Topics in Electronic Structure and Spectroscopy of Cuprates

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ABSTRACT OF DISSERTATION

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Abstract

I have applied first-principles calculations to investigate several interrelated problems concerned with the electronic structure and spectroscopy of cuprates. The specific topics addressed in this thesis are as follows.

1. By properly including doping effects beyond rigid band filling, a longstanding problem of the missing Bi-O pocket in the electronic structure of Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212) is solved. The doping effect is explained in terms of Coulombic effect between layers and is a generic property of all cuprates.

2. A systematic study for Pb/O and rare-earth doping in Bi2212 is carried out to explain the experimental phase diagrams, and a possible new electron doped Bi2212 is predicted.

3. To investigate how the Mott insulators evolve into superconductors with the addition of holes, an analysis of angle-resolved photoemission (ARPES) data of La$_{2-x}$Sr$_x$CuO$_4$ is carried out over a wide doping range of $x = 0.03 - 0.30$. The spectrum displays the presence of the van Hove singularity (VHS) whose location in energy and three-dimensionality are in accord with the band theory predictions. A nascent metallic state is found in the lightly doped Mott insulator and develops spectral weight as doping increases. This metallic spectrum is ‘universal’ in the
sense that its dispersion depends weakly on doping, in sharp contrast to the common expectation that dispersion is renormalized to zero at half-filling. This finding challenges existing theoretical scenarios for cuprates.

4. Self-consistent mean-field three- and four-band Hubbard models are used to study the Mott gap in electron-doped cuprates. The Hubbard terms are decomposed into a Mott-like term which describes the lifting of Cu bands due to energy cost $U$ and a Slater-like term which describes an additional splitting of Cu bands due to antiferromagnetic (AFM) order. While no set of doping-independent parameters can explain the observed gaps for the entire doping range, the experimental results are consistent with a weakly doping dependent Hubbard $U$. These parameters enhance Cu character of the bonding band, producing a charge transfer gap dominated by the Slater-like term.

5. The valence bands of Bi2212 extending from about 1 to 7 eV below the Fermi energy ($E_F$) are primarily associated with various Cu $d$ and O $p$ orbitals. Sorting out these bands would provide valuable information on a number of issues relevant to cuprate physics. In particular, the bonding Cu $d_{x^2−y^2}$ band has an intimate connection with the true lower Hubbard band (LHB), yet its binding energy has never been experimentally determined. An analysis of the ARPES valence band spectrum of Bi2212 is provided. The local-density approximation (LDA) bands are compared with experiments. While O$_{Sr}$ and O$_{Bi}$ bands are in good agreement with LDA, there are disagreements between experiment and LDA associated with bands originating from the CuO$_2$ layers. A necessary correction of the LDA derived TB model is found, and this correction is shown to be related to the Mott physics in such a way that Cu $d_{x^2−y^2}$ weight is evenly distributed into bonding and antibonding bands.
6. Scanning tunneling microscopy/spectroscopy (STM/STS) techniques have entered the realm of high-Tc’s impressively by offering atomic scale real space resolution and meV resolution in bias voltages. STM/STS spectra, however, represent a complex mapping of electronic states of interest related to the CuO$_2$ planes, since the tunneling current must reach the tip after being filtered through the overlayers (e.g. SrO and BiO in Bi2212). We have developed a material specific theoretical framework for treating the normal as well as the superconducting state where the effect of the tunneling matrix element is included by taking into account various orbitals within a few eV’s of the Fermi energy ($E_F$). The tunneling current is evaluated directly including the effect of overlayers. Our computations show the presence of strong matrix element effects, which lead to significant differences between the dI/dV spectra and the local density of states (LDOS) of CuO$_2$ planes. For instance, the $d_{x^2-y^2}$ signal is found to be dominated by non-vertical hopping between the CuO$_2$ and BiO layers. A substantial electron-hole anisotropy of the tunneling spectrum, which is in accord with experiments, is naturally explained by the contribution from $d_{z^2}$ and other orbitals below $E_F$. 
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Chapter 1

Introduction

Theoretical predictions of electronic structures are increasingly proving to be a powerful and necessary tool for understanding and gaining physical insight into spectroscopies of complex materials. In this way critical tests of relevant theoretical models can be identified. Because degrees of freedom involved in complex materials are often large and coupled strongly, the construction of theoretical models for properly describing various phenomena of interest constitutes an interesting problem in its own right.

Due to the complexity of the problems, one usually needs to resort to numerical methods requiring the use of large-scale computations. The most widely applied first-principles method for investigating the electronic spectra of materials is the density functional theory (DFT) [Jon89]-particularly within the local density approximation (LDA), where the many electron problem is simplified into a self-consistent one-electron Schrödinger equation. The standard DFT/LDA construct is ill-suited and inherently limited in being able to handle many important and interesting physical properties such as superconductivity, Mott insulators, and spin or
charge density waves, especially in strongly correlated systems. Progress in this regard can however be made via appropriately developed tight binding Hamiltonians [Sla54] where the physics of strong correlations can be modeled more straightforwardly. The determination of realistic tight-binding parameters in specific cases requires appeal to both experimental studies as well as first-principles calculations.

Within this context, our group has developed and implemented a variety of methodologies for analyzing and exploiting a variety of spectroscopies highly resolved in momentum, energy or spatial dimensions. DFT, tight binding models, and hybrid methods are used as theoretical tools to investigate the electronic structures and
spectroscopic properties of various novel materials. The diagram in Fig. 1.1 provides an overview. Because most complex materials contain transition metals which have d-electrons, all-electron calculations such as Korringa-Kohn-Rostoker (KKR) and linearized augmented plane wave (LAPW) are more appropriate approaches for our research. The electronic structures obtained by LDA can also provide a good starting point for tight binding models. A fitting program was developed to get parameters of tight binding models (see the next two sections). The parameters may be changed or scaled in making comparisons to experimental spectroscopies, such as angle-resolved photoemission spectroscopy (ARPES), scanning tunneling microscopy/spectroscopy (STM/STS), Compton profile (CP), and resonant inelastic X-ray scattering (RIXS).

Cuprates are high-temperature superconductors which contain square CuO$_2$ planes in common. This class of materials is one of the most interesting materials in condensed matter physics. While they offer the highest transition temperature of all existing superconductors, the microscopic mechanism of high-temperature superconductivity is not still understood. The undoped parent compounds are Mott-insulators at half-filling. As doped away from half-filling, the material gradually becomes more metallic and the superconducting phase only emerges in doped cuprates. Electronic structures play a central role in understanding of this exotic material. Several topics in electronic structures of cuprates are discussed in this thesis.

Since the discovery of superconductivity in cuprates, a large number of LDA band structure calculations have been carried out for gaining understanding of the electronic properties of these materials [Pic89]. The most important electronic states are the strongly hybridized copper $d$ and oxygen $p$ states. This is a common feature for all classes of cuprates, including La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$
(Bi2212), and Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO). The $d$ electrons are relatively localized and strong correlation effects are important. LDA is found to be inadequate for strongly correlated electrons and fails to predict the insulating phase for undoped compounds or the Mott metal-insulator transition. In addition, the experimental metallic Fermi surfaces of Bi2212 are not consistent with previous LDA band structures. These failures pose a challenge for physics beyond LDA and are investigated in this thesis.

Doping is one of the most important parameters in cuprate physics and we address two aspects of the doping process. First, the dopants outside the CuO$_2$ plane donate electrons or holes to the CuO$_2$ conduction bands. Potentials of different layers shift differently due to this redistribution of charges among layers. This is beyond the conventional rigid band approximation and accounts for the disagreement between experimental and LDA Fermi surfaces of Bi2212. More details are provided in chapters 2 and 3. Second, the doped electrons or holes within the CuO$_2$ plane can lead to double occupancy of the Cu $d_{x^2-y^2}$ and an energy cost equal to the Hubbard $U$ is important in this strongly correlated material. A proper treatment of this effect, beyond LDA is necessary to understand the Mott metal-insulator transition. While the doping evolution of the band structures of electron-doped cuprates can be reasonably described by tight binding Hubbard models (chapter 5), our ARPES analysis in chapter 4 adds more puzzles to the Mott metal-insulator transition of hole-doped cuprates. In chapter 5, we introduce a Hubbard $U$ correction to LDA, which is able to drive metal-insulator transition near half-filling. The results of ARPES analysis on electron-doped (chapter 5) and hole-doped (chapter 6) cuprates both suggest that $\Delta$ in LDA is too large and the Cu $d_{x^2-y^2}$ weight is more evenly distributed between bonding and antibonding Cu $d_{x^2-y^2}$ - O $p_\sigma$ bands in the metallic states as a precursor to the Mott physics.
Our tight-binding models are flexible in including the interactions beyond the LDA. Besides the Hubbard $U$ and correction to the on-site energies discussed above, the $d$-wave superconducting pair interaction can also be included. The model is applied to a newly developed theoretical framework of tunnelling spectra in chapter 7.

The topics in various chapters are the following. In chapter 2, a rigid band shift is shown to be an inadequate approximation in layered materials like cuprates. The metallic LDA Fermi surfaces agree with ARPES results only when doping is included in the calculation properly. A physical explanation of this generic doping effect on the electronic structures in terms of Coulombic effect between layers is presented. The virtual crystal approximation is found to be able to account for this doping effect and it is simple enough to be directly applied to different dopants. With this new scheme of simulating doping, a systematic study for different dopants is carried out in chapter 3. A prediction of possible new electron doped cuprates is made.

In chapter 4, We analyze ARPES data of hole-doped cuprates over a wide doping range to investigate how Mott insulators transform into metallic states. A preformed metallic state is found in the Mott insulator. The presence of the metallic dispersion fully consistent with LDA calculations in a 3% doped sample is a major surprise. While the metallic state develops finite spectral weight with doping, it undergoes relatively little change in its gross dispersion. This finding is an important constraint on any theory of the transition to a Mott insulator in hole-doped cuprates.

To go beyond LDA, self-consistent mean-field three- and four-band Hubbard models are used to study the collapse of the Mott gap in electron-doped cuprates in chapter 5. In chapter 6, we study higher binding energy regime of the cuprate spectrum to search for strong correlation effects. ARPES data of valence bands from about 1 to 7 eV below the Fermi energy is compared to LDA bands. The necessary correction
to LDA is found by fitting a multi-band tight binding model. This correction can be explained in the sense of a precursor to the Mott physics. Finally, a model for STM/STS spectra of cuprates is discussed in chapter 7. We establish a material specific modeling of the STM/STS in the normal as well as the superconducting state. Because the current originating in the conducting CuO$_2$ layers reaches the tip only after it has been ‘filtered’ through other layers, the STS spectrum is not directly proportional to the local density of states of CuO$_2$ layers. The electron-hole asymmetry observed experimentally can be explained within a conventional picture. This indicates that the effects of strong electronic correlations on the tunneling spectrum are more subtle than has been thought previously.

1.1 Electronic structure of crystals

Crystals are formed by atoms arranged in periodic structures. The atomic spacing is very small on the order of a few angstroms, and a quantum mechanical approach is required for their electronic structures. Since the mass of nuclei is much larger than that of electrons, electrons are moving much faster than nuclei. The quantum mechanical problems of crystals can be simplified by the Born-Oppenheimer adiabatic approximation where the electrons are regarded as instantaneously adjusting to the positions of nuclei. Given the positions of nuclei, $R_\alpha$, we have the electronic Hamiltonian,

$$H_e = \sum_i \frac{p_i^2}{2m} + \sum_{i,\alpha} V_\alpha(r_i - R_\alpha) + \sum_{i,j} V_{ee}(r_i, r_j), \quad (1.1)$$

where $p_i$ is the momentum of the $i$-th electron, $m$ is electron mass, $V_\alpha$ is the nuclear
potential of \( \alpha \)-th atom seen by an electron, and \( V_{ee} \) is due to the electron-electron interaction.

In density functional theory (DFT), the electronic Hamiltonian is further simplified such that the electron-electron interaction is averaged and potentials in Eq. 1.1 are replaced by an effective potential, \( V_{eff} \) which depends on electron density. The problem reduces to solving the one-electron time-independent Schrodinger equation,

\[
\left[ \frac{p^2}{2m} + V_{eff}(r) \right] \psi(r) = E \psi(r),
\]

where \( \psi \) is one-electron wave function. If the nuclei are periodically arranged in the crystal and a Bravais lattice is formed, the effective potential usually has the same periodicity as the lattice, i.e. \( V_{eff}(r + T) = V_{eff}(r) \), where \( T \) is the Bravais lattice vector. The one-electron wave functions also satisfy the Bloch condition,

\[
\psi_k(r + T) = e^{ik \cdot T} \psi_k(r),
\]

where the wave vector \( k \) is crystal momentum. The solution of the eigenvalue problem of Eq. 1.2 can now be labeled by \( k \) and \( n \), where \( n \) is used to indicate the \( n \)-th solution of a particular \( k \). The energy-momentum dispersion relation \( E_n(k) \), known as band structure, as well as the eigen wave function \( \psi_{nk}(r) \) represent the electronic structure of the crystal.

In practice, the band structure calculations solving Eq. 1.2 with boundary condition Eq. 1.3 require numerical methods. Tight-binding (TB), Korringa-Kohn-Rostoker (KKR), linearized augmented plane wave (LAPW), pseudopotential plane-wave
(PW), and linear muffin-tin orbital (LMTO) methods are widely used. Different numerical methods use different basis sets for the wave functions. In the next section, construction of a TB model from KKR wave functions is demonstrated. Having a realistic TB model allows us to go beyond the conventional DFT band theory.

1.2 Construction of tight binding model

In condensed matter physics, many physical properties such as conductivity are determined by states in a small range of energy around the Fermi energy ($E_F$). Instead of an all-electron calculation, a low-energy effective Hamiltonian is enough to capture the essence of the physics. It is computationally efficient and allows us to introduce strong correlation effects. In this section, a scheme for construction of the effective Hamiltonian in a tight-binding formalism is proposed.

We start with eigen wave functions $\psi_{nk}(r)$, the solutions of Eq. 1.2 with the boundary condition Eq. 1.3. Any subset of these wave functions form an orthogonal basis set. The low-energy effective Hamiltonian $H_{eff}(k)$ with this basis set can be expressed simply as a diagonal matrix with selected eigen energies $E_n(k)$ on the diagonal. That is,

$$H_{eff}(k) = \sum_{mn} |\psi_{mk}\rangle H^{diag}_{mn}(k) \langle \psi_{nk}|,$$  \hspace{1cm} (1.4)

with

$$H^{diag}_{mn}(k) = \delta_{mn}E_n(k).$$  \hspace{1cm} (1.5)

We can construct another orthogonal basis set by introducing a unitary transfor-
tion matrix $U_{mn}(k)$. Let us define

$$\tilde{\psi}_{mk} = \sum_n U_{mn}(k)\psi_{nk}. \quad (1.6)$$

These new orthogonal wave functions $\tilde{\psi}_{mk}(r)$ also satisfy the Bloch condition in Eq. 1.3. The Hamiltonian matrix with this new basis set is

$$\tilde{H}(k) = U^\dagger(k)H^{(diag)}(k)U(k). \quad (1.7)$$

A clever choice of $U(k)$ will lead us to a tight-binding formalism where $\tilde{H}(k)$ is built by Fourier transformation of a real space Hamiltonian with a basis set chosen as local orbitals centered at each atom. We then investigate the relation between the momentum space and real space representations.

Wannier wave functions are the most natural way of transforming momentum space Bloch wavefunctions with index $k$ into the real space with index $T$, the Bravais lattice vector. We can obtain the Wannier wave function $\phi_{nT}$ by Fourier transformation,

$$\phi_{mT}(r) = \frac{1}{BZ \text{ volume}} \int_{BZ} dk \ e^{-ikT} \tilde{\psi}_{mk}(r), \quad (1.8)$$

where BZ is an abbreviation for Brillouin zone. Since $\tilde{\psi}_{mk}(r)$ satisfies the Bloch condition in Eq. 1.3, it is trivial that $\phi_{mT}(r) = \phi_{m0}(r-T)$. One can also prove that $\phi_{mT}$ with different index $m$ or at different cell $T$ are orthogonal. The Hamiltonian matrix with Wannier wave functions as basis is
\[ H_{mT',nT''} \equiv \langle \phi_{mT'} | H | \phi_{nT''} \rangle = \langle \phi_{m0}(r) | H | \phi_{n0}(r - T) \rangle \equiv H_{mn}(T), \quad (1.9) \]

where \( T = T'' - T' \). As long as \( \phi_{m0}(r) \) is centered at each atom and has the symmetry of the atomic wave function, each element of \( H_{mn}(T) \) is obtained by an overlap integral of two atomic-like wave functions. We can now recognize that each off-diagonal element of \( H_{mn}(T) \) is the hopping parameter in a tight-binding formalism, while \( H_{mn}(0) \) is the on-site energy of orbital \( m \). The relation between \( \tilde{H}_{mn}(k) \) and \( H_{mn}(T) \) is

\[ \tilde{H}_{mn}(k) = \sum_T e^{ikT} H_{mn}(T). \quad (1.10) \]

The index \( m \) or \( n \) is recognized as a composite index in a tight-binding model, i.e. \( m = (\alpha, L) \), where \( \alpha \) is atom site index and \( L \) is the composite angular momentum quantum number such as \( (lm) \), or \( s, p_x, p_y, p_z \) etc. Suppose the angular part of \( \phi_{m0}(r) \) is a real spherical harmonic function \( Y_L \), the tight binding parameters \( H_{mn}(T) \) follow the Slater-Koster [Sla54] construction rule. Following these rules, the number of independent terms can be reduced by using symmetry arguments.

Now, the question is how to choose the unitary transformation matrix \( U_{mn}(k) \) in Eq. 1.6 such that \( \phi_{m0}(r) \) is an atomic-like wave function centered at each atom. We need not only band energies \( E_n(k) \) but also the wave function information to construct the tight-binding model. In KKR, the space is divided into non-overlapping muffin-tin spheres centered at each atom. The eigen wave function solved by the KKR method inside a muffin-tin sphere can be expressed as
\[ \psi_{nk}(r) = \sum_{\alpha L} C_{\alpha L}^{(nk)} R_{\alpha L}(r; E_n(k)) Y_L(\Omega), \] (1.11)

where \( R \) is a radial wave function and \( Y \) is a (real) spherical harmonic. One may argue that \( R_{\alpha L}(r; E_n(k)) Y_L(\Omega) \) cannot be directly used as a basis wave function because it depends on energy. However, we only take several eV around \( E_F \) for constructing the low-energy effective Hamiltonian. In this small range of energy, we can neglect the change of \( R \) due to the change of energy. This can be validated by the observation that the vectors \( C^{(nk)} \) for fixed \( k \) and different \( n \) are close to orthogonal to each other in our case. By comparing Eq. 1.6 and Eq. 1.11, we choose

\[ U_{nm}^\dagger(k) = \bar{C}_{\alpha L}^{(nk)} \] or equivalently

\[ U_{mn}(k) = \bar{C}_{\alpha L}^{(nk)*}, \] (1.12)

where index \((m) = (\alpha, L)\) and \( \bar{C} \) are obtained from orthogonalization of selected \( C \).

