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by

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Electronic Properties of Strongly Correlated Layered Oxides

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Electronic Properties of Strongly Correlated Layered Oxides

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To my parents and my wife, Chia-Hui Lu,
for their full-hearted support and unconditional love.

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Electronic Properties of Strongly Correlated Layered Oxides

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The two-dimensional electronic systems (2DESs) have kept surprising physicists for the last few decades. Examples include the integer and fractional quantum Hall effects, cuprate superconductivity, and graphene. This thesis is intended to develop suitable theoretical tools which can be generalized to study new types of 2DESs with strong correlation feature.

The first part of this thesis describes the investigation of heterostructures made by Mott insulators. This work is mostly motivated by the significant improvement of techniques for layer-by-layer growth of transition metal oxides in the last few years. We construct a toy model based on generalized Hubbard model complemented with long-ranged Coulomb interaction, and we study it by Hartree-Fock

theory, dynamical mean-field theory, and Thomas-Fermi theory. We argue that interesting 2D strongly correlated electronic systems can be created in such heterostructures under several conditions. Since these 2D systems are formed entirely due to the gap generated by electron-electron interaction, they are not adiabatically connected to a noninteracting electron states. This feature makes these 2D systems distinguish from the ones created in semiconductor heterostructures, and they may be potential systems having non-Fermi liquid behaviors.

The second part of this thesis is devoted to the study of collective excitations in high-temperature superconductors. One important achievement in this work is to develop a time-dependent mean-field theory for $t - U - J - V$ model, an effective low energy model for cuprates. The time-dependent mean-field theory is proven to be identical to the generalized random-phase approximation (GRPA) which includes both the bubble and ladder diagrams. We propose that the famous 41 meV magnetic resonance mode observed in the inelastic neutron scattering measurements is a collective mode arising from a conjugation relation, which has been overlooked in previous work, between the antiferromagnetic fluctuation and the phase fluctuation of the d -wave superconducting order parameter near momentum (π, π) . Furthermore, we find that this collective mode signals the strength of the antiferromagnetic fluctuations which are responsible for the suppression of the superfluid density in the underdoped cuprates even at zero temperature. Finally, we perform a complete analysis on an effective model with parameters fitted by experimental data of Bi2212 within the GRPA scheme and conclude that the short-range antiferromagnetic interactions which are a remnant of the parent Mott-insulator are more likely the pairing mechanism of the High- T_c cuprates.

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Chapter 1

Introduction to Transition Metal Oxides

1.1 Cubic perovskite

In the systems studied in the condensed matter physics, there are always many degrees of freedom involved. One can imagine that in the solid electrons interact not only with each others but also with the cations and anions. The most fascinating feature of such many body systems is that the electrons may have the *collective behaviors*, behaviors not showing up in a single electron, as they interact quantum mechanically. In particular, the transition metal oxides have been one of best platforms for discoveries of novel collective modes, and the well-known examples include Mott insulating state, ferromagnetism and antiferromagnetism, Colossal Magnetoresistance, high-temperature superconductors, and so on.

What are so unique about the transition metal oxides? The name has already revealed answers, transition metals and oxygens. As taught in the quantum mechanics course, we know that the electrons of a transition metal element fill up to $3d$ orbitals. In the atomic limit, the d orbitals have five-fold degeneracy and Hund's

rule tells us how electrons occupy these d orbitals. This five-fold degeneracy, however, does not exist in most transition metal oxides because the transition metal ions are usually surrounded by oxygen and other *spectator* ions which are necessary for stabilizing the crystal structures. Oxygen ions, acting as electron acceptors, usually manifest themselves as O^{2-} , while other spectator ions, acting as electron donors, carry positive valence charge in general. Consequently, these charged ions provide additional electric potentials which break the five-fold degeneracy of the d orbitals in the transition metal oxides.

Obviously how the d -orbital degeneracy is reduced depends critically on the crystal structures. Before discussing the crystal structures, let's discuss about the appropriate representations for d orbitals first. Instead of using the spherical harmonic functions $Y_m^{l=2}$, it is more convenient to use the following combinations for the five d orbitals[1]:

$$\begin{aligned}
d_{xy} &\propto -i(Y_2^2 - Y_{-2}^2) \\
d_{yz} &\propto (Y_1^2 + Y_{-1}^2) \\
d_{zx} &\propto i(Y_1^2 - Y_{-1}^2) \\
d_{x^2-y^2} &\propto (Y_2^2 + Y_{-2}^2) \\
d_{3z^2-r^2} &\propto Y_0^2
\end{aligned} \tag{1.1}$$

The advantage of this representation is that these five eigen-functions are all real functions and their meanings in the real space become very clear. As seen in the Fig. 1.3 in Ref[1], the eigen-functions $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ are much more densed along the x, y axes and z axis respectively, while $d_{\alpha\beta}$ ($\alpha\beta = xy, yz, zx$) are mostly populated on the $\alpha - \beta$ plane but around the lines tilted from the α, β axes by 45° . In literature, it is common to classify $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ as e_g orbital and three $d_{\alpha\beta}$ as t_{2g} orbital.

Now let's consider the most common structure of the transition metal oxides,

the perovskite structure. The simplest perovskite structure might be the *cubic perovskite*, and we will consider mostly this structure in this thesis. Its basic formula is AMO_3 where M is a transition metal element and A is a spectator element which is usually a group II or III element. Because in the unit cell M is surrounded by six O^{2-} located along all three axis directions, the Coulomb interactions due to O^{2-} ions cause energies of electrons on e_g orbitals much higher than those on t_{2g} orbitals. The energy difference between e_g and t_{2g} orbitals can be as high as 3eV in typical perovskites[1]. The two-fold degeneracy of e_g orbitals and the three-fold degeneracy of t_{2g} orbitals can be further broken if the crystal structure has some lattice distortion, for example, elongation of the crystal structure along a certain axis usually results in lowering band energies for orbitals associated with that axis. Typical examples of the materials with cubic perovskite structure are $SrTiO_3$, $LaTiO_3$, $YTiO_3$, $CaVO_3$, $SrVO_3$, etc.

