. The theory describes the pairing up of fermions (known as Cooper pairs) under an attractive interaction that overcomes the mutual Coloumb repulsion. In these so called 'classic' superconductors this attraction is often mediated by phonons. Since breaking a Cooper pair requires a finite amount of energy, the spectrum is characterized by a 'pairing' or 'superconducting gap'. The typical size of the Cooper pairs is 500 Å to 10000 Å which is much larger than the separation between pairs. This inherently allows for a mean field type approach.

However, the BCS theory explains only a very special class of superconductors - compounds whose normal state is a Landau Fermi liquid. In addition, we implicitly assume that the normal state is unstable to a superconducting phase alone and that there are no competing phase transitions. It turns out that this is quite incorrect for many other "exotic" superconductors.

A study of phonon assisted superconductivity had predicted an upper limit to  $T_c$  of about 30 K and the highest known  $T_c$  (in the early 1980's) was that of Nb<sub>3</sub>Ge - about 23.2 K [16]. This led most condensed matter theorists to believe that superconductivity was a well understood phenomenon. But in 1986, J.G. Bednorz and K.A. Muller [1] discovered superconductivity in a lanthanum based cuprate perovskite material (Ba-La-Cu-O system or LBCO) with a  $T_c$  of 35 K. The surprise in the discovery of this "high  $T_c$  superconductor" lay in the fact that this material was a "bad metal" in its normal state. This excitement resulted in a flurry of experiments and search for new exotic materials. Within a year of this remarkable discovery, M.K. Wu *et. al* [2] came up with a yttrium based cuprate with a  $T_c$  of 92 K viz. greater than the boiling point of nitrogen (77 K). At present, a ceramic compound of thallium, mercury, copper, barium, calcium and oxygen has the highest known  $T_c$  of 138 K.

At the time of writing this paper, there is also tremendous excitement about the recent discovery of the Fe-pnictide and Fe-Se superconductors. These compounds are interesting because they may help us understand a possible mechanism of high  $T_c$  superconductivity. In particular, orbital fluctuations seem to be responsible for pairing (compared to spin fluctuations in the case of cuprates). The  $T_c$ 's involved are moderately high (about 20-60 K) in contrast to uranium and cobalt based superconductors, which probably possess similar superconducting mechanisms but with much smaller  $T_c$  's (close to absolute zero). This is why the Fe based superconductors might be easier to study.

In addition to posing an academically exciting and unsolved challenge, a very important objective of the research in this field is to investigate the possibility of a room temperature superconductor. Such a discovery would be remarkable as it may revolutionize many technologies (and possibly solve the energy crisis!). At present, there is no experimental or theoretical evidence that forbids such a possibility and so the search continues.

The study of high  $T_c$  superconductivity began with the discovery of the cuprate superconductors. But even with thousands of papers on the subject, a complete theory of the cuprate superconductors eludes the condensed matter community. However, a lot of progress has been made on many fronts which A. Leggett summarises in his book [7],

1. It is almost sure that Cooper pairing is responsible for superconductivity in the cuprates. However treating them using a BCS mean field approach seems questionable because the pairs are much smaller (coherence length  $\xi \sim 12 - 15 \text{ \AA}$ ) than in the case of the classic superconductors.
2. About 200 odd superconducting cuprates with a variety of chemical compositions and lattice structures are known. The feature common to all of these is the  $\text{CuO}_2$  planes. This leads us to conclude that these planes are responsible for the superconductivity. Also it seems that  $T_c$  is dependent on the number of copper-oxide planes that are close enough to each other (indicating that interplane coupling may be significant).  $T_c$  seems generally to increase with number of planes within a homologous series (i.e. they are structures which differ only in the number of  $\text{CuO}_2$  layers per unit cell).
3. The orbital symmetry of the order parameter is  $d_{x^2-y^2}$  in comparison to  $s$  for the conventional BCS superconductors.
4. The chemical stoichiometry (eg. doping fraction) majorly influences the onset of superconductivity.
5. The route to superconductivity is probably not the electron-phonon interaction.

With this preview, I am ready to outline what is to come in the remainder of the paper. In section 2, I describe the composition and structure of some cuprates and present their generic phase diagram. In section 3, I go on to discuss some model hamiltonians for the  $\text{CuO}_2$  planes. In section 4, I discuss whether these models, correctly explain some observations. In section 5, I present some other aspects of the cuprate structure which influence its electronic structure.

## 2 Composition, structure and phase diagram of cuprates

In this section we analyze the structures of some cuprates. I follow the discussion in [6] as a reference.

## $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

$\text{La}_2\text{CuO}_4$  crystallizes in a body centered tetragonal structure (bct) known as the **T** structure as is shown in figure 1. Each Cu atom is embedded in an octahedron of oxygen atoms. This octahedron is not quite perfect - the inplane Cu-O bond length is significantly shorter (1.9 Å) compared to the Cu-O bond length (2.4 Å) along the  $c$  axis. The oxygens oriented along the  $c$ -axis are known as the 'apical' oxygens or simply  $\text{O}_z$ . They are part of the LaO planes which is the charge reservoir that controls the doping in the copper oxide planes. The  $\text{CuO}_2$  planes are 6.6 Å apart, separated by two LaO planes.

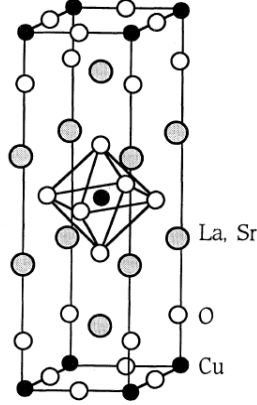


Figure 1: Crystal structure of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  Taken from Almasan and Maple (1991)

The atomic configurations of the elements forming this compound are  $\text{Cu}:[\text{Ar}](3d)^{10}(4s)$ ,  $\text{La}:[\text{Xe}](5d)(6s)^2$ ,  $\text{O}:[\text{He}](2s)^2(2p)^4$  and  $\text{Sr}:[\text{Kr}](5s)^2$ . Oxygen is in the  $\text{O}^{2-}$  configuration completing its  $p$  shell and lanthanum is in the  $\text{La}^{3+}$  configuration making it a stable closed shell electronic configuration. Since the compound is neutral, it follows that Cu must be in the  $\text{Cu}^{2+}$  state i.e. it loses the  $4s$  electron and one  $3d$  electron. Since  $\text{Cu}^{2+}$  has an unpaired spin in its  $d$  orbitals, it has a net spin of  $\frac{1}{2}$ .