We only select the most relevant orbitals \( (\alpha, L) \) in the construction and make the number of orbitals and the number of bands (the number of band index \( n \)) the same to ensure \( U \) is a unitary transformation. The values of \( \bar{C} \) and the original \( C \) are close in our case, implying that \( \phi_{m0}(r) \approx \bar{R}_{\alpha L}(r) Y_L(\Omega) \), where \( \bar{R} \) is an approximation to \( R \) in Eq. 1.11. Thus \( \phi_{m0}(r) \) is an atomic-like wave function centered at the \( \alpha \)-th atom with angular momentum \( L \). This choice of \( U_{mn} \) in Eq. 1.12 does indeed serve our purpose.

From the above, we have all the ingredients for construction of tight binding models from KKR solutions. By having \( E_n(k) \) and \( \bar{C}_{\alpha L}^{(nk)} \) and merging Eqs. 1.5, 1.7, and 1.12, we obtain
\[ \tilde{H}_{\alpha L,\alpha' L'}(k) = \sum_n \bar{C}^{(nk)*}_{\alpha L} E_n(k) \bar{C}^{(nk)}_{\alpha' L'}. \] (1.13)

We programmed Eq. 1.13 to obtain each matrix element of \( \tilde{H} \) as a function of \( k \). On the other hand, we followed the Slater-Koster method [Sla54] to construct a TB model with a limited number of independent hopping parameters. A fitting program was developed to determine these parameters using Eq. 1.10. The residual error left in the fitting is the difference between the actual low-energy Hamiltonian and the TB model Hamiltonian. One can improve the accuracy by increasing the number of hopping parameters until satisfactory results are obtained.

In summary, starting with orthogonal first-principles KKR wave functions \( \psi_{nk}(r) \), by a clever choice of unitary transformation we obtained atomic-like Wannier wave functions \( \phi_{mT}(r) \), and finally a TB model was established by fitting the low-energy Hamiltonian matrix elements. The accuracy can be controlled by the number of hopping parameters included in the TB model. We should also emphasize the special potential of this method here. Although this method is not designed to construct the simplest TB model with the least number of hopping parameters such as the maximally-localized Wannier functions method [Mar97b], it is almost a replica of the low-energy Hamiltonian of KKR and is an ideal match to our various KKR based spectroscopy calculations such as ARPES and Compton profile. It not only preserves the band energies of KKR but also the phase of the wave functions which is important in matrix element calculations of spectroscopies. This construction of TB models makes it possible to include strong correlation effects and simultaneously provides a shortcut to utilize first-principles matrix elements based on KKR wave functions in various spectroscopies.
Chapter 2

Raising Bi-O bands above the
Fermi energy level of hole-doped
\( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) and other
cuprate superconductors

First-principles band theory computations on the cuprates have become a widely accepted tool for gaining insight into their electronic structures, spectral properties, Fermi surfaces (FS’s), and as a starting point for constructing theoretical models for incorporating strong correlation effects beyond the framework of the local-density

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*This chapter is adapted from the following talks and papers.
Hsin Lin, S. Sahraokorpi, R. S. Markiewicz, and A. Bansil, *Raising Bi-O bands above the fermi energy level of hole-doped Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) and other cuprate superconductors*, American Physical Society, APS March Meeting, March 13-17, 2006, abstract V39.010.
Hsin Lin, S. Sahraokorpi, R. S. Markiewicz, and A. Bansil, *Raising Bi-O bands above the fermi energy level of hole-doped Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) and other cuprate superconductors*, Physical Review Letters 96, 097001 (2006).
approximation (LDA) underlying such calculations [Pic89, Pav01, Ban99b, Mar05]. For example, in the double layer Bi-compound Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (Bi2212) – perhaps the most widely investigated cuprate – the LDA generated band structure [Hyb88, Bel04] is commonly invoked to describe the doped metallic state of the system. Band theory however clearly predicts the FS of Bi2212 to contain a FS pocket around the antinodal point $M(\pi, 0)$ as a Bi-O band drops below the Fermi energy ($E_F$), but such FS pockets have never been observed experimentally [Dam03]. This ‘Bi-O pocket problem’ is quite pervasive and occurs in other Bi-compounds. [Sin95] Similarly, Tl- and Hg-compounds display cation-derived FS pockets, presenting a fundamental challenge for addressing on a first-principles basis issues related to the doping dependencies of the electronic structures of the cuprates.

In this chapter, we show how the cation-derived band responsible for the aforementioned FS pockets is lifted above $E_F$ when hole doping effects are properly included in the computations. Detailed results for the case of Bi2212 are presented, where hole doping is generated either by substituting Pb for Bi or by adding excess oxygen in the Bi-O planes. With 20% Pb doping in the orthorhombic crystal structure, the Bi-O band lies $\approx 1$ eV above $E_F$ and the remaining bonding and antibonding FS sheets are in remarkable accord with the angle-resolved photoemission (ARPES) measurements on an overdoped Bi2212 single crystal [Bog01]. Below a critical hole doping level, the Bi-O band falls below $E_F$ and, as a result of this self-doping effect, further reduction in the hole doping level no longer reduces the number of holes in the CuO$_2$ layers. The underlying mechanism at play here is that hole doping reduces the effective positive charge in the Bi-O donor layers, which then reduces the tendency of the electrons to ‘flow back’ and self-dope the material. We have also carried out computations on a number of related compounds, including mono-
layer and trilayer Bi-compounds $[\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta} \text{ (Bi2201)} \text{ and } \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta} \text{ (Bi2223)}]$, and the Tl- and Hg-based compounds, and we find that the lifting of the cation-derived band with hole doping is a generic property of many families of cuprates.

2.1 Theory

Concerning technical details, we have employed both the Korringa-Kohn-Rostoker (KKR) and linearized augmented plane wave (LAPW) band structure methodologies where all electrons in the system are treated self-consistently and the full crystal potentials are considered without the muffin-tin approximation. [Ban99a, Bla01] The KKR scheme is well-known to be particularly suited for a first-principles treatment of the electronic structure of substitutionally disordered alloys. Pb substitution on the Bi sites was considered within the framework of the virtual crystal approximation (VCA), where the Bi nuclear charge $Z$ is replaced by the average of the Bi and Pb charges of what may be thought of as an ‘effective’ Bi/Pb atom, but otherwise the band structure problem is solved fully self-consistently maintaining the charge neutrality of the system. The VCA is expected to be a good approximation in this case since the effective disorder parameter for the Bi-O states, given by $\Delta/W$, where $\Delta$ is the splitting of the Bi-O and Pb-O bands in Bi2212 and Pb2212, respectively, and $W$ is the band width, is estimated to be $\sim 0.3$, so that the system is far from being in the split-band limit. [Ban79] We have also carried out superlattice computations by substituting two Bi atoms by Pb in the orthorhombic Bi2212 as well as KKR-CPA (coherent potential approximation) computations [Ban99a] in 10% Pb doped Bi2201 to independently verify that the VCA provides a good description.
and that Bi/Pb substitution causes little disorder induced smearing of states.

2.2 Band structures of Pb-doped Bi2212

We set the stage for our discussion by considering Fig. 2.1(a) which shows the band structure of undoped Bi2212 predicted by the LDA. Here the lattice is assumed to be tetragonal and the structural parameters used are obtained by minimizing the total energy [Bel04]. A pair of closely placed bands is seen to disperse rapidly through \( E_F \) along the \( \Gamma - X(\pi, \pi) \) line on the right side of Fig. 2.1(a). These are the well-known CuO\(_2\)-bands which are split into bonding and antibonding combinations due to intracell interactions between the two CuO\(_2\)-planes. The problem however is that additional bands of BiO-character drop below \( E_F \) at the \( M(\pi, 0) \) point giving the so-called ‘Bi-O pockets’, leading to a metallic Bi-O layer, [Zha92] in clear disagreement with experimental observations [Dam03].

Fig. 2.1(b) shows how the band structure changes dramatically around the \( M \)-point when 25% Pb is substituted for Bi in Bi2212, where the band structure of the doped compound is computed within the VCA where \( Z \) of the effective Bi atom is reduced from 83 to 82.75 to reflect the average charge of the Bi and Pb atoms. The Bi-O pocket problem is cured as the Bi-O bands are lifted to \( \approx 0.4 \) eV above \( E_F \), and the band structure around the \( M \)-point is simplified and the bilayer splitting of the CuO\(_2\) bands around \( M \) becomes more clearly visible. The extended van Hove singularities (VHSs) in the antibonding and bonding bands appear at binding energies of \( -0.07 \) eV and \( -0.45 \) eV, respectively, and the bare bilayer splitting at \( M \) is \( \approx 400 \) meV. The shape of the antibonding and bonding CuO\(_2\)-bands is very similar to the generally accepted shape in the cuprates. The bands in Fig. 2.1(b) closely
Figure 2.1: Band structure of undoped and 25% Pb-doped tetragonal Bi2212 along various high symmetry directions at $k_z = 0$. 
Figure 2.2: Band structure (at $k_z = 0$) of undoped and 15% Pb-doped Bi2212 assuming orthorhombic lattice structure. Bands are plotted along the high symmetry lines of the tetragonal lattice for ease of comparison with the results of Fig. 2.1.

resemble the bands obtained in previous computations [Ban99b, Lin02] where an ad hoc modification of the LDA potential was invoked to account for the absence of Bi-O pockets in the ARPES spectra of Bi2212. Further computations for a range of Pb-doping levels indicate that the Bi-O pockets are lifted just above $E_F$ at around 22% Pb-doping in the tetragonal structure.

The crystal structure of Bi2212 is more realistically modeled as a $\sqrt{2} \times \sqrt{2}$ orthorhombic unit cell [Sun88]. Accordingly, Fig. 2.2 delineates the effect of doping in orthorhombic Bi2212. Optimized structural parameters for the orthorhombic lattice
from Bellini et al. [Bel04] were used. Similar results are obtained if experimental structure [Mil98] is used. Here one obtains twice the number of bands compared to tetragonal Bi2212 due to the larger size of the unit cell. Comparing Figs. 2.2(a) and (b), we see that 15% Pb doping in the orthorhombic case lifts the Bi-O pockets $\approx 0.4$ eV above $E_F$ and yields a FS consisting of only the bonding and antibonding CuO$_2$ sheets.

A comparison of Figs. 2.1 and 2.2 reveals interesting differences between the band structures of tetragonal and orthorhombic Bi2212 and their evolution with Pb doping. The Bi-O complex of bands is more spread out in energy in Fig. 2.2(a) than in 2.1(a), which reflects the larger atomic displacements in Bi-O layers in the orthorhombic structure. The Bi-O bands display greater sensitivity to Pb doping in the orthorhombic case and only 12% Pb doping pushes the Bi-O pockets above $E_F$ compared to the value of 22% needed in the tetragonal structure. There also are differences in the CuO$_2$ bands. For example, the doping level at which the VHS of the antibonding band lies at the $E_F$ is 22% in the orthorhombic structure and 27% in the tetragonal case. Besides the highly dispersive CuO$_2$ bands, the complex of Cu-O bands below $E_F$ (starting around a binding energy of $\approx 0.8$ eV in Fig. 2.2(a)), which is primarily composed of Cu $d$ and O $p$ bands, is also influenced by the crystal structure and doping as seen with reference to Figs. 2.1 and 2.2. In particular, in the doped orthorhombic system in Fig. 2.2(b), around the $M$-point, these lower lying bands mix significantly with the CuO$_2$ band involved in producing the bonding FS sheet, and change the shape of the associated VHS.

Fig. 2.3 shows that our theoretically predicted FS is in remarkable accord with the experimentally determined FS of an overdoped Bi2212 sample obtained via angle-resolved photoemission (ARPES) measurements [Bog01]. For this purpose,
Figure 2.3: (Color) Theoretical bonding (yellow lines) and antibonding (red lines) FS’s of orthorhombic Bi2212 for 20% (solid lines) and 30% (dashed lines) Pb doping. Other ‘shadow’ FS’s are not shown for simplicity. Experimental FS map taken via ARPES from an overdoped single crystal of Bi2212 is from Bogdanov et al. [Bog01].
computed FS contours for Pb doping levels of 20% (solid lines) and 30% (dashed lines) for the orthorhombic lattice are overlayed on the experimental FS map. [Mar05, Ban05, Sah05] The ‘shadow’ FS’s in the computations are not shown in order to highlight the main bonding and antibonding FS’s. The computed bonding FS (yellow lines) shows relatively little change over 20-30% doping range and its shape and dimensions are in quantitative accord with measurements. The antibonding FS (red lines), on the other hand, is more sensitive to doping and changes from being hole-like at 20% doping (solid red line) to turning electron-like (dashed red line) at 30% doping as the $E_F$ descends through the VHS. Therefore the spectral intensity associated with the antibonding FS in the antinodal region will be sensitive to local variations in hole doping and a careful modeling of the spectral intensities will be required to pin down details of the FS. However, along the nodal direction, neither the antibonding nor the bonding FS is sensitive to doping and here there is good accord between theory and experiment.

2.3 Coulombic effect between layers

The driving mechanism underlying the lifting of the Bi-O pockets with Pb doping in these computations may be understood as follows. The ionization of Bi atoms in the system will in general generate electric fields which tend to attract electrons back into the Bi-O layers and compete with the affinity for the electrons towards the CuO$_2$ layers. The band structures of Figs. 2.1(a) or 2.2(a) which display partially filled Bi-O bands and the associated Bi-O pockets at the FS then imply that the balance of forces in the computations is such that Bi is not fully ionized to 3+ in pure Bi2212 so that we may think of some of the Bi$^{3+}$ electrons as being attracted
back to the Bi-O layers or that the CuO$_2$ layers are self-doped with holes. The fact that the Bi-O bands are moved above $E_F$ with Pb doping in Figs. 2.1(b) or 2(b) then indicates that the substitution of Bi with Pb and the concomitant reduction of positive charge in the Bi-O layers eliminates the need for electrons to ‘flow back’ to the Bi-O layer. In effect then at e.g. 25% Pb doping an empty (Bi/Pb)-O band only donates 0.75 rather than 1.0 electron to the CuO$_2$ layer. It is helpful as well to see how this argument plays out in reverse, i.e. with decreasing Pb doping. When Pb doping decreases, the tendency of the Bi/Pb electrons to flow back to the (Bi/Pb)-O layer increases and below a critical Pb-doping level some of the Bi/Pb electrons actually flow back as the (Bi/Pb)-O band drops below $E_F$. As a result of this self-doping effect, further decrease in hole doping of the CuO$_2$ layers is prevented.

We can quantify the above argument of Coulombic effects by using the ‘atoms in molecules theory’ (AIM) [Ara02] which is implemented in LAPW. AIM is a well established and useful tool for analysis of chemical information. It can be used to divide the crystal into different atomic basins where electrons in a given basin are taken as belonging to the corresponding atom. The result for the tetragonal Bi2212 is shown in Fig. 2.4. A protrusion between Cu and O in the CuO$_2$ layer signals a strong chemical bonding between these two atoms. Here we will only use the partitions to determine net charges from AIM theory. The net charges inside each atomic basin are also obtained. We list the net charge of the reservoir BiO layer, bridging SrO layer, and conducting CuO$_2$ layer in table 2.1 for both undoped and 25% Pb doped Bi2212. While the CuO$_2$ layer gains electron, BiO and SrO layers lose electrons. The electron affinity of the CuO$_2$ layer is the strongest among all oxide layers in the crystal. An electric field between layers due to this uneven distribution of charge induces a driving force inducing electrons to ‘flow back’ to

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Figure 2.4: (Color) Partition of Bi2212 obtained by AIM theory is composed of different atomic basins. Half of the boundary of selected atomic basins is shown in units of Bohr radii (0.529177Å).
the Bi-O layer. Because the net charges are larger in undoped Bi2212 than in the 25%Pb doped case, this force is larger in the undoped case and pulls down the Bi-O bands as shown in Fig. 2.1(a).

By knowing the change of charge distribution of undoped and doped Bi2212, we can estimate the change of Coulomb potential difference between layers. A simple model of two charged parallel plates is used for estimating Coulomb potential difference. We take BiO layer as one plate and CuO$_2$ as the other. Since we are interested in the energy position of the Bi-O band, we assume the parallel plates are charged with the net number of charges $Q$ on the reservoir BiO layer listed in table 2.1. The distance $d \approx 4.56\,\AA$ between the two plates is assumed to be the distance between Bi and Cu. We also have unit cell in-plane area $A = a^2 \approx 13.4\,\AA^2$ as the area of each plate. The potential difference between the two plates is $V = \frac{Qd}{\epsilon_0A}$. Upon 25%Pb doping, the change of Q is $\Delta Q \approx 0.013e$ and causes a change of potential difference $\Delta V \approx 0.8V$. This is very close to the change of energy position of Bi-O bands between Figs. 2.1(a) and (b). Therefore, the Coulombic effect between layers is responsible for the lifting of Bi-O bands upon doping.

### Table 2.1: Net charge on layers (in units of number of electrons)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Undoped $Q$</th>
<th>25%Pb $Q$</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir BiO layer</td>
<td>-0.289</td>
<td>-0.276</td>
<td>0.013</td>
</tr>
<tr>
<td>Bridging SrO layer</td>
<td>-0.295</td>
<td>-0.277</td>
<td>0.018</td>
</tr>
<tr>
<td>Conducting CuO$_2$ layer</td>
<td>1.349</td>
<td>1.315</td>
<td>-0.034</td>
</tr>
</tbody>
</table>
Figure 2.5: Band structures of O-doped Bi2212: (a) $\delta = 0.1$, and (b) $\delta = 0.3$, where $\delta$ denotes excess O per unit cell.
2.4 Excess O-doped Bi2212 and other cuprates

We now consider the effect of adding excess O in Pb-free Bi2212 for hole doping the system. For this purpose, we have carried out extensive computations where O, F, or other pseudo-atoms are inserted in the empty spaces between the Bi-O layers in order to capture varying amounts of Bi electrons to form a closed shell. An added O atom with Z=8 (δ=1.0) captures two additional electrons/unit cell from the Bi-O layers to form a closed shell with Z=10, while an F atom only takes away one electron corresponding to δ=0.5. A Ne atom (Z=10) possesses a closed shell and it has little effect on band structure. The values of δ in the results of Fig. 2.5 were simulated by adding two pseudo-atoms/unit cell with Z=10-δ. Very similar results are obtained if O atoms in Bi-O layers are replaced by pseudo-atoms with Z less than 8.0, so that these atoms attract more than two electrons. Typical modifications in the band structure are shown in Fig. 2.5, where it can be seen that the effect of excess O is to lift the Bi-O pockets much as that of Pb/Bi substitution. The key is to reduce the effective number of electrons available in the Bi-O layers for donation to the CuO$_2$ layers and this can be accomplished via either Pb/Bi substitution or by adding excess O. In Fig. 2.5, the Bi-O pockets lie below $E_F$ for excess O value of δ= 0.1, but lie well above $E_F$ for δ= 0.3. Our analysis indicates that the Bi-O pockets move through $E_F$ at δ ≈ 0.18.