Although the further breaking of degeneracy depends crucially on material details, the splitting between the e_g and t_{2g} bands is very robust and very often seen in the transition metal oxides with perovskite structures, which allows us to use some simplified models to study the physical properties we are interested in. In many cases, we can actually consider a model with single d band, due to the breaking of d orbital degeneracies, to explore a variety of important physics in the transition metal oxides. In the next section, we will briefly discuss the simplified model we will use in this thesis.

1.2 Hubbard model

For the transition metal oxides, the most important model might be the Hubbard model first proposed in 1963[5]. The Hubbard model can be easily generalized to multiband models, but here we only discuss the single band model for a qualitative understanding. There are only two terms in the Hubbard model, and both terms

are purely electronic. The t term describes the hopping between nearest-neighbor sites, which is the largest part of the kinetic energy. The U term represents the energy cost of putting two electrons on the same lattice site due to the Coulomb interaction, and these two electrons can only have anti-parallel spins because of the Pauli exclusion principle. The resulting Hubbard Hamiltonian is:

$$H = - \sum_{\langle i,j \rangle, \sigma} t_{i,j} \left[c_{i,\sigma}^\dagger c_{j,\sigma} + c.c \right] + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (1.2)$$

where $\langle i, j \rangle$ means that i, j are nearest-neighbor.

It is instructive to look at two solvable limits of this model. On the one hand, the Hubbard model becomes a usual tight-binding model for $U = 0$. Therefore in the limit of $U/t \rightarrow 0$, the Hubbard model describes a metal and the U term seems to only have the effect of renormalizing the band structures. On the other hand, for $t = 0$ the Hubbard model describes isolated atoms on a cubic lattice in which the energy gap appears naturally (because it costs an energy of U to put two electrons on the same atom). Therefore it is expected that in the limit of $U/t \rightarrow \infty$ the band structures will split into two bands, usually referred as upper and lower Hubbard bands, separated by a gap with the size of U .

Apparently the Hubbard model in these two limits gives very different physics. This indicates that unusual properties would occur in the Hubbard model with a moderate ratio of U/t , which is just the case for the transition metal oxides. The conduction electrons in the transition metal oxides are the d -electrons which usually have very narrow bandwidth (thus small t) due to the character of d orbitals. This narrow width of the conduction band leads to the large ratio of U/t in the transition metal oxides. For instance, the typical values of U/t could be order of 10 for the simple cubic perovskite AMO_3 . Consequently, the role of electronic correlations becomes dominating in determining the ground state of the solid.

One important feature of the Hubbard model is the Mott insulating state

occurring at the *half-filling*, i.e. one electron per site. Unlike the usual band insulating state formed by fully occupied conduction bands, the Mott insulating state results from the strong short-range Coulomb interactions even though the conduction bands are not fully occupied. In other words, there is an energy gap dynamically generated by local interactions. It is not surprising that whether or not the solid is Mott insulator depends critically on the value of U/t and also on other details of the solid. A good example is the family of cubic perovskite in which LaTiO_3 and YTiO_3 are Mott insulators but CaVO_3 and SrVO_3 are not, despite these four materials have similar lattice structures.

Another important feature of the Hubbard model is its connection to the magnetically ordered ground states such as ferromagnetic (FM) and antiferromagnetic (AFM) states. Qualitatively the appearance of these magnetically ordered ground states can be understood by the delicate balance of the kinetic energy gain and interaction energy cost. In the FM state, the doubly-occupied states which cost interaction energy U are completely eliminated due to the Pauli exclusion principle but the nearest-neighbor hopping which favors the kinetic energy gain is also strongly suppressed as the half-filling is approached. On the other hand, AFM state allows the nearest-neighbor hopping even at the half-filling and the doubly-occupied states are also efficiently avoided by the arrangement of staggered spins. As a result, usually it is seen in the phase diagram of the Hubbard model that AFM state is favored near the half-filling and FM state is favored away from the half-filling. This AFM/FM phase diagram can also be understood by the *Goodenough-Kanamori rule*[2]. To see this, let's first discuss the origin of the spin interaction in the Hubbard model. Although the Hubbard model does not involve any spin operators in its original form given in Eq. 1.2, the spin interaction arises through higher order virtual hopping processes, known as *superexchange processes*, between the nearest-neighbor sites. Goodenough-Kanamori rule states that the superexchange spin interaction is

antiferromagnetic if the two orbitals involved in the virtual hopping processes are both *half-filled*, and is *ferromagnetic* if they are *half-filled and full* or *half-filled and empty*[2, 3]. For the single band Hubbard model we have discussed above, the trend of the magnetic orderings is consistent with Goodenough-Kanamori rule since more and more empty (or full) sites will appear as the electron density is getting away from the half-filling.

It is emphasized that all the above discussions are qualitative and the exact phase diagram of the Hubbard model is still not available so far. Besides the magnetic ordering, the Hubbard model is also found to have instabilities toward the charge density wave states which are connected to the stripe phase observed in the LSCO[4]. In this thesis, we mainly focus on the magnetically ordered and paramagnetic states because these states are more commonly seen in most transition metal oxides. We will explore these magnetically ordered states by the standard Hartree-Fock theory, and the paramagnetic state will be studied by the dynamical mean-field theory which will be formulated in Chapter 2.

Chapter 2

Dynamical Mean-Field Theory

2.1 Introduction

The dynamical mean-field theory (DMFT) has become an important approach to study the strongly correlated systems. The central idea of the DMFT is that by the spatial fluctuations neglected completely, the Hubbard model can be mapped into a solvable model, the Anderson quantum impurity model. With this mapping, the temporal fluctuations are *completely* included, and the mapping becomes *exact* in an non-trivial limit of spatial dimension going to infinity. In this chapter, we will summarize the formalism of the DMFT in details.