Observe that  $\text{La}_2\text{CuO}_4$  compound has one electron per unit cell and so according to the standard (nearly free) electron band structure theory it must be a metal. But it turns out that the electrons are fairly localized and the compound is an insulator. This kind of insulator is known as a Mott insulator.

When the sample is doped with strontium (with the doping fraction indicated by  $x$ ), the  $\text{La}^{3+}$  is randomly replaced by  $\text{Sr}^{2+}$  making few electrons available to the  $\text{CuO}_2$  planes - changing the configuration of oxygen from  $\text{O}^{2-}$  to  $\text{O}^-$ . Thus one "hole" is created in the  $p$  shell of oxygen. It is hole doping which is responsible for superconductivity in this compound.

## YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (YBCO)

The high temperature superconducting property of YBCO was discovered by Wu. et al. in 1987[9]. The structure is called primitive tetragonal. There are two CuO<sub>2</sub> planes per unit cell approximately 3.2 Å apart separated by yttrium ions. The pair of planes within the unit cell is 8.2 Å apart and the volume in between has layers of atoms containing barium, oxygen and copper which form the charge reservoir.

In particular note that there are chains of Cu-O in the **b** direction. The chains are well defined only for the case of  $x = 1$  and absent for  $x = 0$ . It is believed that these chains do not play a major role in the superconductivity, because they are specific to YBCO, but it is known that they do affect properties such as the optical conductivity.

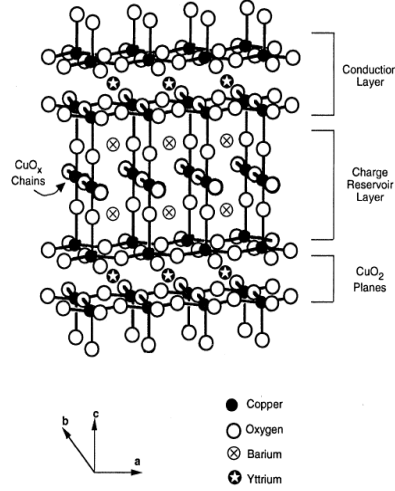


Figure 2: Crystal structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (taken from Jorgensen 1991)

The electronic configuration of the elements is Y:[Kr](5s)<sup>2</sup>(4d), Ba:[Xe](6s)<sup>2</sup>, Cu:[Ar](3d)<sup>10</sup>(4s) and O:[He](2s)<sup>2</sup>(2p)<sup>4</sup>. Y attains a stable configuration by going into the Y<sup>3+</sup> state while barium goes into the Ba<sup>2+</sup> state. Copper is in the Cu<sup>2+</sup> state and oxygen O<sup>2-</sup> state. When oxygens are introduced in the sample, it is believed that it introduces holes into the copper oxide planes, a claim that finds some credit from Hall conductivity measurements. There is an issue with holes existing on the CuO chains which is not very clearly sought out.

## Nd<sub>2-x</sub>Ce<sub>x</sub>CuO<sub>4</sub>

The structure of Nd<sub>2-x</sub>Ce<sub>x</sub>CuO<sub>4</sub> is quite similar to that of La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> except for the location of the oxygens in the charge reservoir. The Nd ions are in the Nd<sup>3+</sup> state and when doped with Ce are replaced by Ce<sup>4+</sup> ions leading to electrons being donated to the copper oxide planes. It is believed that this extra electron completes the *d* shell of

copper. Electron doping is responsible for superconductivity in this compound.

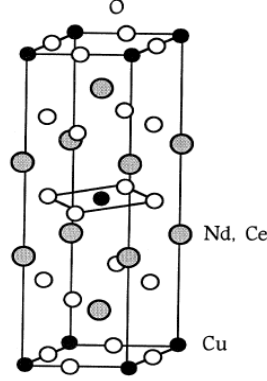


Figure 3: Crystal structure of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  T' phase (taken from Almasan and Maple 1991)

### Generic phase diagram of the cuprates

As seen in the previous section, there are multiple possible routes to superconductivity (hole vs electron doping, or adding oxygens) depending on the compound involved. Despite this diversity amongst the cuprates, some universal features have been observed on their phase diagrams (the variable on the horizontal axis would depend on the cuprate involved). Here we just consider a schematic of a typical cuprate phase diagram.

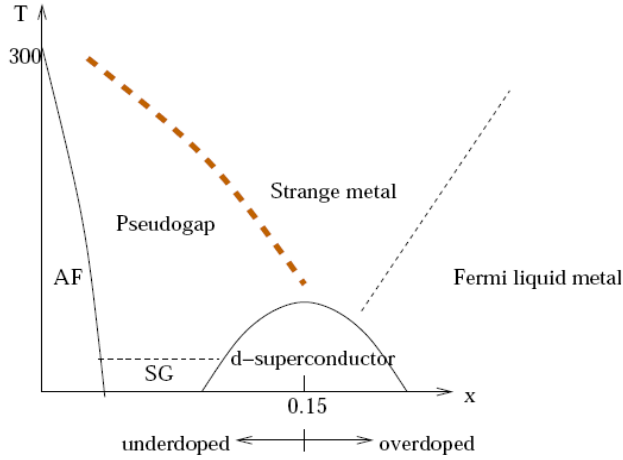


Figure 4: Generic phase diagram of the cuprates (taken from [9] ). This is representative of hole doped compounds. The electron doped side (not shown here) is slightly different. (for eg. it has a bigger AF region). For a discussion of why this asymmetry is present one may refer to [4]

A good description of these phases can be found in [9]. We include a brief overview in Appendix A.