The effect of hole doping on other Bi-compounds is also considered. Fig. 2.6 expands on the discussion of Bi2212 to include the monolayer and trilayer Bi-compounds. The Bi-O bands in the 15% Pb doped Bi2201 and Bi2223 are once again seen to be lifted above $E_F$, even though the band structures of the undoped compounds in both cases display Bi-O FS pockets. Since in Bi2212 the experimental and optimized lattice parameters give similar results in the orthorhombic case, we have used
Figure 2.6: Band structures of 15% Pb-doped Bi2201 and Bi2223. Computations are based on orthorhombic lattice parameters [Tor88, Mie90]. Bands are plotted along the high symmetry lines of the tetragonal lattice for ease of comparison with the results of Fig. 2.1.
Figure 2.7: Band structures of (a) undoped and (b) 24% hole doped TI2201 along the main symmetry directions in the 2D Brillouin zone of the tetragonal lattice.

Going beyond the Bi-compounds, we have studied doping effects on the band structures of Tl- and Hg-based cuprates. Fig. 2.7(a) shows the familiar band structure of undoped (half-filled, \( x = 0.0 \)) TI\(_{2-x}\)Cu\(_x\)Ba\(_2\)CuO\(_{6+\delta}\) (TI2201) with the tetragonal lattice [Shi90]. It displays the CuO\(_2\) band characteristic of the cuprates, with minimum at \( \approx -1.3 \) eV at \( \Gamma \), van Hove singularity (VHS) at \( \approx -0.5 \) eV around the \( M(\pi,0) \)-point, and the non-symmetric inverted parabola along the \( M(\pi,0) \rightarrow X(\pi,\pi) \rightarrow \Gamma \) line. In addition to this CuO\(_2\) band, a second band, which is Tl-O related, is seen to drop below \( E_F \) at \( \Gamma \), giving rise to a \( \Gamma \)-centered electron pocket, which has not

experimental orthorhombic parameters for Bi2201 [Tor88] and Bi2223 [Mie90].
been observed experimentally [Hus03, Pla05]. The problem is similar to that of Bi-O pockets noted above in connection with Bi2212 except that here the pocket is centered around the Γ rather than the $M(\pi,0)$-point.

Fig. 2.7(b) presents results for 24% hole doped Tl2201, where the effects of doping have been taken into account. The Tl-O band has now moved $\approx 0.9$ eV above $E_F$ and the Tl-O pocket of Fig. 1(a) has disappeared from the electronic structure. At 24% hole doping, the rigid band shift (lowering) of $E_F$ will also empty the pocket [Pla05], but the present calculations show that this pocket will be removed very rapidly with doping as the Tl-O band moves to higher energies. Effects of doping beyond the rigid band model are less dramatic on the CuO$_2$ band, amounting to a slight narrowing with doping.

We comment briefly on our theoretical predictions in relation to relevant experimental results on overdoped Tl2201 single crystals. The shape and three-dimensionality of the FS derived from the band structure of Fig. 1(b) is in general accord with that reported in angular magnetoresistance oscillation (AMRO) measurements [Hus03], including delicate variations in the shape of the 3D FS half-way between nodal and antinodal directions, as well as with the angle-resolved photoemission (ARPES) results [Pla05]. However, even though the general shape and the 3D nature of the FS is captured by LDA, the theoretical FS is more squarish than the experimental one (i.e. closer to $X$ in $M-X$ direction and closer to Γ in $\Gamma-X$ direction), possibly reflecting strong correlation physics beyond the conventional picture. Notably, the ARPES lineshapes for emission from $E_F$ in Tl2201 show relatively little broadening even in the antinodal region [Pla05], indicating that interlayer coupling effects in Tl2201 are smaller than in La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) [Ban05, Sah05].

Similar doping effects are also found in Hg-based cuprates. Specifically, for undoped
Hg-based cuprates under a pressure of 10GPa, the Hg-derived bands around \((\pi,0)\) drop below \(E_F\) and induce self-doped holes in the CuO\(_2\) bands [Amb04]. As doping increases, the Hg-derived bands are lifted above \(E_F\), and the self-doping effect is removed.

### 2.5 Summary

In conclusion, our results show clearly that substantial and generic Coulombic effects come into play with hole doping to lift the cation-derived bands in the cuprates. In adducing various physical quantities from spectroscopic data (e.g. size of the pseudogap), changes in the electronic structure with underdoping, especially near the anti-nodal point, should be accounted for, even though most of the existing analysis in the cuprate literature assumes a doping-independent band structure. Finally, the present study provides a first-principles route for exploring self-doping effects and doping dependencies of the electronic structures of this exciting class of materials.
Chapter 3

Possibility of Electron Doped Bi2212*

Local density approximation (LDA) calculations of the cuprates have long been problematic, failing to reproduce the insulating gap at half filling. In Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212) the problem is exacerbated in that a Bi-O derived pocket is predicted to cross the Fermi level ($E_F$), whereas angle-resolved photoemission (ARPES) experiments find only the familiar CuO$_2$-plane Fermi surfaces (FSs). We demonstrated in chapter 2 that the Bi-O pocket problem [Lin06] could be solved away from half filling by properly accounting for hole doping (by Pb or excess oxygen) via the virtual crystal approximation (VCA). It suggests that the Bi-O pocket should *reappear* in the underdoped regime, leading to a self-doping effect in the underdoped regime, wherein a finite hole doping remains on the CuO$_2$ planes even at half filling. In fact, there is some experimental support for this situation, in that an antiferromagnetic

*This chapter is adapted from the following paper.
Hsin Lin, S. Sahrakorpi, R. S. Markiewicz, and A. Bansil, *Possibility of electron doped Bi2212*, unpublished.
(AFM) insulating phase is not typically found in Bi2212 by simply reducing the oxygen content, although it can appear in thin films when some Ca is replaced by a rare earth (RE) element. Here, we further apply the VCA to demonstrate that (1) the pocket can be eliminated even at half filling by co-doping Pb and RE, thereby explaining experimental observations; and (2) excess RE can in principle lead to a net electron doping, into the doping range where superconductivity is found in related materials (Nd$_{2-x}$Ce$_x$CuO$_4$ [NCCO]).

3.1 Computational details

The present calculations were performed within the framework of density functional theory with local density approximation as well as LDA+$U$. The full-potential linearized augmented plane-wave method as implemented in the WIEN2k code [Bla01] was used in all computations. The structural complexity of Bi-based cuprates adds to the difficulty of comparisons between experimental data and theoretical calculations. Incommensurate superstructure close to a $\sqrt{2} \times 5\sqrt{2}$ orthorhombic cell gives the so called Umklapp replicas seen in ARPES FS maps. [Ase03] This superstructure can be suppressed by Pb-doping [Sch95]. The remaining shadow features can be understood in terms of an approximately $\sqrt{2} \times \sqrt{2}$ orthorhombic distortion [Arp06]. Here, we use this orthorhombic cell as a better approximation to the real Bi2212 lattice than the conventional tetragonal cell used in earlier literature [Mas88, Kra88, Hyb88]. Lattice parameters are taken from structurally optimized computations by Bellini et al. [Bel04] where total energy and force minimizations were performed.

There are three types of doping in this study, namely Pb, O, and RE doping. While
Pb and O dopants are in the BiO layer, RE replaces Ca between two CuO$_2$ planes. Since all the three dopants are outside CuO$_2$ layers, Coulombic effects between layers discussed in chapter 2 dominate the change in the band structure. The rigid band model is found to be not adequate for simulating the doping. Instead, VCA captures the Coulombic effect between layers and is used in the following study. In VCA, the ionic charge is changed by the appropriate (fractional) charge averaged over the dopant distribution, and the total number of electrons is adjusted to keep the crystal electrically neutral. All results are fully self-consistent.

### 3.2 Achieving AFM states by RE doping

We set the stage for our discussion by recalling the Bi-O pocket problem. For undoped Bi$_2$212, band theory predicts that the FS contains Bi-O electron pockets around the antinodal point $M(\pi, 0)$ which have never been observed experimentally [Dam03, Bel04]. This ‘Bi-O pocket problem’ is quite pervasive and occurs in other Bi-based cuprates. [Sin95] In chapter 2, we showed that Pb or O doping could lift the Bi-O bands, yielding a CuO$_2$-plane dominated FS whose shape agrees well with ARPES experiments. [Bog01] These results imply, however, that the pockets should reappear in undoped Bi2212. While ARPES has never observed the Bi-O derived FS, it is possible that low enough doping was never achieved, due to uncontrolled oxygen excess.

Interestingly, it is only possible to experimentally reach the AFM insulating state by RE substitution on the Ca site. The RE, typically Y or Dy, acts as a trivalent donor which provides one more electron than Ca. We model this kind of doping within VCA by increasing the nuclear charge $Z$ of the Ca site, neglecting size effects. We will use
the chemical formula $\text{Bi}_{2-2x}\text{Pb}_x\text{Sr}_2\text{Ca}_{1-2y}\text{RE}_{2y}\text{Cu}_2\text{O}_{8+\delta}$ where $x$, $y$, and $\delta$ are doping levels of Pb, RE, and O, respectively. An increase in $x$ or $\delta$ will increase holes per Cu while an increase in $y$ will increase electrons per Cu. To make comparisons to our results for a particular hole doping level, one has to use the sum of Pb content and amount of excess oxygen in experiments as $x+\delta$ holes per Cu. Combining both hole and electron doping, the net hole doping level per Cu would be $x+\delta-y$.

Pb and O doping are two alternative ways to lift the Bi-O bands rapidly and move $E_F$ down. For bands near $E_F$, Pb and O doping give similar results in our VCA calculations. In this work, both the Pb and O doping calculations give the same conclusion. Unlike Pb/O doping, RE doping moves $E_F$ up by filling electrons and changes Bi-O bands relatively little. This is because the Ca layer is very close to the CuO$_2$ layer and far away from BiO layers.

Since Pb/O doping adds holes and lifts the Bi-O bands rapidly while RE doping primarily only reduces the number of holes on the CuO$_2$ planes, it should be possible to get half-filled CuO$_2$ bands by a combination of Pb/O and RE doping. Figure 3.1(a) shows LDA bands for Pb and RE co-doped Bi2212 with $x=0.2$ and $y=0.2$ corresponding to half-filling. The directions in reciprocal space are selected to be the same as in the tetragonal case for ease of interpretation. The Bi-O bands are lifted above $E_F$ by about 0.5 eV. Only half-filled CuO$_2$ bands cross $E_F$ and form two hole-like FS’s centered at $X(\pi, \pi)$. The extended van Hove singularities (VHSs) appear below $E_F$ at the $M$-point as expected. The bare bilayer splitting at $M$ is $\approx 400$ meV.

It is well known that LDA fails to predict a Mott AFM insulator for parent compounds of cuprates [Czy94]. LDA+$U$ is a remedy for too small Coulomb repulsion on the Cu site. While the typical bare value of $U$ for Cu is 7-11 eV [Gra92], part of
Figure 3.1: Band structure of half filled Bi$_{2-2x}$Pb$_x$Sr$_2$Ca$_{1-2y}$RE$_{2y}$Cu$_2$O$_{8}$ with $x=0.2$ and $y=0.2$ along various high symmetry directions at $k_z = 0$. (a) LDA (b) LDA+U with $U=5\text{eV}$. 
the effect of $U$ is already included in LDA, and the optimal value used in LDA+U calculations is generally somewhat smaller. In figure 3.1(b), we employ an LDA+$U$ calculation with $U=5$ eV on Pb and RE doped Bi2212 with $x=0.2$ and $y=0.2$. Again, the Bi-O bands are lifted above $E_F$ by about 0.5 eV and a large gap opens to form an insulating state. In additional LDA+U calculations, we found that as the Pb doping is reduced, the Bi-O bands again cross the Fermi level, even when a large $U$ opens a gap within the CuO$_2$ band. $U$ has little effect on the position of Bi-O bands but changes the CuO$_2$ bands dramatically. The opening of the Mott gap requires both sufficient amount of co-doping and proper value of $U$ in the calculation. This is consistent with experiments that no AFM insulating states are found by reducing Pb/O doping alone. Due to the need for a certain amount of Pb/O doping for lifting the Bi-O bands, half filled AFM insulating phase can only be achieved by adding RE doping additionally to compensate the holes created by Pb/O doping.

3.3 Electron doping

It should be possible to add an excess of RE doping, leading to net electron doping of the CuO$_2$ planes. However, this doping also moves the Bi-O bands closer to $E_F$, so the electron doping level of the CuO$_2$ layer is limited. Here we show how to optimize the electron doping of Bi2212, by combining RE doping with a small amount of Pb/O-doping to keep the Bi-O bands above $E_F$. Figure 3.2 shows the LDA band structure of Pb and RE doped Bi2212 with $x=0.3$ and $y=0.5$. The Bi-O bands are lifted $\sim 1$eV above $E_F$ and the excess electrons provided by RE dope each CuO$_2$ layer to about 20% electron doping. The $E_F$ almost reaches the AFM boundary at $(\pi/2, \pi/2)$. Such a doping level is comparable to optimal doping in the
Figure 3.2: LDA band structure of Pb and RE doped Bi2212 with $x=0.3$ and $y=0.5$ along various high symmetry directions at $k_z = 0$.
electron doped superconductor NCCO. In NCCO, the AFM gap collapses around 15% electron doping level and the superconducting phase emerges.

Figure 3.3(a) provides a calculated co-doping map, illustrating the position of the Bi-O pockets with respect to $E_F$ and the doping range where electron doping might be found. Superimposed on the map are the actual dopings of several experimental surveys. When Pb/O doping levels are low enough (lower than the dashed line), the Bi-O bands cross $E_F$ (red area in figure 3.3(a)). On the other hand, as Pb/O doping levels become high enough (higher than the dot-dashed line), some oxygen bands move up toward $E_F$ and cross $E_F$ (green area in figure 3.3(a)). Between the dashed line and the dot-dashed line is the region where only the main CuO$_2$ bands cross $E_F$. All the doping levels of experimental surveys lie within this region. We suggest that this region is more stable than outside. Partially filled Bi-O bands or partially empty oxygen bands imply the bonds between layers lose their ionic nature. The system could seek other configurations (for example, structural transition or capturing excess oxygens) to have Bi and oxygens fully ionized. Hence, the red and green regions are unstable and not observed by experiments.

Figure 3.3(b) is an experimental phase diagram from Calestani et al. [Cal92] At large enough Pb content, our theoretical dot-dashed line agrees with an experimental boundary where mixed oxides emerge. This proves that green region in figure 3.3(a) is not stable as suggested by our theory. Note that their vertical axis is only Pb content, and the excess oxygen content is missing. Our superimposed lines assume pure Pb doping. In a subsequent study, they also found that Pb and O doping tend to compensate each other [Cal93]. Thus excess O doping is generally found in the low Pb content samples, and net electron doping is not achieved experimentally. To obtain a net electron-doped Bi2212, we suggest that one needs to remove oxygens
Figure 3.3: (Color) (a) Co-doping map. While Bi-O bands are found to cross $E_F$ in the red region below the dashed line, oxygen bands cross $E_F$ in the green region above the dot-dashed line. Several doping levels found in the experiments are indicated as follows. Diamond: modulation free samples in Calestani et al. [Cal92]; square: Harima et al. [Har03]; triangle: Karppinen et al. [Kar03]; cross: Fukushima et al. [Fuk94] (b) Dashed (where Bi-O bands cross $E_F$) and dot-dashed (where oxygen bands cross $E_F$) lines overlaid on experimental phase diagram. [Cal92]
for low Pb content and replace all Ca by RE.

Hence, we find that while it should be possible to make electron-doped Bi2212, that region of the phase diagram has likely not been explored, due to inadvertent oxygen excess. The phase diagram suggests that one could make an electron-doped Bi2212 with net 25% electrons per Cu, by keeping 25% Pb/O doping to avoid the presence of Bi-O pockets and 100% RE doping for providing extra electrons into the system. Since the excess oxygen and Pb doping seem to compensate each other, we suggest that one use ≈ 25% Pb doping or less and remove excess oxygen as much as one can. The discovery of a new bilayer electron-doped superconductor would have a number of potential benefits. First, electron-doped superconductors seem to be less prone to phase separation, and it would be of interest to see if that extends to a very different family of cuprates. If so, much more detailed calculations of the normal state properties are possible, and this would be an ideal test case to compare to its hole-doped analog – in particular, Bi2212 is well suited for scanning tunneling microscopy (STM) studies. Finally, bilayer superconductors tend to have higher transition temperatures. For these reasons, we hope that figure 3.3 can serve as a roadmap to the preparation of this interesting new material.

We note however some possible complications. We have not been able to ascertain the role of the superlattice (or other possible structural instabilities) in controlling the position of the Bi-O pocket. Further, there may be limits on oxygen solubility which we are unable to assess. On the other hand, a sample with a metallic BiO-layer may lose its high quality cleavage plane, thereby making it unsuitable for surface related experiments, such as ARPES and STM.
3.4 Summary

In conclusion, we have explained why rare earth substitution is necessary to reach the AF insulating state in underdoped Bi2212, and have made two experimentally verifiable predictions: (1) that Bi-O pockets should form in Pb/O-free and RE doped Bi2212 and (2) that co-doping with rare earth atoms and Pb could lead to an electron-doped superconductor. While oxygen solubility limitations may restrict the experimental observation of either effect, the novelty of a bilayer electron-doped superconductor is sufficiently great as to make its pursuit worthwhile.
Chapter 4

Appearance of Universal Metallic Dispersion in a Doped Mott Insulator*

Under strong electronic correlations the parent compounds of all cuprates assume the so-called Mott-Hubbard insulating state, rather than the conventional metallic state. By what routes these insulators accomplish the miraculous transformation into superconductors with the addition of electrons or holes is a question of intense current interest, which bears on ongoing debates surrounding the interplay

*This chapter is adapted from the following talks and papers.
between electron correlations, magnetism, lattice effects, and the mechanism of high-
temperature superconductivity. [Dam03] In this study we consider the classic su-
perconductor La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) over the wide doping range of $x = 0.03 - 0.30$,
delineating how the electronic spectrum evolves with doping for binding energies
extending to several hundred meV’s. Our analysis indicates that this Mott insula-
tor contains ‘nascent’ or ‘preformed’ metallic states, which develop finite spectral
weight with doping, but otherwise undergo relatively little change in dispersion over
a wide doping range.