Let's start with the partition function in coherent-state path integral formalism for the Hubbard model:

$$\begin{aligned} \mathcal{Z} &= \int \prod_i D[c_{i\sigma}^*] D[c_{i\sigma}] e^{-S} \\ S &= \int_0^\beta d\tau \left\{ \sum_{i,\sigma} c_{i\sigma}^* (\partial_\tau - \mu) c_{i,\sigma} + H[c_{i\sigma}^*, c_{i\sigma}] \right\} \end{aligned} \quad (2.1)$$

where $\{c_{i\sigma}^*, c_{i\sigma}\}$ are Grassmann variables. The first step of DMFT is to find an effective action S_{eff} such that only the degree of freedom at a single site o is left in

the functional integral:

$$\mathcal{Z} = \int D[c_{o\sigma}^*] D[c_{o\sigma}] e^{-S_{eff}} \quad (2.2)$$

If we are only interested in the solution with full crystal translational symmetry, the choice of this single site does not affect the final results.

The on-site Green's function for the *original Hubbard model* (defined as $G(i\omega_n)$) can be calculated from Eq. 2.2:

$$\begin{aligned} G(\tau - \tau') &= -\langle T c_0(\tau) c_0^\dagger(\tau') \rangle_{S_{eff}} \\ G(i\omega_n) &= \int_0^\beta d\tau G(\tau) e^{i\omega_n \tau} \end{aligned} \quad (2.3)$$

Alternatively, we may also calculate $G(i\omega_n)$ by:

$$G(i\omega_n) = \frac{1}{V} \sum_k \frac{1}{i\omega_n + \mu - \epsilon_k - \Sigma(k, i\omega_n)} \quad (2.4)$$

where ϵ_k is the free ($U=0$) band energy of Hubbard model and $\Sigma(k, i\omega_n)$ is the self energy. These two different ways to calculate the same quantity $G(i\omega_n)$ are the key part of the closed self-consistent equations for DMFT, which we will see in the next section.

Consequently the main question is how to find S_{eff} . It is actually not possible to derive a general form for S_{eff} , except in one non-trivial limit. It has been proven[6] (see Appendix A) that in the limit of $d \rightarrow \infty$, where d is the dimension of the system, S_{eff} can be mapped *exactly* into the Anderson impurity model as:

$$S_{eff} = - \int_0^\beta d\tau d\tau' \sum_\sigma c_{0\sigma}^\dagger(\tau) \mathcal{G}_0^{-1}(\tau - \tau') c_{0\sigma} + U \int_0^\beta d\tau n_{0\uparrow}(\tau) n_{0\downarrow}(\tau) \quad (2.5)$$

Furthermore, in this limit the self-energy does not depend on k at all and there

exists a relation:

$$\mathcal{G}_0^{-1}(i\omega_n) - G^{-1}(i\omega_n) = \Sigma(i\omega_n) \quad (2.6)$$

The above equation builds a connection between the effective theory given in Eq. 2.5 and the original Hubbard model. Furthermore, this relation leads to a closed set of self-consistent relations, which is *exact* in the $d \rightarrow \infty$ limit.

One of the most important success of DMFT is to explain the Mott transition without any magnetic order. This success is a consequence of the fact that although DMFT ignores the spatial dependence, it keeps the dependence on frequency of the Green's function. As a result, the local quantum (or temporal) fluctuations have been *completely* included in the self-consistent equations. Since the Mott insulating state results from the suppression of density of state near the Fermi surface due to the strong local quantum fluctuations, DMFT captures this feature correctly and therefore can give an adequate description for Mott transition even without any magnetic order. In next section, we will discuss the iteration procedure of DMFT.

2.2 Iteration procedure

Eqs. 2.3, 2.4, and 2.6 form a set of closed self-consistent relation. In general, the iteration procedure to solve the DMFT equations is:

1. Give an initial value of self-energy Σ_i .
2. Compute G through Eq. 2.4 with Σ_i .
3. Compute $\mathcal{G}_0$ through Eq. 2.6 with Σ_i and G .
4. Use the $\mathcal{G}_0$ obtained in previous step to calculate the new on-site Green's function G_{new} through Eq. 2.3.
5. Generate the new self-energy Σ_{new} using Eq. 2.6 with $\mathcal{G}_0$ and G_{new} .

6. Repeat until $|\Sigma_i - \Sigma_{new}| \rightarrow 0$.

In this procedure, the most difficult part is the step 4, which is a problem of quantum impurity model. Several numerical techniques have been proposed to solve the quantum impurity model. Two most commonly used methods are the quantum Monte Carlo algorithm and the exact diagonalization method. Although both methods have been applied to study properties of the Hubbard model quite successfully, they both cost a large amount of computation time even just for a 2D single band Hubbard model. As a result, these two methods are not appropriate for cases in which systems with multilayers may be involved. In this dissertation we adopt the newest one, two-site method, proposed by Potthoff[7], which is argued to be computationally inexpensive and reproduces remarkably the scaling of the quasi-particle weight and lower Hubbard band near the Mott transition up to a satisfactory accuracy.

2.3 Two-site method

The two-site method can be considered as the simplest version of the exact diagonalization method. In the exact diagonalization method, in order to generate the necessary self-energy term, some *bath sites* coupled to the impurity site are put into the quantum impurity model. Usually eight to ten bath sites are required to achieve an acceptable accuracy of the self-energy in the whole frequency range for a 2D single band Hubbard model. However, it requires a very heavy computation to solve the iteration equations, and actually an accurate self-energy in the whole frequency range is not required in many cases. For example, as far as the Mott transition is concerned, we only need to know how the self-energy at low frequency changes with U/t . Therefore an impurity model which can capture the physics at low frequency accurately is well enough for the study of Mott transition. This is just the central idea of the two-site method proposed by Potthoff[7]. This method has been used to

study the $\text{LaTiO}_3/\text{SrTiO}_3$ by Okamoto *et. al.*[15].