### 3 Model Hamiltonians for electronic structure calculations

The general philosophy in condensed matter physics (which we adhere to) is to explain observations using a minimalistic model which captures the essential physics of the problem. In order to do so we make some simple (and probably intuitive) assumptions to construct model hamiltonians for the cuprates.

#### Three Band model

Since the Cu-O bonds on the planes are strong bonds in comparison to the weaker inter-planar tunneling interaction, we first try constructing a model in which only the  $\text{CuO}_2$  planes are involved. But one must note that this is far from a complete picture. There is experimental evidence for the dependence of transition temperature on the strength of the inter-layer coupling [7]. Also the  $\text{CuO}_2$  planes might not be perfectly planar - they can buckle as in YBCO. In addition, the presence of electron-phonon coupling, which is expected to be strong in transition metal oxides, is often ignored. One also generally ignores the presence of the apical oxygens. However, this simplified picture may serve as a good starting point to capture the essential low energy physics of the cuprates.

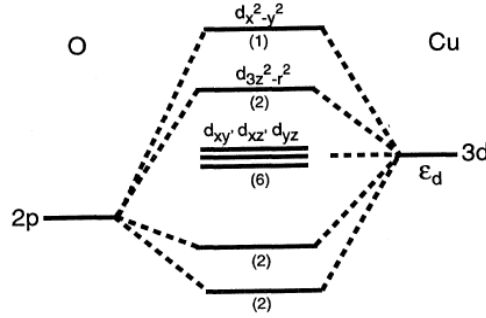


Figure 5: Energy level diagram for bonding between one  $\text{Cu}^{2+}$  and two  $\text{O}^{2-}$  ions. The lowest two levels are unmarked but correspond to linear combinations of  $p_x$  and  $p_y$  orbitals of the oxygens. The numbers in brackets indicate occupation numbers of the level in the undoped compound (from Fulde 1991)

To begin with, let us consider the case where the copper oxide plane is undoped. To write down a model effective hamiltonian, we'll see that we do not necessarily have to consider all the  $d$  electrons of Cu and all the  $p$  electrons of O. We can figure out which orbitals are important by analyzing the effect of the Cu-O interaction on their orbital energies. In  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , each copper atom is surrounded by four in-plane and two apical oxygens. In YBCO, each copper is surrounded by five oxygens. The arrangement of the oxygens in the lattice is responsible for breaking

the  $d$  orbital degeneracy of the isolated copper ion. It turns out that the highest filled orbital has  $d_{x^2-y^2}$  character. (The choice of spatial coordinates used in the remainder of the paper is such that the copper oxide plane is taken to be the X-Y plane). Fig 5 shows how the separation of copper and oxygen orbital occurs in an undoped cuprate. Thus it is sufficient to work with a reduced basis set - the  $d$  orbital of Cu and the  $p$  orbitals of O.

What happens to the additional hole when the compound is doped? It is clear that it probably does not reside at the copper site - there would be a huge energy cost owing to the Coloumb repulsion between two holes. In fact it was the strong repulsion that lead to the compound being an antiferromagnetic insulator instead of a metal! In short, we are in the 'strongly-correlated' regime.

With this picture in mind, we consider each of the contributions to the low energy hamiltonian. For mathematical convenience, we work in the hole representation and take the vacuum to be the state which comprises of Cu 3  $d^{10}$  and O  $p^6$  states.

First, we have different onsite energies for the copper and oxygen atoms. This part of the hamiltonian is given by,

$$H_{on-site} = \epsilon_d \sum_i n_i^d + \epsilon_p \sum_j n_j^p \quad (1)$$

where  $\epsilon_{p,d}$  refer to the energy associated with the  $p_{x,y}$  and  $d_{x^2-y^2}$  orbitals respectively.  $n_i$  is the number operator that counts the total number of holes at site  $i$ . One can set the reference energy to  $\epsilon_d = 0$ .

Now consider the hopping of holes on the Cu-O square lattice. The overlap matrix element  $t_{pd}$  connects the copper  $d$  orbital to the four neighboring oxygen atoms. Similarly, the matrix element  $t_{pp}$  connects an oxygen site and its neighboring oxygens. (These matrix elements are proportional to the overlap between the orbitals involved). Thus we have,

$$H_{hop} = -t_{pd} \sum_{\langle ij \rangle} (p_j^\dagger d_i + h.c.) - t_{pp} \sum_{\langle jj' \rangle} (p_j^\dagger p_{j'} + h.c.) \quad (2)$$

where  $p_j$  ( $d_i$ ) are the fermion operators that destroy holes at the oxygen (copper) ion sites  $j(i)$ .  $\langle ij \rangle$  refer to nearest neighbor copper-oxygen sites while  $\langle jj' \rangle$  refer to nearest neighbor oxygen-oxygen sites.

In addition, we have the Coloumb repulsion terms.  $U_d$  and  $U_p$  are the onsite Coloumb repulsion energies for the copper ( $d$ ) and oxygen ( $p$ ) orbitals respectively.  $U_{dp}$  is the repulsion energy between electrons on neighboring copper and oxygen orbitals. We assume that long range interactions are screened off - this is an approximation that has not been justified here. Thus,



$$H_{Coulomb} = U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d + U_p \sum_i n_{j\uparrow}^p n_{j\downarrow}^p + U_{dp} \sum_{\langle ij \rangle} n_i^d n_j^p \quad (3)$$

where the operators  $n_{i\sigma}$  refers to the number of spin  $\sigma$  electrons at site  $i$ . Thus the total three band hamiltonian is,

$$H_{3-band} = H_{hop} + H_{on-site} + H_{Coulomb} \quad (4)$$

At this point, I feel it is important to clarify a rather confusing nomenclature. The term “three band” could be called “three orbital” model [18]. The three participating orbitals are the  $3d_{x^2-y^2}$  centered on the copper and the  $2p_x$  and  $2p_y$  centered on the oxygens.