We have analyzed extensive angle-resolved photoemission (ARPES) measurements
from LSCO single crystals taken by our experimental collaborators covering a wide
range of dopings, momenta and binding energies. Although the incoherent part of
the spectrum behaves quite anomalously, we find that many-body effects conspire in
such a way that insofar as the coherent part of the spectrum is concerned, at least its
underlying dispersion is reasonably described by the conventional band-theory pic-
ture, significantly broadened lineshapes and ‘kinks’ in the dispersion notwithstand-
ing. Surprisingly, even with the addition of just a few percent holes in the insulator,
the full-blown metallic spectrum seemingly turns on with little renormalization of
the dispersion. In particular, the spectrum displays the presence of the tell-tale van
Hove singularity (VHS) whose location in energy and three-dimensionality are in
accord with the band theory predictions. Furthermore, this metallic spectrum is
‘universal’ in the sense that it depends weakly on doping, in sharp contrast to the
common expectation that dispersion is renormalized to zero at half-filling.
4.1 Methods

The band structure results are based on all electron, full-potential computations within local density approximation (LDA) using the tetragonal lattice structure [Jor87], and include effects of La/Sr substitution within the framework of the virtual crystal approximation [Lin06] introduced in chapter 2. The ARPES data are provided by the group of Prof. Shen in the Department of Physics, Applied Physics and Stanford Synchrotron Radiation Laboratory at Stanford University, Stanford and in the Advanced Light Source (ALS) Division at Lawrence Berkeley National Laboratory. The measurements were carried out on Beamline 10.0.1 at the ALS using Scienta 200, 2002, and R4000 electron energy analysers for 55 eV light with strong in-plane polarization. The energy resolution is 15-20 meV, and the angular resolution is 0.3 degrees for the 14 degrees angular mode. All data were taken at T=20K.

4.2 Nascent metallic states

Fig. 4.1 sets the stage for our discussion showing typical spectra from LSCO in the form of energy distribution curves (EDCs) at two different dopings for a series of momenta. Considering the overdoped case (upper red set), we see a coherent feature dispersing to higher binding energies and becoming broader as one moves away from the Fermi momentum $k_F$. This feature sits on top of a substantial incoherent background extending to quite high energies at all momenta. These basic characteristics are seen to persist in the lightly doped sample (lower blue set), although the greatly reduced spectral weight of the coherent feature in relation to the incoherent part of
Figure 4.1: Illustrative ARPES spectra as a function of binding energy in La$_{2-x}$Sr$_x$CuO$_4$ for a series of momenta along the nodal (i.e. $\Gamma$ to $(\pi, \pi)$) direction. Results from a lightly doped insulating sample ($x = 0.03$, blue lines) and an overdoped metallic sample ($x = 0.22$, red lines) are shown. Coherent spectral peak is seen to disperse to higher binding energies as one moves away from the Fermi momentum, $k_F$. 

55
the spectrum is very evident. Our focus is on the aforementioned coherent feature in the spectrum of LSCO, and especially on delineating the evolution of its dispersion with doping.

The existence of a large, Luttinger-like, metallic ‘nascent’ or ‘underlying’ Fermi surface in LSCO has been established in previous studies, culminating in the recent systematic analysis of Saharakorpi et al. [Sah05] and Yoshida et al. [Yos06]. In contrast, here we consider spectra over a wide energy range of several hundred meV’s, show the presence of the VHS—a unique feature of the band structure—even in the lightly doped insulator, and establish unequivocally the existence of near-universal metallic dispersion in LSCO. These ‘nascent’ Fermi surfaces and dispersions are well defined despite the difficulties of identifying features in the face of loss of spectral weight as the pseudogap develops with underdoping. We emphasize that our focus is on what we may call the ‘gross’ spectrum. In other words, we are not concerned with the fine structure in the electronic spectrum associated with the well-known low energy kinks [Lan01], the recently discovered features at higher energy scales, [Ron05, Gra07, Mee07, Xie07, Val07] or superconducting [Sen07], or other [Kan06] leading-edge gaps.

4.3 Doping evolution

The top row of Fig. 4.2 shows ARPES intensity maps from a lightly doped sample of LSCO \((x = 0.03)\) for a series of binding energies. Cross-sections of the corresponding constant energy (CE) surfaces in the \((k_x, k_y)\) plane computed from the band structure of LSCO, superposed at \(k_z = 0\) (magenta lines) and \(k_z = 2\pi/c\) (black lines) indicate the expected broadening of the ARPES spectra associated
Figure 4.2: Experimental ARPES intensity maps in LSCO are compared with the corresponding cuts in the \((k_x, k_y)\) plane through the theoretical constant energy (CE) surfaces for \(k_z = 0\) (magenta lines), and \(k_z = 2\pi/c\) (black lines). Top Row: \(x = 0.03\) with binding energy varying from 22 meV to 190 meV. Bottom Row: ARPES maps for emission from the Fermi energy for dopings varying from \(x = 0.05\) to \(x = 0.30\).
with interlayer coupling. At zero binding energy, i.e. the Fermi energy $E_F$, such CE contours give the projection of the 3D FS of LSCO on to the $(k_x, k_y)$ plane. Notably, the momentum region enclosed by these CE contours defines the region of allowed ARPES transitions, modulated by the effect of the ARPES matrix element. [Ban99b, Ban05, Sah05] At low binding energies, the CE surface is seen from panels (a-c) to be hole-like around the $X$($\pi$, $\pi$) point for all $k_z$ values. In contrast, at high energy in panel (e), after the VHS has been crossed, the CE surface becomes completely electron-like centered at $\Gamma$. The transition from a hole-to electron-like CE surface does not take place abruptly because the VHS possess a significant 3D character, extending from 85-140 meV in binding energy.

The evolution of the experimental ARPES intensity pattern with binding energy in the top row of Fig. 4.2 clearly follows that of the projected CE surfaces. In particular, the spectral intensity remains confined mainly within the boundaries of these projections as expected, and with increasing binding energy, the intensity first spreads towards the $M$($\pi$, 0)-points and then moves away from the $M$-points along a perpendicular direction, very much the way the CE surfaces transition from being hole- to electron-like. Moreover, first principles ARPES computations show that under the combined effects of the matrix element and $k_z$ dispersion, the spectral intensity develops the characteristic ‘wing-like’ shape seen in Fig. 4.2, and that the spectral weight grows rapidly in the antinodal region as the VHS is approached. [Sah05] These results leave no doubt that metallic states, including the presence of the 3D VHS, appear in the spectrum of the insulator with the addition of only a few percent holes, even though spectral broadening and incoherent background make it hard to see this directly in the individual EDCs. The observed location in energy and three-dimensionality of the VHS is well-described by the conventional
band theory picture, indicating that the energies of these metallic states undergo little renormalization in the lightly doped insulator. The characteristic dispersion of the VHS is quite recognizable in the emission maps of the top row of Fig. 4.2.

The aforementioned metallic dispersion is only weakly dependent on doping. Note that if this is true then the main difference in going from one doping to another would be a shift in the Fermi energy needed to accommodate the right number of holes in the filled portion of the band structure. That is, topologies of the CE surfaces and the associated emission spectra would be comparable for various dopings except for a rigid shift of the energy scales. That this is indeed the case is shown by the results for emission from the $E_F$ for $x = 0.05 - 0.30$, presented in the bottom row of Fig. 4.2. For example, based on parameter free LDA computations for $x = 0.03$ and $x = 0.30$, the $E_F$ for $x = 0.30$ is lower by 190 meV than for $x = 0.03$, so that the ARPES map for emission at a binding energy of 190 meV from $x = 0.03$ in panel (e) can be compared with that for emission from the $E_F$ for $x = 0.30$ in (j). In this vein, the binding energies in the various panels of the top row of Fig. 4.2 for $x = 0.03$ have been chosen to match the $E_F$ shifts involved at the doping levels considered in the panels of the bottom row. Good accord is seen in all cases. These and other similar comparisons among spectra taken at different binding energies and doping levels show clearly that LSCO is characterized by a near-universal metallic dispersion despite dramatic changes in the lineshape due to interactions. This is also true for the theoretical dispersions, although slight doping dependencies can be seen for example by comparing the CE surfaces in the top and bottom frames (c) and (h) in Fig. 4.2.

Further insight is provided by Fig. 4.3, which shows plots of spectral intensity as a function of binding energy along the antinodal line (top row) and the nodal line
Figure 4.3: ARPES intensity maps along the antinodal (top row) and nodal (bottom row) directions over the doping range $x = 0.30 - 0.03$. The corresponding computed band structures are also plotted for three different values of $k_z$: $k_z = 0$ (magenta solid line), $k_z = \pi/c$ (magenta dashed line), and $k_z = 2\pi/c$ (black solid line). Black dots mark positions of the peaks in the experimental spectra. Note that nodal data in the lower row are plotted on an expanded horizontal scale in order to highlight relatively small differences between gross theoretical and experimental dispersions. For each doping, the nodal and antinodal intensities are normalized to a common maximum.
Table 4.1: Estimates of dispersion renormalization factors $Z_{\text{disp}}$ in LSCO for different dopings $x$ in relation to the LDA values. Nodal $Z_{\text{disp}}$ values in parenthesis are an estimate of the upper limit. Stars in the second row denote that for these dopings the values refer to the region in the vicinity of the antinodal point as discussed in the text.

<table>
<thead>
<tr>
<th>Doping $x =$</th>
<th>0.03</th>
<th>0.07</th>
<th>0.12</th>
<th>0.15</th>
<th>0.22</th>
<th>0.30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z_{\text{disp}}$ (nodal)</td>
<td>1.0 (1.2)</td>
<td>0.8 (1.2)</td>
<td>0.6 (0.8)</td>
<td>0.6 (0.8)</td>
<td>0.6 (0.7)</td>
<td>0.6 (0.6)</td>
</tr>
<tr>
<td>$Z_{\text{disp}}$ (antinodal)</td>
<td>1.1±0.2</td>
<td>1.3±0.4</td>
<td>&gt;0.6*</td>
<td>&gt;0.6*</td>
<td>&gt;0.7*</td>
<td>&gt;0.7*</td>
</tr>
</tbody>
</table>

(bottom row) for six different dopings. The corresponding energy bands at $k_z = 0$, $\pi/c$ and $2\pi/c$ are overlaid in each panel. These bands are seen to differ substantially for different $k_z$ values along the antinodal line in the upper panels but are virtually indistinguishable in the lower panels along the nodal line. The VHS, which is marked by the extremum of the band along the antinodal line, is spread over 40 meV at $x = 0.03$ doping due to the effect of $k_z$ dispersion, and its center lies at 110 meV below $E_F$ for $x = 0.03$, but moves to 110 meV above the $E_F$ for $x = 0.30$ with a spread of 70 meV. Along the nodal direction, the theoretical band follows the experimental peak positions given by the black dots reasonably well, although the experimental points are shifted to the right compared to theory in most cases, indicating a slight deviation of FS shape from LDA. Along the antinodal direction, however, the spectral peaks are substantially broader due to $k_z$ dispersion and also possible many body interactions, although most of the spectral weight lies within the $k_z$ dispersed bands as expected in a quasi-2D system. [Ban99b, Ban05, Sah05]
4.4 Dispersion renormalization

We have examined the renormalization of dispersion in relation to the LDA values along the nodal and antinodal directions as a function of doping, and thus obtained the associated renormalization factors $Z_{\text{disp}}$. These results are summarized in table 4.1. Our study provides new insight into the value of $Z_{\text{disp}}$ along the antinodal direction because the VHS is a very robust feature of the LDA band structure. By determining the position of the VHS in the experimental spectrum, and comparing this position with that expected from the LDA, we can uniquely determine the overall renormalization of the spectrum along the antinodal direction with respect to the LDA. At $x = 0.03$ and $x = 0.07$, the VHS lies below the Fermi energy for all $k_z$ values, and in these two cases, by analyzing the CE maps using different renormalization factors to scale the LDA bands, we have obtained $Z_{\text{disp}}$ (antinodal) values of $\sim 1$ within the uncertainty shown in table 4.1, so that the LDA bands are essentially unrenormalized. For $x = 0.12$ and higher dopings, part or all of the VHS lies above the Fermi energy, so that we were only able to estimate a lower limit for $Z_{\text{disp}}$ in the vicinity of the antinodal point. There are of course no filled states at the antinodal point once the VHS moves above the Fermi energy.

Turning to the nodal direction, the effects of $k_z$ dispersion are small, and our analysis is consistent with results available in the literature. For completeness, however, we have estimated the gross $Z_{\text{disp}}$ (nodal) values from the nodal spectra given in Fig. 1 of Zhou et al. [Zho03], reproduced here as Fig. 4.4. In order to gain a handle on the ‘gross’ or underlying dispersion exclusive of the low energy kink (see arrow at 70 meV in Fig. 4.4), values of $Z_{\text{disp}}$ (nodal) given in Table 4.1 are obtained from the slopes of the straight lines joining the point at the Fermi energy with that at 200 meV binding energy, i.e. by lines such as the blue line drawn for the $x = 0.03$
Figure 4.4: Reproduction of Fig. 1 in Zhou et al. [Zho03]. Blue line drawn on the $x = 0.03$ dataset illustrates how the nodal $Z_{\text{disp}}$ value is defined here, while the red line gives the high energy slope used to estimate the corresponding upper limit on $Z_{\text{disp}}$ (nodal) as discussed in the text.
case in Fig. 4.4, and comparing this slope to the corresponding LDA values. Since the LDA values of the nodal radii do not exactly match the measured values, we have estimated $Z_{\text{disp}}^{\text{(nodal)}}$ by comparing LDA and experimental slopes. We also show in parentheses the values of $Z_{\text{disp}}^{\text{(nodal)}}$ obtained from the slopes of the high energy part of the spectrum, as given for example by the red line for $x = 0.03$ in Fig. 4.4, which provides an estimate for the upper limit of $Z_{\text{disp}}^{\text{(nodal)}}$.

Interestingly, at the lowest doping of $x = 0.03$, the nodal as well as the antinodal renormalization factor is seen to be $\sim 1$. In the optimally and overdoped regimes, the nodal renormalization factor is $\sim 0.6$, while the value of the antinodal factor is estimated to be greater than 0.6. In the underdoped $x = 0.03$ case, the renormalization of states in the antinodal and nodal directions is roughly similar, but this is less clear at higher dopings. These results are surprising since we might have expected the LDA to provide a reasonable description in the overdoped regime, and to be renormalized greatly in the underdoped case.

Even though we have shown that the gross dispersion up to several hundred meV’s is described quite well by the band theory picture, this does not mean that the spectrum of LSCO is conventional in nature. As shown in Fig. 4.1, the coherent spectral weight of these dispersive features fades away for underdoping where the pseudogap and polaronic effects kick in. The spectral weight is transferred to an incoherent feature [Yos03, She04, Ros05], reflecting the importance of many-body physics. Our analysis thus suggests that the spectrum of the insulator already contains ‘preformed’ or ‘nascent’ metallic states, which possess zero spectral weight in the half-filled case. With doping, these states develop finite spectral weight, but otherwise undergo relatively little change in their basic character.

It is interesting to study the relationship between the renormalization of the dis-
persion and spectral weight within the simple Green function formalism. The Green function can be approximately written as \( G = Z_\omega [\omega - Z_\omega \epsilon_k / Z_k] \), with \( Z_\omega = 1/(1 - \partial \Sigma / \partial \omega) \), and \( Z_k = 1/(1 + \partial \Sigma / \partial \epsilon_k) \), where \( \Sigma \) is the self-energy. While the spectral weight renormalization is associated with \( Z_\omega \), the band dispersion renormalization is given by \( Z_{\text{disp}} = Z_\omega / Z_k \). It is striking that the spectral weight in LSCO is renormalized greatly but the dispersion is not. This is not consistent with a momentum independent self-energy, since the renormalization of spectral weight would then be accompanied by a similar renormalization of dispersion, suggesting that the self-energy possesses momentum as well as energy dependencies such that the effects of the associated renormalization factors, \( Z_\omega \) and \( Z_k \), [Par04] conspire to approximately cancel each other in renormalizing dispersion. This picture however implies that the heat capacity would be renormalized only weakly with doping, which is not the case experimentally. [Mat04]

Insofar as theoretical models of strongly correlated systems are concerned, a focus of attention in the literature has been the \( t - J \) model, which has been used to describe the physics of the Hubbard Hamiltonian in the large \( U \) regime. One class of \( t - J \) models finds gapped insulating solutions at half-filling, which evolve with doping to yield small Fermi surface pockets [Pre02]. This route appears to be followed in NCCO for electron doping [Arm01, Kus02, Tre06]. But the present results do not show clear evidence for small pockets or other strong violations of Luttinger’s theorem [Kok07]. On the other hand, metallic solutions with a large Luttinger-like Fermi surface have also been reported [Ede06, Sen07], where the spectral weight \( Z_\omega \) is renormalized to zero at half-filling. These solutions are closer to our observations, even though the band width is found to be strongly renormalized near half-filling, \( Z_{\text{disp}} \sim J/t \). A recent variant of the \( t - J \) model succeeds in capturing both the
metallic and insulating aspects of the spectrum simultaneously [Rib05, Tan07]. However, to our knowledge, our finding of a large Fermi surface and a large dispersion, which is weakly dependent on doping, does not fit well within the framework of the currently available scenarios based on simple Hubbard or $t-J$ models or naive application of the classical polaron theory.

4.5 Summary

In conclusion, we have shown that metallic states appear in the electronic spectrum of high temperature superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at all doping levels, ranging from the lightly doped insulating to the overdoped metallic regime. The gross dispersion of these states is not only near-universal in that it is weakly dependent on doping, but it is also conventional in that it is reasonably described by the standard band theory picture up to binding energies of several hundred meV’s. However, the metallic states suffer substantial loss of spectral weight with underdoping and in this respect behave quite unconventionally. Our findings challenge existing theoretical models of the cuprates and indicate the complexity with which many-body physics plays out in this fascinating material.
Chapter 5

Mott vs. Slater Physics in Three-and Four-band Models of Electron-doped Cuprates*

5.1 Introduction: Mott vs. Slater physics

Undoped high $T_c$ cuprates are antiferromagnetic (AFM) insulators with a gap due to the large Coulomb repulsion energy cost $U$ of double site occupation. The evolution of this gap with doping is an important unresolved problem. In this regard, electron-doped cuprates have an important advantage in angle resolved photoemis-

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*This chapter is adapted from the following talks and papers.


sion (ARPES) studies, since the entire lower magnetic band (LMB) and the occupied part of the upper magnetic band (UMB) are observable. Recent ARPES experiments on Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO) [Arm02] suggest a simple evolution: the electrons dope into the bottom of the UMB (starting from $(\pi,0)$), and the gap collapses with doping, vanishing near optimal doping as the FS changes from disconnected pockets to a large FS.