To begin with the general formalism of exact diagonalization method, let's consider the impurity model consisting of one impurity and n_s bath sites. It leads to a Hamiltonian of:

$$H_{imp} = \sum_{\sigma} (\epsilon_o - \mu) c_{o\sigma}^{\dagger} c_{o\sigma} + U n_{o\uparrow} n_{o\downarrow} + \sum_{\sigma, l=1}^{n_s} (\epsilon_l - \mu) a_{l\sigma}^{\dagger} a_{l\sigma} + V_l (c_{o\sigma}^{\dagger} a_{l\sigma} + H.c.) \quad (2.7)$$

where $c_{o\sigma}$ is the same annihilation operator used in previous section associated with the impurity degree of freedom. $\{a_{l\sigma}\}$ are annihilation operators of n_s non-interacting media coupling only to the impurity site. Integrating out $\{a_{l\sigma}\}$ can reproduce the effective action in Eq. 2.5 if the parameters $\{\epsilon_l, V_l\}$ are determined through the self-consistent equations. From comparing Eqs. 2.5 and 2.7, it is found that $\epsilon_o = 0$. We keep this term just to make the Hamiltonian look more familiar to us, and it can be set to be zero at any time we like. It is then straightforward to integrate out the degrees of freedom of the bath sites to give the following term in the action:

$$\begin{aligned} & - \sum_l V_l^2 \int_0^{\beta} d\tau d\tau' G_{bath,l}(\tau - \tau') c_{o\sigma}^*(\tau) c_{o\sigma}(\tau') \\ & = \frac{-1}{\beta^3} \sum_{\omega_n, \Omega_m, \Xi_p} \sum_l V_l^2 \int_0^{\beta} d\tau d\tau' G_{bath,l}(i\omega_n) c_{o\sigma}^*(i\Omega_m) c_{o\sigma}(i\Xi_p) e^{-i\omega_n(\tau - \tau')} e^{i\Omega_m \tau} e^{-i\Xi_p \tau'} \\ & = \frac{-1}{\beta} \sum_{\omega_n} \sum_l V_l^2 G_{bath,l}(i\omega_n) c_{o\sigma}^*(i\omega_n) c_{o\sigma}(i\omega_n) \end{aligned} \quad (2.8)$$

Substituting

$$G_{bath,l}(i\omega_n) = \frac{1}{i\omega_n + \mu - \epsilon_l}, \quad (2.9)$$

we obtain $\mathcal{G}_0^{-1}(i\omega_n)$ in the effective action given in Eq. 2.5:

$$\mathcal{G}_0^{-1}(i\omega_n) = i\omega_n + \mu - \epsilon_o - \Delta(i\omega_n) \quad (2.10)$$

where $\Delta(i\omega_n)$ is the hybridization function defined as:

$$\Delta(i\omega_n) \equiv \sum_{l=1, \sigma}^{n_s} \frac{V_l^2}{i\omega_n + \mu - \epsilon_l} \quad (2.11)$$

In principle, the self-consistent DMFT should be fulfilled rigorously in the limit of $n_s \rightarrow \infty$. However, this will lead to a very complex many-body problem and thus cost a lot of computation time. The spirit of two-site method is to choose $n_s = 1$ so that the H_{imp} contains only two sites, one impurity and one bath sites, hence this H_{imp} can be solved exactly and quickly. Besides, in this case we have only two parameters ϵ_c, V_c to fit and we can replace the original self-consistent relations by fitting the behaviors of on-site Green's function in two limits: $\omega \rightarrow 0$ and $\omega \rightarrow \infty$. As a result, the self-consistent solutions from this simplified two-site model can yield correct behavior in $\omega \rightarrow 0$ and $\omega \rightarrow \infty$ limits, which are just cases we mostly get interested.

The hybridization function then becomes:

$$\Delta(i\omega_n) = \frac{V_c^2}{i\omega_n + \mu - \epsilon_c} \quad (2.12)$$

where V_c, ϵ_c are two real numbers. Substituting the above equation into Eq. 2.10, we have:

$$\mathcal{G}_0(i\omega_n) = \frac{1}{i\omega_n + \mu - \epsilon_o - \frac{V_c^2}{i\omega_n + \mu - \epsilon_c}} \quad (2.13)$$

We will consider the zero temperature case from now on. The major change is replacing $i\omega_n$ by ω in the above Green's functions. We also put $\epsilon_o = 0$ from now on. Therefore the inverse of the free impurity Green's function is:

$$\mathcal{G}_0^{-1}(\omega) = \omega + \mu - \frac{V_c^2}{\omega + \mu - \epsilon_c} \quad (2.14)$$

The interacting impurity Green's function can be calculated exactly by Lehmann

representation:

$$G_{\sigma}^{imp}(\omega) = \sum_m \frac{|\langle g|c_{o\sigma}|m\rangle|^2}{\omega + E_g - E_m + i\delta} + \frac{|\langle m|c_{o\sigma}|g\rangle|^2}{\omega + E_m - E_g - i\delta} \quad (2.15)$$

where $|g\rangle$ is the ground state of the impurity Hamiltonian given in Eq. 2.7 with $n_s = 1$ and $\{|m\rangle\}$ is the set of the eigenstates of the impurity Hamiltonian. The Hamiltonian can be expressed by a basis: $\{|n_{o\uparrow}, n_{o\downarrow}, n_{c\uparrow}, n_{c\downarrow}\rangle\}$ with $n_{o\sigma, c\sigma} = 0, 1$. Therefore the Hamiltonian can be expressed by a 16×16 matrix, which can be diagonalized numerically exact. With this notation, the self-energy $\Sigma(\omega)$ can be obtained by subtracting Eq. 2.15 from Eq. 2.13

Now we have two parameters (ϵ_c, V_c) to be determined by the self-consistent equations. For this two-site model this can be done by fitting the high- and low frequency limits of the Green's function[7]. The first one is:

$$n_{imp} = n \quad (2.16)$$

where $n_{imp} = n_{o\uparrow} + n_{o\downarrow}$ which can be computed from the exact solution of H_{imp} . n is the total particle number computed from the Green's function if self-energy $\Sigma(\omega)$ is known:

$$\begin{aligned} G_{\sigma}(\omega) &= \frac{1}{V} \sum_k \frac{1}{\omega + \mu - \Sigma_{\sigma}(\omega) - \epsilon_{k\sigma}} \\ n &= -\frac{1}{\pi} \int_{-\infty}^0 d\omega \sum_{\sigma} \text{Im} G_{\sigma}(\omega + i0^+) \end{aligned} \quad (2.17)$$

where $\epsilon_{k\sigma}$ is the single-particle band of the original model, which is $2t(\cos(kx) + \cos(ky))$ for single-band 2-d Hubbard model. The full DMFT requires the self-consistency of $G_{\sigma}^{imp}(\omega) = G_{\sigma}(\omega)$, and Eq. 2.16 satisfies it up to an integration. The meaning of it is to guarantee the correct behavior of the $G(\omega)$ at high- ω limit.