A band structure calculation by Hybertsen *et. al* (1989) (we referred to [6]) estimated the values of the parameters (in eV),

$\epsilon_p - \epsilon_d$	$t_{pd}$	$t_{pp}$	$U_d$	$U_p$	$U_{pd}$
3.6	1.3	0.65	10.5	4	1.2

## One Band Models

The three band parameter values are in a range where it may be possible to make further simplifications to the hamiltonian (4) introduced earlier. The whole idea of doing this reduction is to introduce simpler models, those which we relate to more easily! Some simplifying assumptions are,

1. The O-O overlap is small in comparison to the Cu-O overlap  $\implies t_{pp}$  can be ignored.
2. The Coulomb repulsion between two  $p$  electrons of opposite spin is smaller (in comparison to two  $d$  electrons of opposite spin) because the  $p$  orbitals are fairly delocalized  $\implies U_p \ll U_d$
3. The Coulomb repulsion between a  $p$  electron and a  $d$  electron is also small i.e.  $\implies U_{dp} \ll U_d$ .

The hamiltonian thus becomes,

$$H = \epsilon_d \sum_i n_i^d + \epsilon_p \sum_j n_j^p + U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d + H' \quad (5)$$

where  $H'$  is the hybridization term which is given by,

$$H' = \sum_{i,\sigma} \sum_{l \in \{i\}} V_{il} d_{i\sigma}^\dagger p_{l\sigma} + H.c. \quad (6)$$

where  $i$  refers to the location of a copper site and  $l$  is an index over its neighboring oxygen sites indicated by  $\{i\}$ . The hybridization element is given by,

$$V_{il} = (-1)^{M_{i,l}} t_0 \quad (7)$$

where  $t_0$  is the amplitude of the hybridization and is proportional to the overlap.  $M_{i,l} = 2$  if  $l = i - \frac{1}{2}\hat{x}$  or  $l = i - \frac{1}{2}\hat{y}$  and  $M_{i,l} = 1$  if  $l = i + \frac{1}{2}\hat{x}$  or  $l = i + \frac{1}{2}\hat{y}$  where the distances are expressed in terms of Cu-Cu bond length.

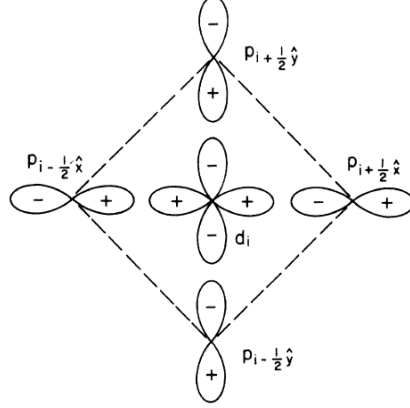


Figure 6: The unit cell in the copper oxide plane showing the minimal orbital set:  $d_{x^2-y^2}$  orbital of Cu and  $p_x$  and  $p_y$  orbital of oxygen per unit cell. Its easy to understand the signs in equation (7) with this picture.

In the case of no doping,  $\text{La}_2\text{CuO}_4$  has a single unpaired  $3d_{x^2-y^2}$  electron per copper viz. equivalent to a single hole. In the hole description of the problem therefore, each Cu site is singly occupied. If there is no tunneling between Cu sites, the compound is an insulator. When the tunneling is turned on ( $t_o$  is small compared to  $U$  but finite), it leads to an antiferromagnetic superexchange interaction (the intermediate being a doubly occupied Cu site and an empty Cu site). This gives rise to the antiferromagnetic Heisenberg hamiltonian with a coupling  $J(t_o, U, \epsilon_p)$  (not calculated here).

$$H_S = J(t_o, U, \epsilon_p) \sum_{\langle i,j \rangle} S_i \cdot S_j \quad (8)$$

where  $S_i$  are the spin 1/2 operators of Cu holes and  $\langle i, j \rangle$  refers to nearest neighbor Cu-Cu pairs.

Now consider what happens when the sample is doped with Sr i.e. holes are introduced into the  $\text{CuO}_2$  planes. In the limit of  $t_o \rightarrow 0$ , we can have one of the two possibilities for the additional holes introduced.

1. The holes go to the Cu sites if  $\epsilon_p > U$ . In this case the oxygen sites can be eliminated (by accounting for the virtual hopping process from hole on Cu to O and then to other Cu) to give a effective Hamiltonian for motion of holes on the Cu sites only. This is described by the one-band Hubbard model.

2. The holes go to the O sites if  $\epsilon_p < U$ . This is the non-trivial case in question and the work of Zhang-Rice (ZR) shows that a reduction to single-band effective Hamiltonian is indeed possible.

In the sections that follow we discuss both the one-band Hubbard model and the ZR singlet.

### One Band Hubbard Model

In 1985, Zaanen, Sawatzky and Allen [13] came up with a general theory for describing band gaps and electronic structures in transition metal compounds. Using their theory, it can be shown that the three band problem can be approximately mapped onto a one band Hubbard model. The onsite Coulomb repulsion  $U_{eff}$  tries to incorporate the effects of the charge transfer gap  $\Delta = \epsilon_p - \epsilon_d$  (ref Fig. 7). The oxygens are completely eliminated from the model (their presence being accomodated in the value of  $U$ ).