Kusko, et al. [Kus02] were able to reproduce this behavior in a one-band mean-field model, where the gap is due to AFM order, and U was found to decrease with doping by about a factor of two, consistent with Kanamori screening [Kan63]. When fluctuation effects are included [Mar04], only short range AFM order is present for $T > 0$, and the gap collapse is associated with a quantum critical point (QCP) where $T=0$ Neel order terminates. Several other one band calculations [Kus03, Sen04, Kyu04] come to similar conclusions. The model also gives a good description of the collapse of the optical pseudogap and of the doping dependence of strictly magnetic properties – the staggered magnetization and magnetic correlation length.

However, extension of these results to a multiband model is nontrivial. In the conventional Zaanen-Sawatzky-Allen (ZSA) scenario [Zaa85], the cuprates are charge transfer insulators at half filling – that is, the copper-like states are split by a large Mott gap, and the actual gap is between the UHB and an oxygen band. There is no obvious connection between this charge-transfer gap and the AFM order of the cuprates. Here, we suggest a resolution to this problem.

We propose a separation of the energy scales of Mott and Slater physics in the multi-band model. The Mott physics involves short ranges and large energies: here double occupancy of Cu atoms is avoided by a new mechanism: strong hybridization with oxygens. On the other hand, the Slater physics arises at a much lower
energy scale, as (short-range) AFM order splits the antibonding Cu-O band. The resulting AFM-split antibonding band now has a dispersion and doping dependence in excellent agreement with the one-band model. However, it has the following advantages: (1) the top of the LMB now has predominantly oxygen character, and is an excellent approximation to the Zhang-Rice singlet. (2) The connection with magnetic properties is now properly explained. (3) The true $U$ parameter $U \sim 7$ eV is much larger than the effective $U_{\text{eff}} \sim 2$ eV of the one-band model, and has a considerably smaller doping dependence, $\sim 20\%$ rather than a factor of 2. (4) The collapse of the Slater gap at a QCP leaves the Mott physics nearly undisturbed.

In more detail, the bands of the three-band model correspond to bonding and antibonding Cu-O bands, with a non-bonding O band in between. The Cu character of the bonding band is a sensitive function of three parameters, Cu-O hybridization energy $\Delta$, Hubbard $U$, and the corresponding $U_p$ on the oxygens. The system can vary from charge transfer to Mott insulator as these parameters change. Hybertsen, Schluter, and Christensen (HSC) [Hyb89] found a large value of $\Delta$ by fitting the local density approximation (LDA) bands. Such a large $\Delta$ would incorrectly place the cuprates in the Mott insulator class, with a relatively small Cu fraction in the bonding band.

We find that a wide variety of parameters can provide a good fit of the three-band model to experimental ARPES spectra in NCCO, but that some parameters must be doping dependent. Minimizing the doping dependence leads to a small value of $\Delta$, and hence to enhanced Cu character of the bonding band, consistent with a charge transfer insulator. In this limit, the Hubbard $U$ term is decomposed into a Mott-like term, associated with the bonding-antibonding gap, and a second, Slater-like spin-density wave (SDW) term, which controls magnetic properties and introduces a gap
at half filling. Now the mean-field parameter is predominantly the AFM moment on
the Cu atoms and a finite moment leads to the splitting of all three bands. These
three-band model results are valid in a more realistic four-band model which is also
presented in this chapter.

5.2 Three band model

The quasi two-dimensional energy bands originating from the CuO$_2$ layer are present
near the Fermi level in all cuprates [Pic89]. The Emery three-band model [Eme87]
has been widely used to describe the dominant Cu$_{x^2-y^2}$, O$_{px}$, and O$_{py}$ orbitals. Our
model Hamiltonian is

\[
H = \sum_j \Delta_{d0} d_j^\dagger d_j + \sum_{\langle ij \rangle} t_{dp} [d_i^\dagger p_i + (c.c.)] + \sum_{\langle ii' \rangle} t_{pp} [p_i^\dagger p_{i'} + (c.c.)] \\
+ \sum_j U n_{dj\uparrow} n_{dj\downarrow} + \sum_i U_p n_{pi\uparrow} n_{pi\downarrow}
\]  

(5.1)

where $\Delta_{d0}$ is the (bare) difference between the on-site energy levels of Cu$_{x^2-y^2}$ and
O$_p$, $t_{dp}$ the copper-$d$–oxygen-$p$ hopping parameter, $t_{pp}$ the oxygen-oxygen hopping
parameter and $U$ ($U_p$) the Hubbard interaction parameter on Cu (O). $n_{dj} = d_j^\dagger d_j$ and
$n_{pi} = p_i^\dagger p_i$ are the number operators for Cu-$d$ and O-$p$ electrons respectively. The
equations were solved at Hartree-Fock (HF) level and a self-consistent mean-field
solution was achieved. The HF decomposition of $U$ is

$$n_{d\uparrow}n_{d\downarrow} \rightarrow <n_{d\uparrow}> n_{d\downarrow} - <n_{d\downarrow}> n_{d\uparrow} = \frac{n_{d\uparrow} <n_d> - (n_{d\uparrow} - n_{d\downarrow}) <m_{d\uparrow}> + <m_{d\uparrow}>^2 - \frac{<n_d>^2}{4}}{2}, (5.2)$$

where $<n_d>$ and

$$<m_d>=<n_{d\uparrow} - n_{d\downarrow}>/2 \quad (5.3)$$

are the average electron density and staggered magnetization on Cu, with a similar decomposition for $U_p$. It is assumed that $<m_d>$ corresponds to a simple antiferromagnetic (AFM) order on the Cu sites. The renormalization of $\Delta_{d0}$ comes in two stages. First, Hartree corrections lead to a renormalized Cu-O splitting parameter

$$\tilde{\Delta}_{d0} = \Delta_{d0} + U <n_{d\uparrow}>/2 - U_p <n_{p\uparrow}>/2. \quad (5.4)$$

Secondly, the conventional, or ZSA splitting is defined with respect to the upper Hubbard band, or

$$\Delta_d = \tilde{\Delta}_{d0} + Um_d. \quad (5.5)$$

For $\tilde{\Delta}_{d0} < Um_d$, $\Delta_d$ describes a charge transfer gap, while if $\tilde{\Delta}_{d0} > Um_d$, $U$ opens a Mott gap $\sim 2Um_d$ without oxygen bands in between. Self-consistency involves (1) adjusting the chemical potential $\mu$ to get the correct doping $x$, (2) satisfying Eq. 5.3 for the staggered magnetization, and (3) finding the correct average $<n_d>$, $<n_p>$ for Eq. 5.4. In general, there could also be a magnetization on the oxygens, but for the AFM order on the coppers, magnetic order on oxygen is frustrated, and we generally find $<m_p>=0$. Note from Eqs. 5.4 and 5.5 that $U$ is split into one part which renormalizes $\tilde{\Delta}_d$, as well as a residual term proportional to the staggered magnetization, $<m_d>$. The former term is a Mott-like term which describes the
lifting of Cu bands due to energy cost $U$. The latter is a Slater-like SDW term which describes an additional splitting of Cu bands due to magnetic order. Even when the AFM order on the coppers vanishes and the Slater-like SDW goes to zero, the Mott-like term persists on both the coppers and oxygens.
Table 5.1: Three band model parameters for LDA, HSC [Hyb89], and three-band model of different doping levels $x$.

### 5.3 Comparison to LDA and LDA+U

In the absence of AFM order ($< m_d > = 0$), the model has three bands. Fig. 5.1 compares the LDA calculation of the NCCO valence bands with the three-band model, while Figs. 5.2 (a) and (b) compare the corresponding densities of states (DOS). Our fit parameters, listed in column 1 of table 5.1, confirm the results of HSC (column 2). Note that for both LDA and three-band parameters, the bonding band (BB) DOS is predominantly of oxygen character, while the antibonding band (AB) carries most of the Cu weight. Thus, a gap in the AB band would be predominantly a Mott gap due to $\tilde{\Delta}_{d0} > Um_d$. This is in contradiction to the conventional ZSA scenario [Zaa85], where the BB should have a predominantly Cu character (as the lower Hubbard band), while the AB is of mixed Cu-O character, leading to a charge transfer-like gap.

A charge transfer gap can be opened by going to an LDA+U calculation, with $U=7$ eV, Fig. 5.2(d). This also pushes considerable Cu weight into the BB near -8 eV. A very similar DOS is found from our 3-band model with $\tilde{\Delta}_{d0} = -0.3$ eV and
Figure 5.2: (Color) Comparison of DOS of Cu $3d_{x^2-y^2}$ and O $2p$ (bonding) character of NCCO from (a) the paramagnetic (PM) three-band model, (b) the full LDA band structure calculation, (c) the antiferromagnetic (AFM) 3-band model, and (d) LDA+U calculation, with $U=7$ eV. Area shaded red = Cu partial DOS.
Figure 5.3: (Color) Comparison of DOS of up and down spin on Cu $3d_{x^2-y^2}$ of one sublattice in NCCO from (a) the one band model with $U_{1b} = 1.96$ eV and $x = 0$, (b-d) the three band model, with $x = 0$ (b), 0.1 (c), 0.15 (d), and (e,f) LDA+U calculations, with $U = 7$ eV and $x = 0$ (e) and $U = 1.24$ eV and $x = 0.15$ (f). Blue line = up spin. Red line = down spin.
Figure 5.4: Three-band model band structures of different electron doping levels with constant $U=7.2$ eV. Parameters ($\Delta_{d0}=-0.76$ eV, $U_p=5$ eV, $t_{dp}=0.8$ eV, $t_{pp}=-0.4$ eV) are chosen such to give an indirect gap of 1.3 eV at $x=0$. The gaps at $x=0.1$ and $x=0.15$ are too large compared with experimental results [Arm02].
staggered magnetization $m_d = 0.29$, Fig. 5.2(c); the parameters used are listed in the fourth column (labeled ‘$x = 0$’) of table 5.1. These parameters are chosen to fit the ARPES experiments at half filling. Note that the parameters are close to those of HSC, renormalized by a factor $Z = 0.6$ (third column of table 5.1 – the model is insensitive to the value of $U_p$). A similar renormalization is found in one-band models when comparing LDA and ARPES spectra. In the following, we will refer to the two split components of the AB band as the upper magnetic band (UMB) and lower magnetic band (LMB).

These models also produce a similar spin polarization on Cu, Fig. 5.3. The cuprates are AFM, so the figure illustrates the polarization of one sublattice, with up and down spins reversed on the other sublattice. Recall that the LDA already incorporates $U$ in an average sense, so the $U$ in LDA+U is a correction. By comparing Fig. 5.3(e) and (f), the $U$ in LDA+U is also doping dependent, with the correction $U$ scaling to zero in the nonmagnetic phase.

5.4 Doping dependence

When AFM order is included, each band splits into two subbands. Fig. 5.4 shows the calculated band structures at different electron doping levels, assuming doping-independent parameters $\Delta_{d0}$, $U$, and $U_p$ such that the indirect gap $[(\pi/2, \pi/2) \to (\pi,0)]$ for zero doping has the experimentally observed value 1.3 eV. As the doping level $x$ increases, the gap decreases. However, the gap for $x=0.1$ and $x=0.15$ is too large when compared to the experimental results [Arm02]. We explored a wide range in parameter space, $-5 < \Delta_{d0} < 5$, $2 < U < 13$, and $0 < U_p < 7$, but always found that when the gap at half filling is fixed at 1.3 eV, the (self-consistent)
indirect gap of x=0.1 is about 1 eV (not shown), much larger than experiment. It is necessary to have at least one of the three parameters \( U, U_p, \) or \( \Delta_{d0} \) be doping dependent. Fig. 5.5 illustrates the parameter range explored, and compares some earlier estimates of the parameter values [Hyb90, Hyb89, Ste88, Ent90, Sim97].

Since the one band models find a good correlation between the gap closing and the magnetic properties, we chose to let \( U \) be doping dependent. While only the combination in Eq. 5.4 enters the mean field theory, the fit retains some sensitivity to \( \Delta_{d0} \) and \( U_p \) individually, since \( < n_d > \) (and hence \( < n_p > \)) varies with these parameters. We again find that a wide range of parameter choices can lead to good fits of the ARPES data. In choosing values for \( U, U_p, \) and \( \Delta_{d0} \), the following points should be noted. (1) For any value of \( U \) and \( U_p \), a value of \( \Delta_{d0} \) can be found which gives an indirect gap of 1.3 eV between the UMB and LMB. LMB was found at binding energy 1.3 eV in ARPES and we assume the Fermi level is pinned near the bottom of the UMB which is consistent with resonant inelastic X-ray scattering (RIXS) [Mar08]. Consistent with Eq. 5.4, we find that for any \( U \) [in the range 2.2-7.2 eV explored], the full band structure at half filling depends only on the combination

\[
\Delta_U = \Delta_{d0} - U_p < n_p > / 2 ,
\]

where \( \Delta_U \) and \( < n_p > \) depend only on \( U \), Figs. 5.5(b) and (c). Note that \( < n_p > / 2 \) is close to 1, and \( \Delta_U \) is generally negative, requiring a large value of \( U_p \) to keep \( \Delta_{d0} \approx 0 \). (2) The larger the value of \( U \), the smaller (percentage-wise) is its doping dependence. (3) The larger \( U \), the more Cu character is transferred to the lowest-lying of the six bands. Thus, in Fig. 5.5(d), \( Um_d \) and \( \tilde{\Delta}_{d0} \) are plotted as functions of \( U \). For \( U < 4 \) eV, \( \tilde{\Delta}_{d0} > Um_d \) and the gap near \( E_F \) is a Mott gap. For \( U > 4 \) eV, \( \tilde{\Delta}_{d0} < Um_d \) and the gap near \( E_F \) is a charge-transfer gap. (4) A larger \( U \) also
Figure 5.5: (a) Lines denote those sets of parameters $U$, $U_p$, and $\Delta_{d0}$ which can correctly model the undoped case, with an indirect gap of 1.3 eV at $x=0$. $\Delta_{d0}=-5,-3,-1,1,3,$ and 5 are used for the lines from top to bottom. Square: Simon et al [Sim97] adjusted by our $t_{pp} = -0.4$ eV; cross: Stechel et al [Ste88]; diamond: Entel et al [Ent90] and Hybertsen et al [Hyb90]. (b) Plot of $<n_p>$ as a function of $U$ at half-filling. (c) Plot of $\Delta_U$ as a function of $U$ at half-filling. (d) Plot of $U m_d$ (solid line) and $\Delta_{d0}$ (dashed line) as functions of $U$ at half-filling.
enhances the energy separation between the bonding and nonbonding bands.

For the above reasons, we chose a large value $U = 7.2$ eV for the undoped case, and fixed $U_p = 5$ eV, $\Delta_{d0} = -0.76$ eV for a good fit to the ARPES data. We stress that only the combination in Eq. 5.6 is relevant. To optimize the fits to the doped samples, the doping dependent $U$’s displayed in table 5.1 were chosen. The resulting values of $< n_d >$ were calculated, leading to the values of $\tilde{\Delta}_{d0}$ and $\Delta_d$ given in table 5.1. In Fig. 5.6, our results are overlayed on ARPES results on NCCO [Arm02]. The Fermi level goes into the UMB at low doping and gives rise to the $(\pi, 0)$ or $(0, \pi)$ electron pockets. As doping increases, the gap decreases, and the maximum in the LMB near $(\pi/2, \pi/2)$ approaches the Fermi level. For $x$ higher than 0.15, the bands resemble the uncorrelated band structure. The full electron-doped dispersions for this set of parameters is shown in Fig. 5.7. We find that for all the parameter sets in Fig. 5.5, reducing $U$ by 1.2 eV at $x = 0.1$ causes a similar near collapse of the AFM gap. In general, the dispersions of the UMB and LMB found in the three-band model are in good agreement with those found earlier in the one-band model, as noted previously [Mar04].

The doping dependence of $U$ does not harm the aforementioned hybridization scenario. In Fig. 5.3 (b), (c), and (d), we show the DOS of up and down spins on one sublattice of Cu $3d_{x^2-y^2}$ in the three band model with $x = 0, 0.1$, and 0.15, respectively. For all dopings, the up spins are concentrated in the LHB – the narrow Cu peak at the lowest energy, with a second peak at intermediate energies, while most of the unoccupied states above $E_F$ are down spins. As doping increases, the gap around $E_F$ between UMB and LMB decreases but the Cu peak in the DOS persists. This is similar to the Mott-like behavior where we expect a filled Cu band at deep energy and an empty band near $E_F$. On the other hand, the UMB and LMB have
Figure 5.6: (Color) Effect of doping dependent $U$ on bands near Fermi level overlaid on ARPES results on NCCO [Arm02]. $U=7.2$, 7.00, 5.90, and 5.65 for $x=0$, 0.04, 0.1 and 0.15 respectively.

quite different DOS for different spins and this captures the Slater physics where we expect that AFM order induces the magnetic gap. As we can see in Fig. 5.3(a), the one band model open a similar gap between UMB and LMB due to AFM order as captured by Slater physics.

The staggered magnetization $m_d(x)$ decreases with increasing doping and vanishes slightly above optimal doping (Fig. 5.8). The good agreement with experiments [Ros91, Man04] found in the one band model [Mar04, Man04] is retained in the three band model. This can be understood from Eq. 5.5 and table 5.1: since $\tilde{\Delta}_0d \sim 0$, $\Delta \sim Um_d$. In the one-band model, $\Delta = 2U_{1b}m_d$, but the parameter $U_{1b}$ has a different meaning and a very different numerical value from $U$ and the one-band $m_d$ is somewhat larger.

Fig. 5.2(c) compares the partial DOS for a fit with a large $U$ to the earlier LDA and HSC fits. It is readily apparent that the present parameter choice yields a DOS quite similar to the LDA+U calculation. Thus, the present parameter choices at
Figure 5.7: Three-band model band structures of different electron doping levels with a reduction of $U$. 

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Figure 5.8: Doping dependence of staggered magnetization: diamond: three band model, star: four band model, cross: one band model [Mar04], square: Rosseinsky et al [Ros91], circle: Mang et al. [Man04]
half filling are consistent with the ZSA picture for the cuprates as charge-transfer
insulators, and in good agreement with LDA+U calculations.