The other self-consistent equation is obtained by fitting the low energy behavior $\omega \rightarrow 0$. By carefully expanding the self-energy in powers of ω , Potthoff

derived the following equation:

$$V_c^2 = z M_2^{(0)}, \quad (2.18)$$

where

$$z = \left(1 - \frac{d\Sigma(0)}{d\omega}\right)^{-1} \quad (2.19)$$

is the quasi-particle weight, and

$$M_2^{(0)} = \sum_{j \neq i} t_{i,j}^2, \quad (2.20)$$

where $t_{i,j}$ is the hopping integral from i to j . With Eqs. 2.16 and 2.18, the self-consistent equations for DMFT can be solved and the results are accurate in both low and high frequency limits.

Using the same spirit, the two-site method can be generalized to the multi-band Hubbard model. There will be a two-site impurity model for each band, and the self-consistent equations will become

$$\begin{aligned} n_{imp}^r &= n^r \\ V_c^{r2} &= \sum_{r',i'} z^r \left(t_{i,i'}^{r,r'}\right)^2 \end{aligned} \quad (2.21)$$

where r is the band index and $t_{i,i'}^{r,r'}$ is the hopping integral between r th band on site i and r' th band on site i' . The detailed derivation can be found in Potthoff's original paper[7], and we will use this generalized formalism in our calculations for Mott insulator heterostructures discussed in Chapters 5 and 6.

Chapter 3

Time-Dependent Mean-Field Theory

In this chapter, we will summarize the time-dependent mean-field theory (TDMFT) which handles the quantum fluctuations around the mean-field states obtained by the standard Hartree-Fock theory. The main advantage of the TDMFT is that it is formally equivalent to the generalized random phase approximation (GRPA) including both bubble and ladder diagrams, hence it is suitable for systems in which both the direct and exchange interactions are important.

3.1 Linear Response Theory

The standard Hartree-Fock theory, also known as mean-field theory, allows us to decouple the two-body interactions into effective one-body potentials characterized by a set of order parameters which are constant in time. The resulting mean-field Hamiltonian is usually simple because only few non-zero order parameters are required at the mean-field level. This simplification no longer exists in the TDHFT. For TDHFT, every effective potential is assumed to fluctuate in time around its

mean-field value. To be specific, for any particle-hole or particle-particle channels $\hat{O}$ (for exmaple, $\hat{O} = c_i^\dagger c_j, c_i^\dagger c_j^\dagger, etc.$), the effective potential is:

$$\langle \hat{O} \rangle = \langle \hat{O} \rangle_{MF} + \delta \langle \hat{O} \rangle(t) \quad (3.1)$$

where $\langle \hat{O} \rangle_{MF}$ is the expectation value of the operator $\hat{O}$ evaluated in the mean-field state. Therefore, the effective Hamiltonian becomes:

$$\mathcal{H} = H^{MF} + H^{fluc}(t) \quad (3.2)$$

where H^{MF} is just the standard mean-field Hamiltonian. Since $H^{fluc}(t)$ is small by construction, we can take H^{MF} as the 'unperturbed' Hamiltonian and then apply the time-dependent perturbation theory to treat $H^{fluc}(t)$.

If an external perturbation $H^{ext}(t)$ is applied, the total potential which the quasiparticles will respond to is: $H'(t) = H^{ext}(t) + H^{fluc}(t)$. Using the linear response theory, we can compute the change in element of density matrix $\delta \langle \rho_{ab} \rangle$ by:

$$\delta \langle \rho_{ab}(t) \rangle = \frac{i}{\hbar} \int_{-\infty}^{\infty} dt' \theta(t - t') \langle [H'(t'), \rho_{ab}(t)] \rangle_{MF}. \quad (3.3)$$

Fourier transforming to the frequency-momentum space $(\omega, \vec{q})$ and expressing the density matrix in the quasiparticle basis (i.e. the eigen-states of H^{MF}), we finally arrive at

$$(\omega \hat{I} - \hat{M}) \bar{\rho}(\vec{q}, \omega) = H^{ext}, \quad (3.4)$$

where $\bar{\rho}$ is a column representing the change in the quasiparticle density matrix. Due to the translational invariance, the excitation momentum $\vec{q}$ is a good quantum number, and the excitation energies $\{\omega_i\}$ for a given $\vec{q}$ are the eigenvalues of $\hat{M}$ whose elements as well as H^{ext} are evaluated from the commutator appearing in Eq. 3.3. Diagonalizing the matrix $\hat{M}$ gives the same results of performing the

bubble and ladder sums in GRPA perturbation theory[11, 12], and the proof will be given in the end of this chapter.

It would be more convenient to order $\bar{\rho}(\vec{q}, \omega)$ such that $\hat{M}$ can be written as $\hat{M} = \hat{\eta}\hat{A}$ where $\hat{A}$ is a hermitian matrix and

$$\hat{\eta} = \begin{pmatrix} \hat{I} & 0 \\ 0 & -\hat{I} \end{pmatrix}. \quad (3.5)$$

This special structure of $\hat{M}$ echoes that used in the Bogoliubov theory for interacting boson system, which indicates that the excitations are actually bosonic. Accordingly, we can borrow results from the Bogoliubov theory to calculate several physical properties, for example, the correlation energy.