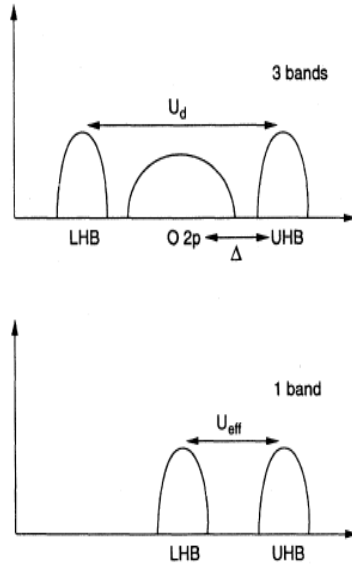


Figure 7: Schematic band structure of the  $\text{CuO}_2$  planes showing the effective reduction of the three band model to the one band model (taken from [6]).

The Hubbard hamiltonian comprises of a hopping part parametrized by ( $t$ ) and an onsite Coloumb repulsion part ( $U$ ),

$$H = -t \sum_{\langle i,j \rangle} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (9)$$

where  $c_{i\sigma}^\dagger$  is the fermion operator that creates a spin  $\sigma$  electron at site  $i$  of a square lattice. Sometimes, the second

term is written as  $\sum_i (n_{i\uparrow} - \frac{1}{2})(n_{i\downarrow} - \frac{1}{2})$ . The factors of 1/2 are present just for mathematical convenience (especially when we are interested in studying the deviation from half filling) and do not change the physics. (The only relevant term is  $\sum_i n_{i\uparrow}n_{i\downarrow}$ . The other terms  $\sum_i n_{i\uparrow} + n_{i\downarrow}$  are constant anyway)

Although the Hubbard model is used extensively in the literature, a justification for why it is a valid reduction is not so obvious. It can be shown that this model captures the essential physics of the AF phase ( $t/U \ll 1$ ) and Fermi liquid phase ( $t/U \gg 1$ ), but the issue of superconductivity in the model seems unresolved.

### Zhang Rice Singlet

In 1988, Zhang and Rice [3] derived an effective one band model for the cuprates. We have gone through some mathematical steps from this paper in Appendix B to try understanding how effective low energy hamiltonians can be arrived at using second order perturbation theory. (This is a theme that has been emphasized throughout the P636 course)

The basic idea is that the doped hole introduced to the Cu-O plane resonates on the four oxygen sites surrounding a copper. The spin of this hole combines with the spin of the hole at the Cu site. ZR showed that the motion of this singlet is described by the  $t - J$  model.

$$H_{eff} = H_t + H_s = \sum_{i \neq j, \sigma} t_{ij} (1 - n_{i, -\sigma}) d_{i\sigma}^\dagger d_{j\sigma} (1 - n_{j, -\sigma}) + J(t_o, U, \epsilon_p) \sum_{\langle i, j \rangle} S_i \cdot S_j \quad (10)$$

This interpretation is not without controversy. V. Emery and G. Reiter challenged this result in their paper [5]. Their study indicated that the quasi particles in the case of the three band Hubbard model had charge and spin, in contrast to the singlet states involved in the  $t - J$  model. However, some further work on the subject seems to indicate that this reduction is quite valid.

The ZR idea can also be applied to the case of electron doping (for eg.  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4+\delta}$ ) [4] i.e. this case is well described by the  $t - J$  model. But it represents a very different physical situation from the spin-singlet case. In the hole doping case the object that is hopping over the lattice is the ZR singlet, whereas the object that hops in the electron doping case is the Cu  $d^{10}$  configuration.

## 4 Inferences from electronic structure calculations

### Ring exchange in AFM phase

Most features of the antiferromagnetic phase can be well explained by the nearest neighbor Heisenberg model. However, additional interactions do show up in the dispersion of spin waves, mainly along the Brillouin zone edge. This can be probed using inelastic neutron scattering with high energy and wavevector resolution. One such experiment

was performed on  $\text{La}_2\text{CuO}_4$  by Aeppli *et. al* [17].

In order to explain their experimental observations, [17] worked with a hamiltonian given by,

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\langle i,i' \rangle} \mathbf{S}_i \cdot \mathbf{S}_{i'} + J'' \sum_{\langle i,i'' \rangle} \mathbf{S}_i \cdot \mathbf{S}_{i''} + J_c \sum_{\langle i,j,k,l \rangle} \{(\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_k \cdot \mathbf{S}_l) + (\mathbf{S}_i \cdot \mathbf{S}_l)(\mathbf{S}_k \cdot \mathbf{S}_j) - (\mathbf{S}_i \cdot \mathbf{S}_k)(\mathbf{S}_j \cdot \mathbf{S}_l)\} \quad (11)$$

where  $J$ ,  $J'$ ,  $J''$  are the first, second and third nearest neighbor couplings.  $J_c$  is the ring exchange interaction between four spins (labelled clockwise) at the corners of a square plaquette.

To begin with, they set  $J'' = J_c = 0$  and were able to obtain a very good fit to their data. However, this yielded a ferromagnetic  $J'$  which was inconsistent with theoretical predictions. Moreover, experiments on  $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  with similar exchange path between  $\text{Cu}^{2+}$  ions as in  $\text{La}_2\text{CuO}_4$  predicted an antiferromagnetic coupling  $J'$ .

This (possible) inconsistency led them to try out the one band Hubbard model in the limit of strong correlation viz.  $t/U \ll 1$ . When expanded perturbatively to order  $t^4/U^3$  (i.e. 4 hops) we get,  $J = 4\frac{t^2}{U} - 24\frac{t^4}{U^3}$ ,  $J_c = 80\frac{t^4}{U^3}$  and  $J' = J'' = 4\frac{t^4}{U^3}$ . They were able to get a good fit to  $t$  and  $U$  and these values were found to be in good agreement with those obtained from photoemission and optical spectroscopy.