It is important to stress this result: a large $U$ and a small $\Delta_{d0}$ combined produce
a charge-transfer insulator consistent with the ZSA scheme. If at half filling with
fixed $U_p$ we try to use a larger value of $\Delta_{d0}$, then $U$ must be smaller to produce
the same indirect gap across the Fermi level, and there is a crossover from charge-
transfer insulator to Mott insulator. This result can be related to three-band Slave
Boson model results. Slave boson calculations have been used to explore the di-
rect, Brinkman-Rice scenario of the Mott transition within the three-band models.
However, the gap opening and effective mass divergence at half filling are found
only if the parameter $\Delta$ exceeds a threshold value, $\Delta_c = 3.353t_{CuO} + 2.94|t_{OO}|$.
[Cas92, Mar97a] The present calculations shed insight on this result. (1) A large $\Delta$
transforms the CuO$_2$ plane from a charge transfer insulator to a Mott insulator. As
$\Delta$ increases, the hybridization with oxygen decreases, leading to a one-band (copper
only) model much closer to Mott’s original model. Thus, slave boson calculations
find a Brinkman-Rice transition ($\Delta > \Delta_c$) only in the Mott limit of the three-band
model, and not in the charge transfer limit expected for the cuprates. (2) Moreover,
the strong band renormalization (effective mass divergence) has not been seen, con-
firming that $\Delta < \Delta_c$, and suggesting that a different route is taken to the insulating
phase of the cuprates.

5.5 Zhang-Rice singlets

In the conventional (three-band) picture, the UMB and LMB are denoted as the
upper Hubbard band (UHB) and O-derived Zhang-Rice singlet (ZRS) band [Zha88].
Figure 5.9: (Color) Orbital character of the first holes. The four oxygens surrounding the copper contribute the character with phases like $d_{x^2-y^2}$. 
In fact, the LMB provides an excellent description of the ZRS. In our three band model, the first hole in the LMB appears at \((\pi/2,\pi/2)\) and has 15% copper character and 85% oxygen character. Moreover, this hole has the same orbital symmetry as the ZRS. Fig. 5.9 illustrates the charge distribution and relative phases at the top of the LMB for the AFM unit cell, for the spin up electrons. The central Cu has the spin down hole associated with the UMB, while the corner Cu’s have the corresponding spin up hole. Thus the four oxygens contribute equally to the first hole, with relative phases consistent with d-wave symmetry, in such a way that the spin up oxygen hole combines with the spin down Cu hole; on the alternate sublattice, the spin up and spin down states are reversed. Superficially, it appears that the oxygens have the same d-wave symmetry with respect to the corner Cu’s. However, the wave function is at \((\pi/2,\pi/2)\), or \((0,\pi)\) in the AFM Brillouin zone, so the wave functions change sign when shifted one AFM cell and do not have d-wave symmetry with respect to the corner Cu’s. Hence the O-holes are decoupled from the corner Cu’s. Note that this Cu does not contribute to the first hole wave function. While Zhang and Rice considered the situation with \(\tilde{\Delta}_{d0} > 0\) (the effective on-site energy of copper higher than that of oxygen), our results indicate the first holes have the same orbital symmetry as ZRS even with slightly negative value of \(\tilde{\Delta}_{d0}\).

### 5.6 Four band model

While the three-band model is generally in good agreement with the one-band and experimental results, there is one problem: near \(x = 0.15\), experiment finds a second, hole-like FS pocket developing near \((\pi/2,\pi/2)\). In the one-band model, this can be fit by including a \(t''\) hopping parameter in the dispersion. Such a parameter is absent
Table 5.2: Four band model parameters

<table>
<thead>
<tr>
<th>(eV)</th>
<th>x=0.0</th>
<th>0.04</th>
<th>0.10</th>
<th>0.15</th>
</tr>
</thead>
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<tr>
<td>$t_{dp}$</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>$t_{sp}$</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>$\Delta_{d0}$</td>
<td>-0.76</td>
<td>-0.76</td>
<td>-0.76</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\Delta_s$</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>$U_p$</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>$U$</td>
<td>6.63</td>
<td>6.23</td>
<td>4.83</td>
<td>4.53</td>
</tr>
<tr>
<td>$m_d$</td>
<td>0.35</td>
<td>0.30</td>
<td>0.14</td>
<td>0.07</td>
</tr>
<tr>
<td>$n_d$</td>
<td>1.29</td>
<td>1.37</td>
<td>1.60</td>
<td>1.67</td>
</tr>
</tbody>
</table>

in the present 3-band model but is present in the 4-band model by adding copper 4s. The four-band model in general can provide an equally good fit to the doping dependence, but again with doping-dependent $U$.

For the four-band model [And94], Eq. 5.1 is rewritten as

$$H = \sum_j \Delta_s s_j^\dagger s_j + \sum_j \Delta_{d0} d_j^\dagger d_j + \sum_{<i,j>} t_{sp}[s_j^\dagger p_i + (c.c.)] + \sum_{<i,j>} t_{dp}[d_j^\dagger p_i + (c.c.)] + \sum_j U n_d d_j n_d^\dagger + \sum_i U_p n_p n_p^\dagger,$$  \hspace{1cm} (5.7)

where $\Delta_s$ is the difference in on-site energy between copper $s$ and oxygen and $t_{sp}$ is the copper-$s$–oxygen-$p$ hopping parameter, and the other parameters have their original interpretation. Also, the term $t_{pp}$ is set to zero, as an indirect O-O hopping term arises via the Cu 4s orbital. An advantage of the four-band model is that $t_{sp}$ also induces an additional effective hopping parameter, absent in the present three-band model, which corresponds to the parameter $t''$ of the one-band model. This parameter is necessary to reproduce a hole pocket FS in the intermediate doping range.

Fig. 5.10 shows the corresponding doping-dependent dispersions in the four band
Figure 5.10: Four-band model band structures of different electron doping levels with a doping-dependent U.
Figure 5.11: (Color) Comparison of three- (top row) and four-band (middle) model Fermi surfaces at several electron doping levels with the experimental results[Arm02] (bottom). Doping levels are $x = 0.04$ (left column), 0.10 (center), and 0.15 (right).
model, using the parameters of table 5.2. The two highest bands are the split 4s band, while the remaining bands are similar to those found in the three-band model. Again, a doping dependent $U$ is needed to reproduce the observed gap collapse. The net change in $U$ is quite similar in the two cases, a 22% reduction in the three-band model vs an 18% reduction in the four-band model. A subtle difference is in the 15% doping case, the lower right frame of Fig. 5.10, where the LMB crosses the Fermi level, due to the effective $t''$ parameter. This can be seen most clearly in Fig. 5.11, which compares calculated Fermi surfaces for the three-band (top row) and four-band (middle row) with experimental ARPES Fermi surfaces for NCCO [Arm02] (bottom row). At 15% doping the experiment shows a clear second pocket along the zone diagonal, due to the LMB, which is well reproduced by the four band model, but is just vestigal in the three-band model. Finally, in Fig. 5.12 we show that the four band model dispersions are also consistent with the experimentally measured dispersions [Arm02].

Figure 5.12: (Color) Four-band model dispersions with a doping dependent $U$ compared to ARPES results on NCCO [Arm02].
5.7 Routes to a Mott gap

To clarify our new route to a Mott gap, we compare it to several other models. The Mott transition is usually considered in real space, but when looked at in momentum space, it reveals a topologically nontrivial aspect: how can a single sheet of an energy-dispersion surface be split into two halves without the electrons being aware of the seam? So far, only one direct solution to the problem is known, but nature has devised several techniques for avoiding the singularity.

We are aware of four routes to the Mott transition:

- In the **direct scenario**, the effective mass diverges as the electron density approaches half filling, so the band dispersion collapses and the electrons never reach the jump discontinuity at half filling, between lower and upper Hubbard bands. This approach goes back to Brinkman and Rice, and arises in several slave boson calculations. It does not appear to be relevant to the cuprates, where the dispersion is only renormalized by a factor of two or so.

- In the **superlattice scenario**, the divergence is avoided. A larger real space cell leads to a smaller Brillouin zone. Half filling in the original zone corresponds to an exactly filled new zone, so the discontinuity migrates to the new zone boundary. Among the possible ordered phases are charge-density wave, flux phases, and SDWs in (electron-doped) cuprates.

- In the **gossamer scenario**, the dispersion remains finite at half filling but the spectral weight of in-gap states vanishes. Such a scenario may be associated with (nanoscale) phase separation, and seems to be relevant in hole-doped cuprates.

- The new **hybridization scenario** works as follows. By hybridizing with the
CuO$_2$-plane oxygens, the single copper band splits into two bands, one bonding (BB) and one antibonding (AB), with a third non-bonding, predominantly oxygen band. Neglecting the non-bonding band for simplicity, the other two bands play the role of lower and upper Hubbard bands. When $\Delta$ is small, the BB and AB are both approximately half filled with Cu-electrons, and the remainder composed of electrons on oxygens, which play a role analogous to holons in a one-band model.

5.8 Summary

In conclusion, we find that (1) a large variety of parameter sets can correctly describe the dispersion of the gap in the AB band at half filling, in good agreement with ARPES experiments. Within the present model the gap is due to AFM order – i.e., it is a Slater gap. However, (2) we have been unable to explain the doping dependence of the gap, unless at least one parameter is doping dependent. (3) Ascribing the doping dependence to $U$, we can correctly reproduce the doping dependence of the ARPES data. The results also explain the reasons for the good agreement of both one- and three-band models with experimental staggered magnetization data. (4) There is still a large ambiguity in choice of parameter sets. We have resolved this by choosing a large value for $U$ at half filling, which minimizes the fractional change in $U$ with doping. The final parameter sets at half filling are quite similar to the HSC parameter set, modulo an overall renormalization of the experimental data by $Z \sim 0.6$. We should caution that this renormalization is based exclusively on the UMB and LMB, and recent ARPES data on the waterfall features at higher energy scales [Ron05, Gra07, Mee07, Xie07, Val07] suggests a possible binding energy dependence of $Z$. 
This final choice of parameters suggest a very different picture from the conventional one for the three-band model. (1) We find that the LDA calculation (and the HSC parametrization derived from it) fail to predict the expected ZSA behavior for the cuprates: the Cu weight is concentrated mainly in the AB band, with no sign of a large Mott gap. This may be why LDA fails to find AFM order. (2) Both defects are corrected in the LDA+U model, and we find that our new parameter set provides a partial DOS in good agreement with the LDA+U result. (3) Hence, (unlike the LDA) the Mott physics is correctly built into our three-band model – that is, both the large splitting of the Cu levels into the BB and AB – as well as the Slater physics, which is responsible for the AFM gap at half filling. (4) The usual three-band picture of UHB, ZRS, and LHB neglects the AFM band splitting, and hence has little connection with the one-band results. In contrast, the present calculation naturally explains the one-band results, and why magnetic properties (staggered magnetization, correlation lengths) are correctly predicted by the model.

We note that very similar parameters are found in RIXS experiments in NCCO [Mar08], which directly accesses the magnetic gap and its collapse. Furthermore, RIXS experiments find a strong satellite feature at \( \sim 6 \) eV which we identify as a transition from the lower BB to the AB above the Fermi level. Extension of these results to hole-doped cuprates may be complicated by effects related to nanoscale phase separation (‘stripe’ physics).
Chapter 6

Extracting the CuO$_2$ Bonding Band from the Valence Band

ARPES in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

The valence bands of the cuprates pose an interesting challenge for analysis. For Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212), there is a broad array of bands extending from about 1 to 7 eV below the Fermi energy ($E_F$) [Tak89, Wel89, Lin89, Eis90, Gol91]. The array consists of 34 bands, primarily associated with 10 Cu $d$ orbitals, 24 O $p$ orbitals. These orbitals include in particular the hybridized bands of the in-plane Cu $d_{x^2-y^2}$ – O $p_{\sigma}$ orbitals, of relevance in three-band models of the cuprates.

Sorting out these bands would provide valuable information on the strengths and

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*This chapter is adapted from the following talk.
weaknesses of LDA-ARPES analysis, particularly the roles of broadening and individual orbital $U$ corrections, and would also tackle a number of issues relevant to cuprate physics. For instance, how does band broadening vary with binding energy, how significant are strong correlation ($U$) effects in higher bands, how does renormalization/kink physics manifest itself at ever increasing energies, and where do other d-bands lie? More specifically, the apical oxygen and Cu $d_{z^2}$ orbitals have been implicated in some mechanisms of $T_c$, yet we have no clear ideas of where the associated bands are. These bands also play an important role in scanning tunneling spectroscopy (STS) where the asymmetry between the processes of electron injection vs extraction is due to the opening of Cu $d_{z^2}$ and other tunneling channels for the negative bias voltage and which will be discussed next chapter. Finally, the bonding Cu $d_{x^2-y^2}$ band has an intimate connection with the true lower Hubbard band (LHB), yet its binding energy has never been experimentally determined. How do these features change as the system is doped from a Mott insulator to a high-$T_c$ superconductor?

Here we provide a preliminary analysis of these features using angle-resolved photoemission (ARPES) in Bi2212. First, LDA bands are compared with experiments. Second, a necessary correction of the LDA derived TB model is found. Third, this correction is shown to be related to the Mott physics.

6.1 LDA bands

The LDA band structure of undoped Bi2212 was calculated within the all-electron full-potential KKR method [Ban99a]. The conventional tetragonal cell was used and the crystal parameters were taken from structurally optimized computations by
Bellini et al. [Bel04] where total energy and force minimizations were performed.

The ARPES results were provided by the group of Prof. Lanzara in the Physics Department at the University of California, Berkeley and in the Materials Sciences Division at the Lawrence Berkeley National Laboratory. Two Bi2212 samples with different dopings are used. One is underdoped (UD) $x = 0.12$ with $T_c = 70 - 80 \text{K}$. The other is overdoped (OD) $x = 0.22$ with $T_c = 65 \text{K}$. Several photon polarizations directions and energies in the range from 27eV to 60eV are used.

We begin by making direct comparisons between LDA band structures and ARPES intensity. Figure 6.1 shows ARPES intensity maps (left column) for an overdoped sample at two photon energies. The bands crossing the Fermi level are the well-studied antibonding Cu $d_{x^2-y^2} - \text{O}_\text{Cu} p_\sigma$ bands, but here our main interest is in the deeper lying bands. To enhance weak features, the plots also display second derivative maps of smoothed ARPES intensity (center), and a series of EDCs (energy distribution curves) taken at equally spaced $k$-values (right). Black circles on the intensity maps and colored dots on the EDC curves are LDA bands. Larger size of the circles or dots highlight $\text{O}_{\text{Sr}}$ and $\text{O}_{\text{Bi}}$ contribution. While there are characteristic differences between the spectra, due to ‘matrix element effects’, the main features are consistent for both photon energies. There are some features well predicted by LDA. Around $-3 \text{ eV}$ where LDA gives a flat complex of predominantly $\text{O}_{\text{Sr}}$ and $\text{O}_{\text{Bi}}$ character, the corresponding ARPES intensity is large. Larger dispersive bands between $-4 \text{ eV}$ and $-7 \text{ eV}$ are $\text{O}_{\text{Bi}} p_{x,y}$ bands. The dispersion of the bands also agrees between experiment and LDA. These bands come from outside the CuO$_2$ layers and are primarily related to $\text{O}_{\text{Sr}}$ and $\text{O}_{\text{Bi}}$. Note that they account for almost all of the most intense features (red and yellow) in the ARPES spectra, consistent with an electron escape depth smaller than the distance to the nearest CuO$_2$ layer.
Figure 6.1: (Color) ARPES intensity (left), second derivative maps of smoothed ARPES intensity (center), and EDCs taken at equally spaced $k$-values (right) for OD Bi2212 are shown along nodal direction (indicated by the black line in the inset of the left column) with out of plane polarization 33 eV photon energy (top row) and in-plane polarization 60 eV photon energy (bottom row). High intensity regions in the intensity maps, blue area in the second derivative maps, or peaks and shoulders in the EDCs suggest the positions of bands. LDA bands (circles in the left column and color dots in the right column) with $O_{Sr}$ and $O_{Bi}$ character have good agreement with experimental bands particularly around -3 eV.
We will see that the CuO$_2$ layer orbitals are not only weaker, but also in poorer agreement with LDA, suggesting that large corrections to LDA are associated with strong correlation effects only in the CuO$_2$ planes.

To begin our exploration of the CuO$_2$ plane, we look at the extrema – the bands in the ‘spaghetti’ lying at the lowest and highest energies. The lowest band of this bundle of valence bands is analyzed in figure 6.2. Both experiment and LDA clearly show a gap below the bottom of these bands. However, LDA has an isolated band with O$_{Cu} p_{\sigma}$ character around −7.7 eV at X($\pi, \pi$), while the ARPES band bottom is at a lower binding energy. Extended searches for bands around −7.7 eV in ARPES found no features. A weak feature with similar dispersion can be seen at the same k-point, X, at −7.1 eV with 52 eV photon energy (arrows in figure 6.2).

The top of this bundle of valence bands along X-M(0, $\pi$) is basically flat in both experiment and theory, but the position is different, too. The experimental large intensity starts at ≈−1.2 eV [Gra07, Mee07, Xie07], whereas the LDA gives −0.6 eV with Cu $d$ and O$_{Cu} p$ character. In other words, the bandwidth of this bundle of valence bands is ≈1 eV smaller in experiment than in LDA. Given that the top of this bundle of valence bands is lower in experiment than in LDA while the bottom is higher, we can exclude an overall constant renormalization. This provides an alternative evidence to the commonly known failure of LDA in the strongly correlated CuO$_2$ plane.