3.2 Correlation energy

To compute the correlation energy, it is much easier to see from the viewpoint of an interacting boson system. If we approximate every element of the density matrix as a bosonic creation (annihilation) operator $b_\mu^\dagger(b_\mu)$, we can write H^{fluc} as:

$$H^{fluc} = \sum_{\mu, \nu} B_{\mu, \nu} b_\mu^\dagger b_\nu + \left(D_{\mu, \nu} b_\mu^\dagger b_\nu^\dagger + h.c. \right), \quad (3.6)$$

or in a matrix form of

$$H^{fluc} = \frac{1}{2} \bar{\beta}^\dagger \hat{A} \bar{\beta} - \frac{1}{2} \sum_n B_{n, n}. \quad (3.7)$$

$\bar{\beta} \equiv (b_1, b_2, \dots, b_1^\dagger, b_2^\dagger, \dots)$, and $\hat{A}$ is the hermitian matrix defined as:

$$\hat{A} = \begin{pmatrix} \hat{B} & \hat{D} \\ \hat{D} & \hat{B} \end{pmatrix}, \quad (3.8)$$

and related to $\hat{M}$ used in the last section through $\hat{M} = \hat{\eta}\hat{A}$. Applying the generalized Bogoliubov transformation, H^{fluc} can be diagonalized by $\bar{\alpha} \equiv (a_1, a_2, \dots)$ with corresponding eigenvalues $(\omega_1, \omega_2, \dots)$ where $\{\omega_n\}$ here contain only the positive eigenvalues of $\hat{M}$. In terms of new eigen vectors, we have the diagonalized H^{fluc} :

$$H^{fluc} = \sum_n \omega_n a_n^\dagger a_n + \frac{1}{2} \left[\sum_n \omega_n - B_{n,n} \right] \quad (3.9)$$

Therefore, the correlation energy at zero temperature is:

$$E^{cor} = \frac{1}{2} \sum_n \omega_n - B_{n,n} \quad (3.10)$$

3.3 Response Functions

Besides the correlation energy, we can also compute response functions once the change in density matrix $\delta\langle\bar{\rho}_q\rangle$ is known. In this section we derive the numerical formalism to calculate the response functions within the TDHFT.

The 'generalized' response function can be defined as:

$$\chi^{\hat{O}, \hat{K}}(\vec{q}, \omega) = i \int dt e^{i\omega t} \theta(t) \langle [\hat{O}_{\vec{q}}(t), \hat{K}_{-\vec{q}}(0)] \rangle_{MF}. \quad (3.11)$$

The physical meaning of the response function is the change in the expectation value of observable $\hat{O}$ in the ground state of H^{MF} with the small external potential $\hat{K}$ applied to the system. If both $\hat{O}$ and $\hat{K}$ are single-particle potentials, we can then define the columns $\bar{C}_{\hat{O}}$ and $\bar{C}_{\hat{K}}$ such that

$$\hat{O} = (\bar{C}_{\hat{O}})^\dagger \bar{\rho}(\vec{q}, \omega), \quad \hat{K} = (\bar{C}_{\hat{K}})^\dagger \bar{\rho}(\vec{q}, \omega). \quad (3.12)$$

Consequently Eq. 3.11 becomes

$$\chi^{\hat{O},\hat{K}}(\vec{q},\omega) = (\bar{C}_{\hat{O}})^\dagger (\omega\hat{I} - \hat{M})^{-1} \hat{\eta} \bar{C}_{\hat{K}}, \quad (3.13)$$

where $\hat{M}$ and $\hat{\eta}$ are the same matrices given in Chapter 3.2.

Since $(\omega\hat{I} - \hat{M})$ and $\hat{M}$ have the same eigenvectors, we could introduce $\hat{T}$ being a matrix such that:

$$\left(\hat{T}^{-1}\hat{M}\hat{T}\right)_{ij} = \omega_i \delta_{ij} \quad (3.14)$$

where $\{\omega_i\}$ is the set of collective mode energies including both positive and negative ones. Then we have:

$$\left(\hat{T}^{-1}(\omega\hat{I} - \hat{M})\hat{T}\right)_{ij} = (\omega - \omega_i) \delta_{ij} \quad (3.15)$$

It leads to:

$$\left(\hat{T}^{-1}(\omega\hat{I} - \hat{M})^{-1}\hat{T}\right)_{ij} = \frac{\delta_{ij}}{(\omega - \omega_i)} \quad (3.16)$$

So finally it is straightforward to express the response function as:

$$\begin{aligned} \chi^{\hat{O},\hat{K}}(\vec{q},\omega) &= (\bar{C}_{\hat{O}})^\dagger(\vec{q})(\omega\hat{I} - \hat{M})^{-1} \hat{\eta} \bar{C}_{\hat{K}}(\vec{q}) \\ &= (\bar{C}_{\hat{O}})^\dagger(\vec{q})\hat{T}\hat{T}^{-1}(\omega\hat{I} - \hat{M})^{-1}\hat{T}\hat{T}^{-1} \hat{\eta} \bar{C}_{\hat{K}}(\vec{q}) \\ &= \sum_i \frac{W^i(\vec{q})}{\omega - \omega_i} \\ W^i(\vec{q}) &= \left(\sum_\alpha ((\bar{C}_{\hat{O}})^\dagger(\vec{q}))_\alpha \hat{T}_{\alpha,i} \right) \left(\sum_\beta \hat{T}_{i\beta}^{-1} \hat{\eta}_{\beta\beta} (\bar{C}_{\hat{K}}(\vec{q}))_\beta \right) \end{aligned} \quad (3.17)$$

With this formalism, most response functions can be obtained as long as the diagonalization of $\hat{M}$ can be done.