## Fermi surface

ARPES (Angle Resolved Photoemission spectroscopy) experiments such as those performed by [15] show that at optimal doping, the Fermi surface is large and encloses an area of about half of the Brillouin zone. This seems consistent with the Luttinger theorem which states that the 'volume' of the Fermi surface of interacting electrons is the same as in the non interacting case (Refer to P636 notes). However, for the underdoped cuprates, it seems that the Fermi surface is "small" and exists only as pockets around  $(\frac{\pi}{2}, \frac{\pi}{2})$  and symmetry related points. But there has been some controversy regarding interpretation of ARPES data and we refer the more interested reader to the brief discussion of this issue in [15].

A pertinent question to ask then is - can a model explain the characteristic hole pockets that form in underdoped cuprates? [14] made progress in this direction. They considered a nearest (with coupling  $t$ ) and next to nearest neighbor (with coupling  $t'$ ) one band Hubbard model, and applied the spin density wave (SDW) formalism to it. In this method the quartic terms arising in the Hubbard model (from the number operators) are decoupled using the relation,

$$\langle \sum_k c_{k+Q,\uparrow}^\dagger c_{k,\uparrow} \rangle = - \langle \sum_k c_{k+Q,\uparrow}^\dagger c_{k,\uparrow} \rangle = \langle S_z \rangle \quad (12)$$

where  $Q$  is the antiferromagnetic ordering momentum and is equal to  $(\pi, \pi)$  for a square lattice.

The idea is that the Hubbard hamiltonian is converted into a completely quadratic form, which is diagonalized by a Bogoliubov transformation.

Using this approach and by varying  $\Delta \equiv U < S_z >$ , they saw the evolution of a large Fermi surface into a small Fermi surface (i.e. the appearance of hole pockets). This is shown in figure 8.

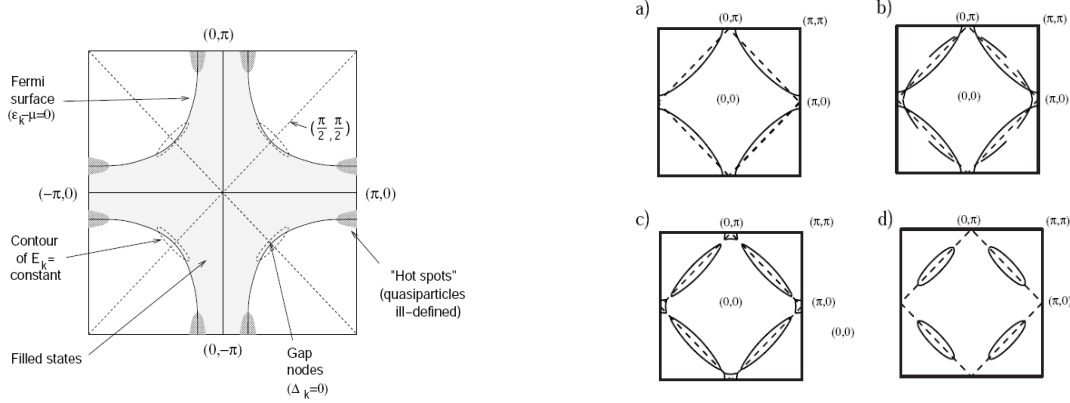


Figure 8: *Left*: Schematic of an experimental observation such as that from ARPES (Figure taken from [3]) *Right*: Schematic evolution of the Fermi surface in the  $t$ - $t'$  Hubbard model (with  $t'=-0.2t$ ) with  $\Delta = U < S_z >$  (a)  $\Delta = 0$  (b)  $\Delta = 0^+$  (c) For intermediate  $\Delta$  we see electron and hole pockets (d) For large  $\Delta$  pockets around  $(\frac{\pi}{2}, \frac{\pi}{2})$  are formed. The dashed line indicates the boundary of the magnetic Brillouin zone (Figure taken from [14])

### Superconductivity in three and one band models?

It is seen from numerical simulations that the one band Hubbard model shows no superconductivity within the range of lattice sizes and temperature ranges considered [6]. This follows from a computation of the pair-pair correlation function, which shows no long range correlations.

Does the  $t$ - $J$  model demonstrate superconductivity in some range of parameter values of  $t$  and  $J$  ? The answer is unfortunately a very tricky one - maybe! Based on exact diagonalization results, for  $J/t > 0.3$  and near half filling it is believed that there are attractive forces involved in the model which may lead to some sort of pair condensation, thereby explaining superconductivity. (I believe) It is still quite an open question.

## 5 Other aspects of cuprate models

In the discussions above we have dealt with the simplest models in the literature. However, there have been studies that do not make extreme simplifications in the hope of capturing a larger chunk of the low energy physics of the cuprates. Here we discuss two such cases - (1) where the  $p$  orbitals of the in-plane oxygens are taken into account and (2) where the effect of apical oxygens is not ignored.

### Conjectural state with spontaneous currents

We briefly present a development in the theory of cuprates proposed by C.M. Varma in 1997 [10]. According to the theory, high  $T_c$  superconductivity in the cuprates could be explained by the enhancement of quantum fluctuations over thermal fluctuations as the temperature is decreased. These fluctuations are those of currents that circulate from Cu to O orbitals.

The theory starts off with a two band model of Cu and O bonding and antibonding bands and predicts the existence of a novel ground state - a fourfold pattern of circulating current within a unit cell - giving it the name “circulating current” (CC) phase. Since, the pattern is the same across all the cells translational symmetry is preserved. Observe that though the hamiltonian has fourfold rotational symmetry and is time reversal invariant, the ground state does not have these symmetries - i.e. these symmetries are spontaneously broken. However, the product of time reversal and four fold rotation is preserved.

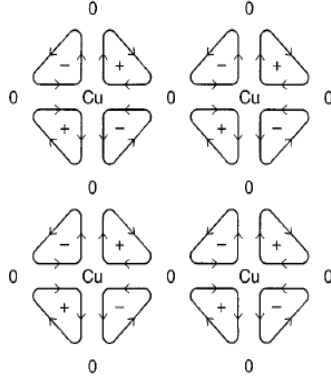


Figure 9: Ground state current distribution in the circulating current phase drawn for four cells. The + and - indicate magnetic fields pointing up and down.