**6.2 Intensity anomaly**

Besides the dispersion, we also found an anomaly in the intensity. The ratio of the intensity of the antibonding Cu $d_{x^2-y^2}$ − O$_{Cu} p_{\sigma}$ in the low binding energy region to
Figure 6.2: (Color) ARPES intensity (left), second derivative maps of smoothed ARPES intensity (center), and EDCs taken at equally spaced $k$-values (right) for UD Bi2212 are shown along $X(\pi, \pi)$ to $M(0, \pi)$. The actual $k$-points are indicated by the black line in the inset of intensity map. The data were taken at photon energy $= 52$ eV and 80% out-of-plane polarization. High intensity regions in the intensity map, blue area in the second derivative map, or peaks and shoulders on the EDCs suggest the positions of bands. LDA bands (circles) with Cu and $O_{Cu}$ character are overlaid on the ARPES intensity map, showing discrepancies near -1 eV and -7 eV. The arrows indicate the bottom of the experimental bonding Cu $d_{x^2-y^2}$ – $O_{Cu} p_{\sigma}$ bands.
Figure 6.3: (Color online) Blue line shows averaged EDC of figure 6.2. Red line is the EDC after Shirley background subtraction. The vertical dashed line at -0.6 eV separates the spectrum into low binding energy region and high binding energy region.
the spaghetti bands lying at higher binding energies is much lower than the expected value in LDA. The typical EDC of Bi2212 is shown as the blue line in figure 6.3. We use -0.6 eV (dashed line) to separate the area into two regions, low and high binding energy regions. We assume that the bottom of the valence bands lies above -8 eV, so the spectral weight at lower energies must be due to Shirley background [Shi72] (note that this assumption gives us an upper limit to the Shirley background). After Shirley background subtraction the corrected spectrum is given by the red curve. The intensity of the high binding energy region is reduced much more than that of low binding energy region, with essentially no change to the area in the low binding energy region associated with the antibonding Cu $d_{x^2-y^2} - O_{Cu} p_o$ bands. From the corrected spectra we define $R_{Exp}$, the ratio of the area of low binding energy region to that of high binding energy region, which can be compared to the LDA ratio, $R_{LDA} \approx 0.4$. The experimental values are much lower. $R_{Exp}/R_{LDA}$ ranges from 0.1 to 0.3 for various experimental conditions, including in-plane and out-of-plane polarization and different photon energies. In other words, 70% to 90% of the spectral weight is lost in the low binding energy region. A simple explanation is a finite electron escape depth, $\ell_{esc}$, with $e^{-\ell/\ell_{esc}} \sim 0.2$, or $\ell_{esc} \sim 0.6\ell$, where $\ell = 4.5\text{Å}$ is the distance from the CuO$_2$ plane to the surface BiO layer. Our results are consistent with Norman et al. [Nor99] where $\ell_{esc} \sim 3\text{Å}$. 

6.3 TB model

To quantify the changes in the ARPES spectra, we first introduce a multi-band tight binding (TB) model which reproduces the LDA band dispersions as well as band characters. The most relevant orbitals for the velance bands are included in the
TB model. They are $s, d_{z^2}, d_{xz}, d_{yz}, d_{x^2-y^2}$ for Cu; $p_x, p_y, p_z$ for O; $s, p_x, p_y, p_z$ for Bi; and $s$ for Sr and Ca. The symmetry of the orbitals is taken care of by using the Slater-Koster results [Sla54] for the angular dependence of the overlap integrals. The hopping parameters for the overlap integrals are determined by the method introduced in Chapter 1 where the TB Hamiltonian as a function of $k$ is fitted to the derived Hamiltonian from KKR. In figure 6.4, we show the LDA (a) and TB bands (b), highlighting the Cu $d$ character and displaying the Cu $d$ partial density of states (DOS). The LDA dispersions as well as characters of the complex valence bands are captured by the TB model. Cu $d$ are centered around -2eV and split into bonding and anti-bonding bands due the interaction to the surrounding oxygens. The anti-bonding bands form the top of the valence bands around -1eV. The bonding bands spread into a wider energy range, and Cu $d$ DOS has long tail below -3eV until the bottom of the valence bands which can be seen in both LDA and TB Cu $d$ DOS.

Having determined the TB parameters, we find that very simple changes are sufficient to describe the experimental ARPES dispersions. It is sufficient to shift only the on-site energies of various Cu $d$ and O$_{Cu}$ $p$ levels. Specifically, we had to (1) raise O$_{Cu}$ $p_\sigma$ from the LDA value -3.3 eV to -2.5 eV, (2) lower all Cu $d$ orbitals by 0.8 eV and (3) lower O$_{Cu}$ $p_\pi$ and $p_z$ by 0.3 eV. On-site energies of other layers and all hopping parameters were kept unchanged, except Bi $p$. Since we are comparing to ARPES experiment, we have ‘lifted’ the BiO bands as discussed in chapter 2 by raising the on-site energies of Bi $p$ by 1.2eV to simulate the effect of hole doping [Lin06]. The resulting renormalized TB bands are shown in figure 6.4(c), while a comparison to experiment is shown in figure 6.5. We note in particular that the overall width of the experimental bands is now well reproduced, and both the band
Figure 6.4: (Color) Bi2212 band structure calculated in LDA (left) is compared with TB fit (center). Modified TB fit matched to ARPES is shown in the right. Shading indicates degree of Cu $d$ character, with lighter indicating strong Cu character and black bands essentially no Cu $d$. To the right of each dispersion is the partial density of states of Cu $d$. 
Figure 6.5: (Color) ARPES intensity (left), second derivative maps of smoothed ARPES intensity (center), and EDCs taken at equally spaced $k$-values (right) for UD Bi2212 are shown along $X(\pi, \pi)$ to $M(0, \pi)$. The actual $k$-points are indicated by the black line in the inset of intensity map. The data were taken at photon energy $= 27$ eV and 80% out-of-plane polarization. High intensity regions in the intensity map, blue area in the second derivative map, or peaks and shoulders on the EDCs suggest the positions of bands. Black dots are modified TB bands showing good agreement between theory and experiment.
Figure 6.6: (Color) Band structures and partial DOS of modified TB model which describe ARPES dispersions. Various Cu \( d \) band characters are shown in different colors.

tops and bottoms are well represented. Experimentally, the top of the valence bands constitute a mixture of flat and highly dispersive bands along \((\pi,0)\) to \((\pi,\pi)\). These are well fitted in the modified TB model with bands of mixed Cu \( d \) and O\(_{Cu}\) \( p \) character. In addition, the good agreement with non-CuO\(_2\)-plane orbitals is preserved.
The flat complex of O\(_{Sr}\) and O\(_{Bi}\) bands around \(-3\) eV is clearly seen. The modified TB bands also fix the bottom of the valence bands in figure 6.2. We have studied numerous spectra taken under different conditions of polarization and photon energy, on samples at two different dopings \(x=0.12\) and \(x=0.22\), and find a uniform and consistent degree of agreement between experiment and renormalized theory.

By having a TB model which describes the ARPES dispersions, we discuss the bands from various Cu \( d \) orbitals. In figure 6.6, the band structures as well as various Cu
partial DOS of the modified TB model are shown. Due to the symmetry, various Cu $d$ orbitals have different strength of interaction with O $p$ orbitals. The largest interaction is between Cu $d_{x^2-y^2}$ and O$_{Cu}$ $p_{\sigma}$. The large dispersive bands with $d_{x^2-y^2}$ character are located at the bottom of the valence bands and near $E_F$. Cu $d_{z^2}$, $d_{yz}$, $d_{xy}$ have slightly smaller interaction with O$_{Cu}$ $p_{\pi}$. Their band dispersion as well as the separation of their bonding bands around -5eV and antibonding bands around -1.5eV are smaller. Those bands with Cu $d_{z^2}$ character near -2.5eV are relatively flat due to the small interaction with O$_{Cu}$.

The broadening of the valence bands is estimated by convoluting the modified TB model with a finite width. A Lorentz distribution in energy is assumed for the broadening of each eigenstate. Initially, the overall half width was estimated to be 0.5eV. However, at the lower binding energy around 1eV, the experimental EDCs are sharper and a smaller width is needed for this energy range. In figure 6.7, an energy dependent width is shown in the inset. While the width is constant below -3eV, it decreases as binding energy decreases. Theoretical EDCs using this energy dependent width are compared with experimental EDCs. The weight for each eigenstate is indicated by the height of the bars at each eigen energy position. The weight is calculated by adding 100% components of O$_{Sr}$ and O$_{Bi}$ (magenta) and 25% components of CuO$_2$ (green). This only accounts for the short escape depth effect discussed above where 75% of the spectral weight of CuO$_2$ is lost. More complex matrix element effects are not included, leading to the residual discrepancy between theoretical and experimental curves. The EDC peak around -3eV is due to O$_{Sr}$ and O$_{Bi}$ bands. This is a robust feature in all experimental conditions explored. The data shown in figure 6.7 are selected because they are the dataset with the smallest width. The -3eV peak is composed of several eigenstates, which could be further
Figure 6.7: (Color) Shirley background subtracted experimental EDCs (blue solid lines) at 4 k-points ($k_x$, $k_y$ in units of $2\pi/a$) are compared with theoretical EDCs (red dashed lines). The experimental EDCs are taken from the bottom row of figure 6.1 where the polarization is in-plane and photon energy is 60eV on OD Bi2212. The Shirley background is subtracted from the experimental EDCs, and all EDCs have been shifted vertically for clarity. An energy dependent width for theoretical EDCs is shown in the inset. The weight of each eigen state for the theoretical EDCs is indicated by the height of the bar at the eigen energy position. Magenta and green indicate the fully counted weights from out-of-plane oxygens (O$_{Sr}$ and O$_{Bi}$) and the reduced weights from CuO$_2$ respectively.
separated in energy due to orthorhombic distortions or structural modulation which are not included in the computation. Therefore, the estimated width 0.5eV should be considered as the upper bound.

### 6.4 The CuO$_2$ Bonding bands

Here we would like to concentrate on one issue of some importance – the dispersion of the bonding bands of the CuO$_2$ layer, essential for understanding the true Mott transition in this material. The lowest bands in the bundle of valence bands in figure 6.4 are the bonding bands of Cu $d_{x^2-y^2}$ and O$_{Cu}$ $p_{\sigma}$. Their antibonding bands form the bands at $E_F$ which are intensively studied in the literature. According to the Zaanen-Sawatzky-Allen (ZSA) [Zaa85] classification scheme, the undoped cuprates are charge-transfer insulators, with a charge transfer gap near $E_F$, and a larger Mott gap associated with copper states. An understanding of the bonding band, and more generally of the three-band model which is studied in Chapter 5, is essential for understanding the Mott physics in the cuprates.

Within the ZSA scheme, a material is a charge transfer insulator if the Hubbard $U$ is larger than the on-site energy difference $\Delta$ between the metal and the oxygen levels. As shown in Chapter 5, this has posed a problem for the LDA bands in the cuprates, since a large value of $\Delta$ is found [Hyb89]. Here, we confirm the problem with LDA, and show that it is greatly ameliorated when using the experimental dispersions. To see this, we introduce a simple three-band model, including Cu $d_{x^2-y^2}$ and two
Our model Hamiltonian is

$$H = \sum_j \epsilon_d d_j^\dagger d_j + \sum_i \epsilon_p p_i^\dagger p_i + \sum_{\langle ij \rangle} t_{dp}[d_j^\dagger p_i + (c.c.)]$$

$$+ \sum_{\langle ii' \rangle} t_{pp}[p_i^\dagger p_{i'} + (c.c.)] + \sum_{\langle \langle ii' \rangle \rangle} t_{pp}'[p_i^\dagger p_{i'} + (c.c.)] \quad (6.1)$$

where $\epsilon_d$ ($\epsilon_p$) is the on-site energy of Cu $d_{x^2-y^2}$ ($O_{Cu} p_{\sigma}$), $t_{dp}$ the copper-$d$–oxygen-$p$ hopping parameter, $t_{pp}$ and $t_{pp}'$ are the nearest-neighbor and second-nearest-neighbor oxygen-oxygen hopping parameters respectively. This three-band model is slightly different from that used in Chapter 4 where only nearest-neighbor hopping terms are included. The corresponding parameters extracted from our multiband fit to the LDA bands are shown in the first column of table 6.1. However, these parameters by themselves give a poor representation of the three bands, due to strong hybridization with the Cu 4s band. Andersen et al. [And95] have shown how to project out the Cu 4s orbital by means of down-folding, leading to renormalized values for $\epsilon_p$, $t_{pp}$, and $t_{pp}'$, while $\epsilon_d$ and $t_{dp}$ are unchanged. The downfolding procedure introduces an energy-dependent correction $t_C = t_{sp}^2/(\epsilon_s - \epsilon)$ to the dispersion coefficients, $\epsilon_p \rightarrow \epsilon_p - 2t_C$, $t_{pp} \rightarrow t_{pp} + t_C$, and $t_{pp}' \rightarrow t_{pp}' - t_C$, where $t_{sp}$ is Cu 4s - $O_{Cu} p_{\sigma}$ hopping parameter and $\epsilon_s$ is the on-site energy of Cu 4s. We approximate $\epsilon = -3.5\text{eV}$ which is close to the center of the BB and AB bands. This yields $t_C = 0.6\text{eV}$ and gives a good overall fit to the multiband model. The dressed values for the LDA bands are shown in column 2 of table 6.1.

The same procedure was also applied to the modified TB model which describes ARPES and the downfolded results are shown in column 3 of table 6.1. One can see that $\Delta = \epsilon_d - \epsilon_p$ is greatly reduced from 2.22eV in column 2 to 0.62eV in column 3. In other words, the dressed Cu $d_{x^2-y^2}$ and $O_{Cu} p_{\sigma}$ orbitals are much closer to each
Table 6.1: Three band model parameters

<table>
<thead>
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<th></th>
<th>(eV)</th>
<th>bare</th>
<th>dressed</th>
<th>modified</th>
</tr>
</thead>
<tbody>
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<td>$\epsilon_d$</td>
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<td>-2.24</td>
<td>-3.04</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_p$</td>
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<td>-4.46</td>
<td>-3.66</td>
<td></td>
</tr>
<tr>
<td>$t_{dp}$</td>
<td>1.59</td>
<td>1.59</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>$t_{pp}$</td>
<td>0.17</td>
<td>0.77</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>$t'_{pp}$</td>
<td>0.46</td>
<td>-0.14</td>
<td>-0.14</td>
<td></td>
</tr>
<tr>
<td>$\epsilon_d - \epsilon_p$</td>
<td>1.02</td>
<td>2.22</td>
<td>0.62</td>
<td></td>
</tr>
</tbody>
</table>

other in ARPES than LDA.

Figure 6.8 shows the partial DOS per spin associated with the Cu $d_{x^2-y^2}$ and $O_{Cu} p_\sigma$ orbitals, with frame (a) referring to the multiband fit to the LDA, (b) the multiband fit to the ARPES, and (c) and (d) the three-band fits to LDA and ARPES, respectively. The blue curves indicate the total DOS associated with the three orbitals, the red curves are the Cu contribution. The overall agreement between the three-band and corresponding many-band DOS’s is good, although the multiband models have an additional weak peak at intermediate energies, due to hybridization with other bands. In all cases the antibonding (AB) band is reasonably well separated from the others, while the nonbonding (NB) band overlaps the top of the bonding band (BB). Since the three- and multiband results are so similar, we confine our remarks to frames (a) and (b).

We believe that the red shaded areas represent the most significant difference, as far as strong-correlation effects are concerned. Strong correlation is usually taken to indicate small or no double occupancy (NDO) of the Cu sites. Since the degree of double occupancy can be treated as a variational parameter, NDO is approximately equivalent to requiring that all singly occupied Cu sites are stabilized by a large energy, $\sim U$. Figure 6.8 indicates that in LDA, only 35% of the Cu electrons
Figure 6.8: (Color online) Partial DOS per spin for (a) the multiband fit to the LDA, (b) the multiband fit to the ARPES, and (c) and (d) the three-band fits to LDA and ARPES, respectively. The blue curves indicate the total DOS associated with the three orbitals (one Cu $d_{x^2-y^2}$ and two O$_{Cu}$ $p_{\sigma}$ orbitals), and the red curves are the Cu $d_{x^2-y^2}$ contribution. The red regions with a number indicate Cu $d_{x^2-y^2}$ contribution in the bonding bands.
are stabilized, while for the renormalized parameters 46% are stable – close to one electron per Cu. Thus, the latter parameters are much more conducive to strong correlation effects.

This can be readily understood. As $\Delta \to 0$, the Cu and one symmetrized O band hybridize better, so the Cu is evenly distributed between BB and AB bands. As $\Delta$ increases, Cu weight shifts to AB bands. It is interesting to recall that early calculations [Zaa88] suggested a small value of $\Delta$, and that x-ray photoemission spectroscopy (XPS) measurements typically find small values for $\Delta$ in the cuprates ($\sim 0.3 - 1.2$ eV) [Fuj87, She87, Chi95, Leo98].

### 6.5 Summary

In conclusion, the bundle of valence bands extending from about 1 to 7 eV below $E_F$ was studied by ARPES experiment and LDA theory. Shirley background effects are found to be relatively weak, and the low spectral weight of CuO$_2$ plane features is likely associated with the finite electron escape depth. While O$_{Sr}$ and O$_{Bi}$ bands are in good agreement with LDA, there are disagreements between experiment and LDA associated with bands originating from the CuO$_2$ layers. The necessary corrections to LDA were found to be only the changes of on-site energies of Cu $d$ and O$_{Cu}$ $p$. The paramagnetic TB band structure which describes ARPES results has more Cu weight shifted to the bottom of the BB, and in this sense has a precursor to the Mott physics built in, even in a strongly doped regime.
Chapter 7

Importance of Matrix Element Effects in the Scanning Tunneling Spectra of High-Temperature Superconductors*

Scanning tunneling spectroscopy (STS) has entered the realm of high-temperature superconductors powerfully by offering atomic scale spatial resolution in combination with high energy resolution. The STS spectrum represents a complex superposition of myriad tunneling paths via which electrons travel to the tip from the conducting layers after being filtered by the effects of insulating overlayers. The

*This chapter is adapted from the following talks and papers.
A. Bansil, Jouko Nieminen, R. S. Markiewicz, Hsin Lin, Importance of matrix element effects in the scanning tunneling spectra of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, American Physical Society, 2008 APS March Meeting, March 10-14, 2008, abstract A10.005.
Jouko Nieminen, Hsin Lin, R. S. Markiewicz, A. Bansil, Importance of matrix element effects in the scanning tunneling spectra of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, eprint arXiv/cond:0805.1675, unpublished.
tunneling signal thus involves what we may refer to as a generalized ‘matrix element’ which connects the STS spectrum with the characteristics of the underlying electronic states of interest. Much of the existing interpretation of the spectra is based however on the fundamental assumption that the STS spectrum is directly proportional to the local density of states (LDOS) of the cuprate layer, and amounts to neglecting the effect of the tunneling matrix element. So motivated, we have developed a material specific theoretical framework for treating the normal as well as the superconducting state where the effect of the tunneling matrix element is included by taking into account various orbitals in the semi-infinite solid. Results for $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) show clearly that the matrix element strongly modifies the STS spectrum. In accord with experimental observations, the computed spectrum displays a remarkable asymmetry between the processes of electron injection vs extraction. This asymmetry arises because $d_{z^2}$ and other tunneling channels begin to open up as the bias voltage between the tip and the sample becomes increasingly negative. The LDOS of the Cu $d_{x^2−y^2}$ orbitals does not possess this asymmetry.