3.4 Relationship to the generalized random phase approximation

The equivalence relationship between the TDMFT and the GRPA can be proved by comparing the response functions obtained from both approaches. The proof described in this section closely follows the one given by Joglekar and MacDonald[12]

Let's start with the diagrammatic approach. Assume that $\{\alpha_n\}$ are the eigenstates of H^{MF} and n includes all the label indices such as band index, momentum, spin, etc. Then the 'non-interacting' quasiparticle response functions can be expressed as:

$$\begin{aligned}\chi_0^{ijkl}(i\omega_n) &= \frac{1}{\beta} \int_0^\beta d\tau e^{i\omega_n \tau} \langle T_\tau \alpha_i^\dagger(\tau) \alpha_j(\tau) \alpha_k^\dagger(0) \alpha_l(0) \rangle \\ &= \left[\frac{n_F(E_k - \mu) - n_F(E_i - \mu)}{i\omega_n - \epsilon_{ki}^{ph}} \right] \delta_{il} \delta_{jk} \\ &\equiv D^{ik} \delta_{il} \delta_{jk}\end{aligned}\tag{3.18}$$

where $\omega_n = 2\pi n/\beta$ is the bosonic Matsubara frequency, $\epsilon_{ki}^{ph} = E_k - E_i$ is the quasiparticle particle-hole energy, and $\{E_n\}$ are the quasiparticle energies of H^{MF} . Summing the ladder and bubble diagrams plotted in the Fig. 3.1 produces the GRPA response function. The diagrams on the top of the Fig. 3.1 represents the response function χ_{ladder} summing over all ladder diagrams connected by exchange interaction V^{ex} , and it gives:

$$\chi_{ladder}(i\omega_n) = D(i\omega_n) [1 - V^{ex} D(i\omega_n)]^{-1}\tag{3.19}$$

Note that in this notation, all the response functions and the interactions are expressed in the matrix form whose basis is the quasiparticle density matrix ρ_{ab} the same as that used in previous sections.

The GRPA response function can then be obtained by summing the bubble

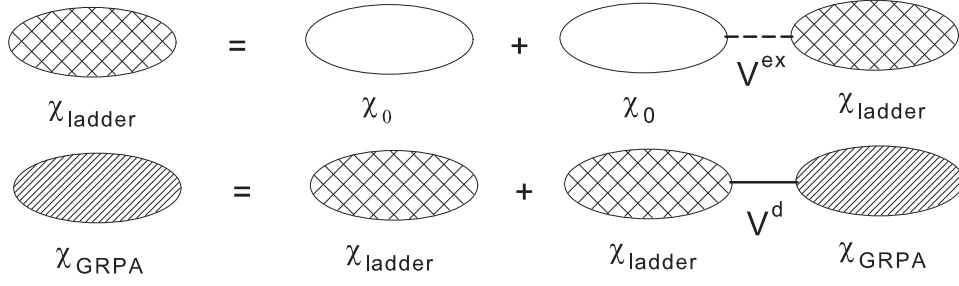


Figure 3.1: Diagrammatic representation of the GRPA response function. V^{ex} is the exchange interaction while V^{d} is the direct interaction. This figure is a reproduction of Fig. 1 given in Phys. Rev. B **64**, 155315 (2001).

diagrams with the ladder diagrams included. To do this summation, we can simply replace the χ_0 by χ_{ladder} and the interaction line by the direct interaction V^{d} , which are described by the diagrams on the bottom of the Fig. 3.1. Consequently, the GRPA response function becomes:

$$\chi_{\text{GRPA}}(i\omega_n) = \chi_{\text{ladder}}(i\omega_n) \left[1 + V^{\text{d}} \chi_{\text{ladder}}(i\omega_n) \right]^{-1} \quad (3.20)$$

After doing some algebra, we finally have:

$$\chi_{\text{GRPA}}(i\omega_n) = D(i\omega_n) \left[1 + D(i\omega_n)(V^{\text{d}} - V^{\text{ex}}) \right]^{-1} \quad (3.21)$$

The excitation energies are identified with the poles of $\chi_{\text{GRPA}}(i\omega_n)$, which are the zeros of $[1 + D(i\omega_n)(V^{\text{d}} - V^{\text{ex}})]$ and $D^{-1}(i\omega_n)$. While the zeros of $D^{-1}(i\omega_n)$ are the quasiparticle particle-hole energies constituting the particle-hole continuum, those of $[1 + D(i\omega_n)(V^{\text{d}} - V^{\text{ex}})]$ are the collective excitations which are responsible for the peaks observed in various experiments. The zero-temperature response functions can be obtained by the analytic continuation $i\omega_n \rightarrow \omega + i\delta$, and then after carefully evaluating the Eq. 3.3, it can be easily found that $\omega\hat{I} - \hat{M}$ in the TDMFT can be

expressed as:

$$\omega \hat{I} - \hat{M} = \left[(\omega - \epsilon^{ph}) \hat{I} \right] \left[1 + D(\omega)(V^d - V^{ex}) \right]. \quad (3.22)$$

Therefore the eigenvalues of the matrix $\hat{M}$ are just the zeros of $[1 + D(i\omega_n)(V^d - V^{ex})]$ and $D^{-1}(i\omega_n)$, and consequently we can conclude that the TDMFT is identical to the GRPA calculation with both bubble and ladders diagrams summed.

Technically the TDMFT can be considered as the matrix representation of the GRPA, and there are several advantages of using the TDMFT. Since in principle we can obtain the matrix $\hat{M}$ for any interactions, we can perform the GRPA calculations accurately by simply doing the diagonalization of $\hat{M}$. Therefore the TDMFT is very powerful to treat the systems with complicated interactions. Besides, the TDMFT can be done with respect to any mean-field states, and this flexibility allows us to study the quantum fluctuations around any ordered states in which we are interested. In Chapters 8 and 9, we will use the TDMFT to investigate the collective modes observed in the inelastic neutron scattering measurements, and we will see that performing the GRPA calculations accurately provides new understanding of the High- T_c superconductors.

Chapter 4

Recent Progress of Transition Metal Oxide Heterostructures

4.1 LaTiO₃/SrTiO₃ Superlattice

Partly motivated by the rich physics that the semiconductor heterostructures have brought to us, recently intensive attentions have been paid to the physics of transition metal oxide heterostructures from both theoretical and experimental points of view[13]. In the last decade, remarkable improvements in the techniques of growing thin films and heterostructures with the transition metal oxides have opened doors to several new fields of study. For example, one important question for theory is how the strong electron-electron correlations influence the electronic states in systems with a reduced space coordination, such as thin films, surfaces, heterojunctions, etc.