Bourges *et. al* [12] seem to have verified the existence of these current loops using polarized neutron diffraction.

### Role of apical oxygens in superconductivity

Upto this point we have assumed that the high  $T_c$  superconductivity can be explained by models that simply model the  $\text{CuO}_2$  planes. Here we shed light on the possible role of apical oxygens.

It was observed that when  $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$  (electron doped) is subjected to pressure, its  $T_c$  remained unchanged, in comparison to the strong pressure dependence that was seen for  $\text{Nd}_{1.3}\text{Ce}_{0.2}\text{Sr}_{0.5}\text{CuO}_{4-\delta}$ . This was attributed to the fact that the former has no apical oxygens while the latter has oxygen pyramids in its structure. The dependence on apical oxygens is clearer in  $\text{YBa}_2\text{Cu}_4\text{O}_{7-\delta}$  with a  $T_c \approx 80\text{K}$  - it is seen that a pressure of 1 GPa changes the  $\text{Cu-O}_z$

distance by about 2.5% toward the in-plane Cu and leads to  $T_c$  increasing by about 5 K.

Taking lead from these experiments [11] did a theoretical study on the issue. They concluded that presence of the apical oxygens modifies the  $p$  hole band structure - it turns out that the long range hopping integrals of the Zhang Rice singlet bound state around Cu-spins is increased which in turn is related to the transition temperature. Decreasing the distance between Cu and  $O_z$  makes the effect more prominent, as can be seen by subjecting the sample to pressure.

## 6 Conclusion

I briefly summarize the term paper here. We saw the structure of the cuprates and observed the feature common to them was the presence of the copper-oxide planes, which lead us to believe that it is the seat of high  $T_c$  superconductivity. The universality of the phase diagram leads us to believe that some general models applicable to most cuprates are capable of describing it. With the hope of understanding the electronic structure of the cuprates and hence the mechanism of superconductivity, we saw some model Hamiltonians for the copper-oxide planes. We saw that the one band Hubbard model satisfactorily explained the AFM phase and showed promise when it came to describing the Fermi surface of underdoped cuprates. The issue of superconductivity in the model seems to be an open question. We then went on to briefly present a conjectured circulating current phase in which the oxygen orbitals have a role to play - i.e. they are not eliminated from the effective model. In addition, we saw that the apical oxygens might also have a non trivial role to play in electronic structure.

## Appendix A - Cuprate phase diagram

Here we briefly describe the cuprate phase diagram introduced in section 2.

1. **Antiferromagnetic phase:** At no doping, we have a Mott insulator i.e. one electron per unit cell. Neutron diffraction studies confirm that it is an antiferromagnet with the magnetic unit cell size twice as large as the size of the crystal unit cell. This phase is quite simply described by the AF Heisenberg model.
2. **Spin glass:** At low doping and low temperatures just beyond the AF phase, we observe a spin glass regime. We have a few holes in a mostly antiferromagnetic background. It turns out that holes tend to favor local ferromagnetic order. Thus we have the possibility of frustrated interactions which in turn lead to history dependent effects, characteristic of a spin- glass system.
3. **Pseudo-gap:** In the underdoped regime and well above  $T_c$ , it is found that electronic properties vary with direction in momentum space - a 'gap' (much like the superconducting gap) is seen by electrons travelling in



certain directions. This is a phase that is not well understood at the present moment. One of the emerging theories is that it is a phase where the Cooper pairs have been formed, but have not condensed.

4. **Superconducting phase:** As can be seen from the two-dimensional Brillouin zone in Fig 8, there are four points around  $(\pm\frac{\pi}{2}, \pm\frac{\pi}{2})$  – where the Fermi surface intersects the gap nodes  $\Delta_k = 0$ . Around these points, the energy grows linearly, (much like what we see in graphene) and a linearized theory around those points is well described by the Dirac equation (from quantum field theory) - so these are called “Dirac points.” As pointed out in the preview, it is well established that the superconducting mechanism is via cooper pairing but the BCS explanation seems out of place since the pairs are small (only  $\sim 10$  electrons within a pair radius  $\sim$  coherence length)
5. **Strange metal:** The thermodynamic properties of the compound in this phase are similar to the behaviour of a Fermi liquid. However, this region is characterized by simple but unusual power laws in its transport properties (such as resistivity, optical conductivity, thermal conductivity, magnetoresistance etc.) as a function of temperature. For example the resistivity scales as  $T$  in comparison to  $T^2$  for a normal Fermi liquid. It is believed that the physics of this region is controlled by a quantum critical point under the superconducting dome (Castellani *et. al.* 1997)
6. **Fermi liquid:** In the limit of large doping it becomes easy for electrons to hop from one unit cell to another. The Landau “quasiparticle” picture holds here and we have a normal Fermi liquid.

## Appendix B - Reduction of 3-band model to ZR singlet

In section 3, we spoke about Zhang-Rice reduction of the 3 band model to a one band model ( $t - J$  model). In this section we try to sketch some mathematical details from their paper [3].

To begin with, let us consider a single square- one copper surrounded by four oxygens. Consider linear combinations ( $P_{i\sigma}$ ) of the O hole states ( $p_{l\sigma}$ ),

$$P_{i\sigma}^{(S,A)} = \frac{1}{2} \sum_{l \in \{i\}} (\pm 1)^{M_{i,l}} p_{l,\sigma} \quad (13)$$

where  $-(+)$  correspond to the S(A) state.  $M_{i,l}$  is the same as that defined earlier in section 3 (also refer figure 6, for a clearer understanding).