We focus on the Bi2212 system, which has been the subject of an overwhelming amount of experimental work [McE05, Hud01, Bal06, Fis07, Hoo03], although our results bear more generally on the STS spectra of the cuprates. In a tunneling experiment (see figure 7.1), one measures the current drawn when the tip is placed on the surface and a bias voltage is applied between the tip and the sample. Note that the current originating in the conducting CuO$_2$ layers reaches the tip only after it has been ‘filtered’ through the overlayers of SrO and BiO and depends sensitively on the nature and orientation of the various Bi, Sr, Cu and O orbitals. The measured tunneling current thus is not a simple reflection of the LDOS of the CuO$_2$ layers, but it represents a complex mapping of the electronic structure of the system.
7.1 Band structures

In order to construct a realistic framework capable of describing the STS spectrum of the normal as well as the superconducting state, we start with the normal state Hamiltonian

\[
\hat{H}_1 = \sum_{\alpha\beta\sigma} \left[ \epsilon_\alpha c_{\alpha\sigma}^\dagger c_{\alpha\sigma} + V_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta\sigma} \right],
\]

(7.1)

which describes a system of tight-binding orbitals created (or annihilated) via the real-space operators \( c_{\alpha\sigma}^\dagger \) (or \( c_{\alpha\sigma} \)). Here \( \alpha \) is a composite index denoting both the type of orbital (e.g. Cu \( d_{x^2−y^2} \)) and the site on which this orbital is placed, and \( \sigma \) is the spin index. \( \epsilon_\alpha \) is the on-site energy of the \( \alpha^{th} \) orbital. \( \alpha \) and \( \beta \) orbitals interact with each other through the potential \( V_{\alpha\beta} \) to create the energy eigenstates of the system.

We model the Bi2212 sample as a slab of seven layers in which the topmost layer is BiO, followed by layers of SrO, CuO\(_2\), Ca, CuO\(_2\), SrO, and BiO, as shown in figure 7.1(a). The tunneling computations are based on a \( 2\sqrt{2} \times 2\sqrt{2} \) real space supercell consisting of 8 primitive surface cells with a total of 120 atoms (see figure 7.1(b)). The coordinates are taken from the tetragonal crystal structure of Ref. [Bel04]. An \( s \) orbital is used to simulate the tip. The tip is allowed to scan across the substrate for generating the topographic map of figure 7.3(b), or held fixed on top of a surface Bi atom for the computed spectra presented in figures 7.3 and 7.4. The tight-binding parameters of the normal state Hamiltonian of Eq. 7.1 produce the detailed band structure of Bi2212 shown in figure 7.2(a). This band structure is quite similar to the LDA band structure of Bi2212 that underlies for example the extensive angle-resolved photoemission analysis of chapter 6. The Slater-Koster results [Sla54, Shi04] are used to fix the angular dependence of the tight binding.
Figure 7.1: (a) Side view of tip placed schematically on top of seven layers used to compute the tunneling spectrum of Bi2212, where the surface terminates in the BiO layer. Tunneling signal from the conducting CuO$_2$ layers reaches the tip after passing through SrO and BiO layers. (b) Top view of the surface showing arrangement of various atoms. Eight two-dimensional real space primitive unit cells used in the computations are marked by dashed lines.
overlap integrals. The specific orbitals sets used for various atoms are: \((s, p_x, p_y, p_z)\) for Bi and O; \(s\) for Sr; and \((4s, d_{3z^2-r^2}, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2})\) for Cu atoms. This yields 58 orbitals in a primitive cell and a total of 464 orbitals in the \(2\sqrt{2} \times 2\sqrt{2}\) simulation supercell. We have repeated the computations of the tunneling spectra using a larger number of layers and found our results and conclusions to be insensitive to computational details.

Superconductivity is included by adding a pairing interaction term \(\Delta\) in the Hamiltonian of Eq. 7.1 as follows

\[
\hat{H} = \hat{H}_1 + \sum_{\alpha\beta\sigma} \left[ \Delta_{\alpha\beta} c_{\alpha\sigma}^\dagger c_{\beta-\sigma}^\dagger + \Delta_{\alpha\beta}^\dagger c_{\alpha\sigma} c_{\beta-\sigma} \right] 
\]

We take \(\Delta\) to be non-zero only between \(d_{x^2-y^2}\) orbitals of the nearest neighbor Cu atoms, and to possess a d-wave form, i.e. \(\Delta\) is given in momentum space by

\[
\Delta_k = \frac{\Delta}{2} \left[ \cos k_x a - \cos k_y a \right],
\]

where \(a\) is the in-plane lattice constant. The pairing interaction of Eq. 7.3 allows electrons of opposite spins to combine to produce superconducting pairs such that the resulting superconducting gap is zero along the nodal directions \(k_x = \pm k_y\), and is maximum along the antinodal directions. The superconducting state in figures 7.2(b), 7.3 and 7.4 uses a gap parameter value of \(|\Delta| = 0.045\text{eV}\), and is chosen to model a typical experimental spectrum [McE05] for the generic purposes of this study.

Figure 7.2 shows how the Hamiltonians of Eqs. 7.1 and 7.2 provide a realistic description of the electronic structure of Bi2212 in the normal as well as the superconducting state. The normal state band structure in figure 7.2(a) is seen to properly
Figure 7.2: (a) Normal state electronic spectrum of Bi2212. Cu $d_{x^2-y^2}$ weight of states is given by the color of dots. Inset shows the energy region of the VHS’s on an expanded scale. (b) Electronic spectrum of the superconducting state. Electron weight of states is given by the color of dots. Inset highlights the region of the superconducting gap near the antinodal point.

display the presence of various major features. These include: The pair of bands crossing the Fermi energy ($E_F$) due to the two CuO$_2$ planes with the associated van Hove singularities (VHS’s) marked VHS-a (antibonding) and VHS-b (bonding), which are split by 250 meV at the $(\pi, 0)$ point due to interaction between the two CuO$_2$ planes; BiO bands lying about 1 eV above $E_F$; and, the ‘spaghetti’ of bands involving various Cu and O orbitals starting at a binding energy of around 1 eV below $E_F$. Although states near $E_F$ are mainly of Cu $d_{x^2-y^2}$ and O $p_{x,y}$ character, they also contain some Bi and Cu $d_{z^2}$ admixture. In the superconducting state in figure 7.2(b), due to the pairing interaction, the number of bands is doubled as the normal state spectrum is mirrored through $E_F$ to reflect electron-hole symmetry, and additionally, a d-wave superconducting gap appears in both CuO$_2$ bands near $E_F$. However, the spectral weight in the electron channel given by the redness of the dots dominates in the bands derived from the normal state, while the mirrored
states are dominated by the hole component (blue color).

7.2 Tunneling spectra

Having discussed the electronic structure of the normal and superconducting states, we turn now to consider the computation of the tunneling spectra. For this purpose, we apply the conventional form of the Todorov-Pendry expression [Tod93, Pen91] for the differential conductance $\sigma$ between orbitals of the tip $(t, t')$ and the sample, $(s, s')$,
which in our case is straightforwardly shown to yield

$$\sigma = \frac{dI}{dV} = \frac{2\pi e}{\hbar} \sum_{tt' ss'} \rho_{tt'}(E_F)V_{tt'}\rho_{ss'}(E_F + eV)V_{ss'}^\dagger,$$  \hspace{1cm} (7.4)

where the density matrix

$$\rho_{ss'} = -\frac{1}{\pi} \text{Im}[G_{ss'}^+],$$  \hspace{1cm} (7.5)

is given in terms of the retarded Green function or propagator $G_{ss'}^+$. Eq. 7.4 differs from the more commonly used Tersoff-Hamann approach [Ter85] in that it takes into account the details of the symmetry of the tip orbitals and how these orbitals overlap with the surface orbitals. We now express the imaginary part of the Green function in Eq. 7.5 as the difference between the retarded propagator $G_{ss'}^+$ and the corresponding advanced propagator $G_{ss'}^-$, i.e.

$$\rho_{ss'} = \frac{1}{2\pi i} (G_{ss'}^- - G_{ss'}^+) = -\frac{1}{\pi} \sum_\alpha G_{s\alpha}^+ \Sigma''_{\alpha} G_{\alpha s'},$$  \hspace{1cm} (7.6)

where in writing the second equality we have introduced the complex self-energy for orbital $\alpha$,

$$\Sigma_\alpha(E) = \Sigma'_\alpha(E) + i\Sigma''_\alpha(E),$$  \hspace{1cm} (7.7)

in order to allow modeling of possible effects of various bosonic couplings and correlation effects in shifting and broadening electronic states. Here, for simplicity, we have assumed the self-energy to be diagonal in the basis set.

With Eq. 7.6, the tunneling current of Eq. 7.4 can be recast into the form

$$\sigma = \sum_{t\alpha} T_{t\alpha},$$  \hspace{1cm} (7.8)
where

\[ T_{t\alpha} = -\frac{2e}{\hbar} \sum_{t'ss'} \rho_{tt'}(E_F)V_{ts}G_{sa}^+ \Sigma''_{ao} G_{a's'} V_{st}', \]  

(7.9)

and the Green functions and the self-energy are evaluated at energy \( E = E_F + eV_b \).

Eqs. 7.8 and 7.9 are similar to the Landauer-Büttiker formula for tunneling across nanostructures [Mei92], and represent a slight reformulation of Frederiksen et al. [Fre07].

The nature of Eq. 7.9 can be understood straightforwardly: \( G_{sa}(E) \) gives the amplitude with which electrons of energy \( E \) residing on the \( \alpha \)th orbital in the solid tunnel to the surface after being broadened via the self-energy \( \Sigma''_{ao} \). The term \( V_{st} \) is the overlap between the surface orbital and the tip, while \( \rho_{tt'} \) gives the available states at the tip. Hence, \( T_{t\alpha} \) gives the contribution of the \( \alpha \)th orbital to the current, and the summation in Eq. 7.8 collects these individual contributions to yield the total tunneling current which reaches the tip. Eq. 7.9 thus provides a very powerful and transparent scheme for understanding how the total tunneling current is composed of contributions from various ‘tunneling channels’ or paths [Sau97, Mag99] through the solid and for delineating the specific manner in which different orbitals and atoms take part in this complex process.

In considering the tunneling spectrum of Bi2212, we focus first on figure 7.3(a), which presents spectra over the broad energy range of ± 1 eV. Concentrating on the computed spectrum (black line), we see that at high positive bias voltage the spectrum is fairly structureless. At low energies around zero volts, it displays the characteristic peak-dip-hump and gap features. At negative bias voltages the theory shows the presence of the anti-bonding (VHA-a) and bonding (VHS-b) van Hove singularities, followed by a broad dip around -0.7 eV, and then a rapid rise. In all these respects the theory and experiment (red line) are in good accord. Moreover,
Figure 7.4: **Main frame:** Partial contributions to the tunneling current from various orbitals in the two cuprate layers. The CuO$_2$ layer closest to the tip is identified as layer 1 or L1, while the second layer is denoted by L2. Specific contributions are: $d_{x^2-y^2}$ orbitals of the four nearest neighbor Cu atoms (L1-nn, blue line); $d_{x^2-y^2}$ orbitals of the four next nearest neighbor Cu atoms of the first layer (L1-nnn, green line); $d_{x^2-y^2}$ orbitals of the Cu atoms of the second layer (L2, red line); $d_{z^2}$ of the central Cu atom (magenta line). **Inset:** Decomposition of the current from the second cuprate layer: Total contribution (red line); contribution of the four nearest neighbours (blue line); and the next nearest neighbours (green line).

theory reproduces the remarkable observed asymmetry of the tunneling spectrum between positive and negative voltage in that the current is low at high positive bias, but becomes much higher at negative biases. The rapid increase in current at high negative bias results from the turning on of Cu $d_{z^2}$ and other Cu and O orbitals comprising the 'spaghetti' of bands starting around 1 eV binding energy (see figure 7.2(a)).

We emphasize that the local density of states of the Cu $d_{x^2-y^2}$ levels (green line in figure 7.3(a)), which has been widely used to interpret the spectra in the high-$T_c$
literature, fundamentally does not provide a good description of the spectrum. In particular, the Cu \( d_{x^2-y^2} \) LDOS possesses an asymmetry which is opposite to that of the tunneling spectrum, being high at high energies and low at low energies. Figures 7.3(b) and (c) further highlight the importance of the tunneling matrix element. Figure 7.3(b) shows the computed ‘topographic map’ of the BiO surface, where the current is held fixed and the vertical movements of the tip are used to generate a map of the surface much like in atomic force microscopy. Bi atoms appear as bright spots in this image in accord with experimental observations, while O atoms sit at the centers of dark regions. However, when we analyze the current we find that the \( d_{x^2-y^2} \) orbital of the Cu atom lying right under the Bi atom gives zero contribution \[Mar02\], and that the \( d_{x^2-y^2} \) contribution to the tunneling current comes mainly from the four nearest neighbor (NN) Cu atoms as indicated schematically in figure 7.3(c), although there are contributions from more distant Cu atoms in the first CuO\(_2\) layer as well as from the Cu atoms in the second CuO\(_2\) layer, a point to which we return below.

Figure 7.3(d) gives a blow up of the low energy region of \( \pm 0.2eV \), shown by gray shading in figure 7.3(a). The generic form of the real and imaginary parts of the self-energy applied to the Cu \( d_{x^2-y^2} \) orbitals (solid and dashed blue lines, respectively) and the self-energy applied to all other orbitals is given in the inset. The computed spectrum is seen to properly reproduce the coherence peaks and the characteristic peak-dip-hump feature.

Figure 7.4 delineates contributions from a number of different tunneling channels or paths by which electrons can reach the tip as a function of the applied voltage. Paths starting from Cu atoms in the CuO\(_2\) layer closest to the tip, referred to as layer 1 or L1, as well as from the second cuprate layer L2 are considered. The
current is dominated by the \( d_{x^2-y^2} \) orbitals on the four nearest neighbour (nn) Cu atoms in layer 1 up to about -0.7 eV (blue line). At higher negative biases, the contribution from the \( d_z^2 \) electrons from the Cu atom lying right below the Bi atom or the tip grows rapidly (magenta line). The contribution from the four next nearest neighbour (nnn) \( d_{x^2-y^2} \) orbitals in layer 1 is also significant and it is spread over a wide energy range with little structure in the region of the van Hove singularities (green line, main figure). In contrast, the total current originating from the \( d_{x^2-y^2} \) orbitals of the second cuprate layer is quite localized over zero to -0.6 eV bias (red line, main figure), but it is mainly made up of contribution from the nn-Cu atoms in the second layer (blue line in the inset). nnn-Cu or other orbitals in the second layer do not yield substantial current. Here we have emphasized the nature of the current associated with the cuprate layers and how an intrinsic electron-hole asymmetry in the tunneling signal comes about through the \( d_{z^2} \) orbitals. We note however that the Bi and O orbitals in the surface Bi-O layer can also play a role in producing an asymmetric background current.

### 7.3 Summary

In conclusion, we have presented a framework for a material specific modeling of the scanning tunneling spectra in the normal and superconducting states of complex materials where effects of multiple orbitals and the associated tunneling matrix element are properly taken into account. In this way, we provide a realistic basis for identifying signatures of specific electronic states in the tunneling spectrum, and for realizing thus the full potential of the tunneling spectroscopy. The scheme can be extended to incorporate effects of impurities and various nanoscale inhomogeneities.
by using appropriately larger basis sets in the computations. Our results on Bi2212 show that the matrix element strongly modifies the spectrum, and reveal new insights into how different tunneling channels contribute to the spectrum, and how much of the striking electron-hole asymmetry observed experimentally is not due to the nature of the local density of states of the Cu \( d_{x^2-y^2} \) orbitals, but that it can be explained within the conventional picture due to the turning on of Cu \( d_{z^2} \) and other channels with increasing bias voltage. This indicates that the effects of strong electronic correlations on the tunneling spectrum are more subtle than has been thought previously. However, we should note that we have not analyzed spectra associated with the deeply underdoped regime where charge order has been reported. [Koh07]
Chapter 8

Conclusion

I have performed LDA band structure calculations on various kinds of cuprates and compared the results with experiments. Topics discussed in previous chapters show the predictive power as well as limitation of LDA. The metallic states near $E_F$ of hole doped cuprates are found to be reasonably described by LDA. In particular, the Fermi surfaces of Bi2212 predicted by LDA agree with ARPES results if doping is included in the calculation properly beyond rigid band filling. The doping evolution of the LSCO Fermi surface maps in ARPES also agree with LDA. Even at the edge of the insulating phase, the nascent metallic states in 3% doped LSCO have the dispersion fully consistent with LDA. On the other hand, the loss of spectral weight of these metallic states in the underdoped region cannot be explained by LDA. This is an important constraint on theoretical models involving strong correlation effects.

LDA with the virtual crystal approximation is able to capture the interlayer charge redistribution effects associated with doping. This is applied to solve the long-standing problem of the Bi-O Fermi surface pocket in Bi2212, and also applied to predict a new class of electron-doped Bi2212. This relative simple scheme could be
further applied to other layered materials to address how the doping changes the relative energy positions of different bands associated with different layers.

On the other hand, the doping effect within CuO$_2$ is dominated by strongly correlated electrons and LDA is inadequate. Three- and four-band Hubbard models are carried out to explain the doping evolution of electronic structures in NCCO. The on-site energy difference between Cu $d_{x^2-y^2}$ and O $p_{\sigma}$ is found to be too large in LDA. The model with more evenly distributed Cu $d_{x^2-y^2}$ weight among bonding and antibonding bands has better agreement with ARPES results in NCCO. This is also confirmed in chapter 6 where the entire ARPES valence band spectrum extending from about 1 to 7 eV below $E_F$ of Bi2212 is analyzed. This is a starting point for studying the strong correlation effects by multi-band models. The multi-band model covers much wider energy range than the one-band model and allows different treatments on different atoms.

By having a realistic model of Bi2212, we demonstrate that STM/STS spectra are sensitive to matrix element effects which are due to the fact that the current originating from the CuO$_2$ plane is filtered by other layers before reaching the tip. The electron-hole asymmetry observed experimentally can be explained within a conventional picture. This indicates that the effects of strong electronic correlations on the tunneling spectrum are more subtle than has been thought previously. This theoretical framework of STM/STS provides a realistic basis for identifying signatures of specific electronic states in the tunneling spectrum, and for realizing thus the full potential of the tunneling spectroscopy. The scheme can be extended to incorporate effects of impurities and various nanoscale inhomogeneities by using appropriately larger basis sets in the computations.

We have developed an approach in which LDA is used as template for building
a tight binding model, which can easily be adjusted either by experiments or by including interactions beyond LDA such as Hubbard $U$ or superconducting pairing. The STM/STS simulation based on this approach is shown to be a useful tool for understanding the tunneling spectra. In the future, this model can be combined with first-principle matrix elements to simulate other spectroscopies, such as angle-resolved photoemission spectroscopy, Compton profile, and resonant inelastic X-ray scattering. This makes it possible to have direct comparisons between theory and various spectroscopies. Hopefully, by revealing features hidden in matrix element effects, one can gain more insights into the physics of complex materials.
Bibliography