These hole states combine with the  $d$  orbital on copper to form spin singlet or triplet states. From use of second order perturbation theory it can be shown that the singlet state associated with the  $S$  state has an energy much lower than the  $A$  state This energy of this spin singlet is given by  $-8(t_1 + t_2)$  where  $t_1 = \frac{t_o^2}{U}$  and  $t_2 = \frac{t_o^2}{U - \epsilon_p}$ . (One may

recall that  $t_0$ ,  $U$  and  $\epsilon_p$  are the amplitude of the hybridization element, the onsite Coloumb repulsion on the Cu site and the energy of the  $p$  orbital respectively.) One hopes (and that turns out to be the case) that when we consider the entire system this local singlet picture is not severely affected. Thus, we work in the subspace of  $S$  states alone. Observe however, that the localized  $S$  states are not orthogonal. In fact, we can calculate a mathematical expression for the overlap between  $P_{i\sigma}^{(S)}$  and  $P_{j\sigma'}^{(S)}$  quite easily.

First realize that the  $P$  states are formed from combinations of orthogonal  $p$  states, where,

$$\langle p_{l\sigma} | p_{m\sigma'} \rangle = \delta_{\sigma,\sigma'} \delta_{l,m} \quad (14)$$

From the above expression it is clear that for  $\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)} \rangle$  to be non zero, the spins at sites  $i$  and  $j$  have to match i.e.  $\sigma = \sigma'$ . For  $i = j$ , it follows quite trivially that  $\langle P_{i\sigma}^{(S)} | P_{j\sigma}^{(S)} \rangle = 1$ . If  $i$  and  $j$  are neighboring copper sites, then they have one oxygen neighbor in common and so the overlap is  $-(\frac{1}{2})(\frac{1}{2}) = -\frac{1}{4}$ . All other overlaps are zero. Thus we may write  $\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)} \rangle$  compactly as,

$$\langle P_{i\sigma}^{(S)} | P_{j\sigma'}^{(S)} \rangle = \delta_{\sigma,\sigma'} \left( \delta_{ij} - \frac{1}{4} \delta_{<i,j>} \right) \quad (15)$$

where the symbol  $\delta_{<i,j>} = 1$  for  $i, j$  being nearest neighbors and 0 otherwise.

The natural thing to do next is to orthogonalize this set of wavefunctions. One may construct such a set from our earlier knowledge of Wannier functions (which we came across when we did the tight binding model from Ashcroft and Mermin). First, the delocalized Bloch states ( $\tilde{P}_{\mathbf{k}\sigma}$ ) can be expressed in terms of a linear combination of a localized (but non orthogonal) basis set  $\{P_{i\sigma}\}$ . The orthogonal localized Wannier functions ( $\phi_{i\sigma}$ ) can be expressed in terms of these Bloch states. We have,

$$\phi_{i\sigma} = \frac{1}{\sqrt{N_s}} \sum_{\mathbf{k}} \tilde{P}_{\mathbf{k}\sigma} \exp(i\mathbf{k} \cdot \mathbf{R}_i) \quad (16)$$

$$\tilde{P}_{\mathbf{k}\sigma} = \frac{1}{\sqrt{N_s}} \beta_{\mathbf{k}} \sum_i P_{i\sigma}^{(S)} \exp(-i\mathbf{k} \cdot \mathbf{R}_i) \quad (17)$$

where  $N_s$  is the number of copper sites (or equivalently the number of  $\text{CuO}_4$  squares) in the system.  $\beta_{\mathbf{k}}$  is a normalization factor given by,

$$\beta_{\mathbf{k}} = [1 - \frac{1}{2}(\cos k_x + \cos k_y)]^{-1/2} \quad (18)$$

To understand the computation of the normalization factor, simply consider the overlap of  $\tilde{P}_{\mathbf{k}\sigma}$  and  $\tilde{P}_{\mathbf{k}'\sigma}$  and impose the orthonormality constraint and use the expression of overlap from (14).

The O-hole states combine with the Cu-hole to form a singlet  $(-)$  or triplet  $(+)$  state.

$$\psi_i^\pm = \frac{1}{\sqrt{2}}(\phi_{i\uparrow}d_{i\downarrow} \pm \phi_{i\downarrow}d_{i\uparrow}) \quad (19)$$

Again as was the case for a single square, the energy of the triplet turns out to be  $\gg t$  and so it is possible to project out  $\psi_i^+$  and work with  $\psi_i^-$  alone. In fact, the energy associated with the singlet is not significantly different from the one obtained for a single square.

Now consider the motion of this singlet. When  $\psi^-$  moves from  $i$  to  $j$ , we have to take into account that the hole at the Cu  $d$  orbital moves from  $j$  to  $i$  ! This leads to a kinetic energy term of the form,

$$H_t = \sum_{i \neq j, \sigma} t_{ij} (\psi_j^- d_{i\sigma})^\dagger (\psi_i^- d_{j,\sigma}) \quad (20)$$

with  $t_{ij}$  being computed from perturbation theory.

What the above expression tells us is that when a  $d$  hole is created at site  $i$ , a singlet is destroyed at the same site. This in turn means that we cannot have two  $d$  holes at one site - because that would mean applying a singlet destruction operator twice! Thus we can simply project out the doubly occupied states with the operator  $(1 - n_{i,-\sigma})$ . Thus equation (20) becomes,

$$H_t = \sum_{i \neq j, \sigma} t_{ij} (1 - n_{i,-\sigma}) d_{i\sigma}^\dagger d_{j\sigma} (1 - n_{j,-\sigma}) \quad (21)$$

Thus the combined hamiltonian from (21) and (8) is,

$$H_{eff} = H_t + H_s = \sum_{i \neq j, \sigma} t_{ij} (1 - n_{i,-\sigma}) d_{i\sigma}^\dagger d_{j\sigma} (1 - n_{j,-\sigma}) + J(t_o, U, \epsilon_p) \sum_{\langle i,j \rangle} S_i \cdot S_j \quad (22)$$

and is referred to as the  $t$ - $J$  model in the literature. In fact, the one band Hubbard model reduces to the  $t - J$  model in the limit of  $U/t \gg 1$ .

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