Among these developments, the superlattice of LaTiO₃/SrTiO₃ first fabricated by Ohtomo *et. al.*[14] is an important milestone in this field. Both materials are insulators, despite LaTiO₃ is a Mott insulator while SrTiO₃ is a band insulator. With an *atomically precise* technique of the layer by layer growth, Ohtomo *et. al.* demonstrated that the superlattice with n layers of LaTiO₃ and m layers of SrTiO₃

exhibits a significant metallic behavior near the interface which can be engineered by the number of LaTiO_3 layers n . This finding shed a light on new possibilities of creating novel two-dimensional electronic (2DES) systems other than the one found in the semiconductor heterojunctions.

It was then quickly realized by Okamoto and Millis[15] that this new finding can be understood as an *electronic surface reconstruction*, reminiscent of the purely electronic[16] reconstructions imposed by space-charge physics on systems with polar surface terminations[17]. A simple way to understand this is given as following. Let's first consider the number of electrons on the d -bands in both bulk materials; LaTiO_3 has average number of d electrons $n_d = 1$ (denoted as d^1 material) while SrTiO_3 has $n_d = 0$ (denoted as d^0 material). With these configurations, it would been thought naively that the electrons would spread out on the d bands in both materials after the superlattice was made. This, in fact, does not happen because the LaO layers provide the additional positive background charges while the SrO layers are mostly neutral layers. Consequently, the electrons tend to be trapped in the LaTiO_3 materials, resulting a profile of charge density being almost 1 deep inside the LaTiO_3 and almost 0 in the SrTiO_3 . If the quality the interface is good, the charge density must change smoothly. Therefore it will be expected that the d -bands on the layers near the interface are only *partially occupied* corresponding to a crossover from d^1 to d^0 , and these partially filled d -bands are the origin of the metallic behaviors observed by Ohtomo *et. al.*

All the above mentioned physics can be demonstrated by a simple toy model containing Hubbard model plus the long ranged Coulomb interaction, although first principle calculations showed[18] that some additional details like orbital degeneracy and lattice distortion may have some influences on the physical properties of the interface states. Nevertheless, this series of study suggests that the simple toy model can correctly capture the trend of the charge distribution in the transition metal

oxide heterostructures, and we will follow this spirit to investigate more possibilities of the heterostructures.

4.2 $\text{LaAlO}_3/\text{SrTiO}_3$ Superlattice

The apparent electronic interface reconstruction (EIR) discovered[19, 20, 21] at the heterojunction between the band insulators LaAlO_3 and SrTiO_3 is unique in complex oxide interface studies and does not have an analog in semiconductor heterojunction systems. The reconstruction is forced by the polarity difference between LaAlO_3 and SrTiO_3 . Polarity discontinuities are normally weaker at semiconductor heterojunctions and, when present, the electric fields to which they give rise are usually screened by relaxation of atoms near the interface[31]. In complex transition metal oxides, however, it was discovered[16, 20] that the polarity discontinuity field can be screened electronically by transferring electrons between surface and interface layers, changing the valence of transition metal ions in these layers. Electrons dodge the *polar catastrophe*[20] without essential atomic assistance, resulting in an interfacial reconstruction mostly from the electronic degrees of freedom.

However, there is still some uncertainty about the role of oxygen vacancies in the measured conductivity. For example, it has been proposed that the oxygen vacancies are responsible for the insulating behavior observed at the *p*-type interface[22] and might be the source of the carrier density at the *n*-type interface[23, 24]. Besides, the groundstate of the interfacial system at the low temperature has also attracted many attentions. Transport measurements[25] indicated the possible occurrence of superconductivity at the interface with the superconducting transition temperature of ≈ 200 millikelvin, though there are still debates on whether or not this superconductivity originates from the two-dimensional electron gas at the interface. Another interesting issue is whether this interface has magnetic orderings. A recent first principle calculation[26] showed that the Ti^{+3} atoms at the

interface have a non-zero magnetic moment, suggesting the interface is magnetic. It is noted that there is still no experimental support of the existence of magnetism at the $\text{LaAlO}_3/\text{SrTiO}_3$ interface partly due to lacking of appropriate probes for the interface magnetism.

Despite difficulties in reducing the oxygen vacancy and finding reliable methods to probe the properties of interface system, the progress in the layer-by-layer growth sheds a light on engineering of the transition metal oxides. For example, it has been shown[21] that such an interface can be tuned between metallic and insulating states by relatively modest electric fields, suggesting the possibility of novel electronic devices. In the following two chapters, we will demonstrate the our proposals for creating novel two-dimensional systems from transition metal oxide heterostructures.

Chapter 5

Modulation Doping near Mott Insulator Heterojunctions

*Parts of this chapter have been published on Physical Review B **74**, 075106 (2006).*

5.1 Introduction

We consider in this chapter the modulation doping near an interface between two different Mott insulators, a MIMI heterojunction. This idea is mainly motivated by making an analog of the semiconductor heterostructures, and therefore we aim at seeking for possibilities of finding new types of two-dimensional systems with the transition metal oxides.

The model system that we have in mind is sketched in Fig. [5.1]. Most classes of transition metal compounds are either ternary or quaternary, with additional *spectator* atoms that donate electrons to hybridized transition metal-oxygen orbitals near the Fermi energy. These systems can be doped by replacing the spectator atoms by atoms with a different valence. Modulation doping of a MIMI heterojunction is achieved by doping the larger gap material at a spectator atom location

that is removed from the heterojunction. The extra electrons then enter the upper Hubbard band of the lower gap Mott insulator, creating a two-dimensional doped Mott insulator that is trapped near the heterojunction by space charge electric fields. The spatial separation between dopants and the carriers that reside in the upper or lower Hubbard bands should give rise to strongly correlated metals that are relatively free from disorder due to chemical doping, and are two-dimensional in character. These systems are illustrated schematically in Fig.[5.2]. We study these systems using both HFT and DMFT as in previous studies, and also demonstrate that a generalized Thomas-Fermi theory (TFT) can be employed to capture key qualitative physics of strongly-correlated heterostructures in a very direct way. TFT yields accurate results for charge-density profiles and for the critical doping δ_c associated with the onset of parallel conduction. We conclude that both the doping fraction δ_D and the distance between the heterojunction and the doping layer play a role in the competition that occurs between different magnetically ordered states.

In the next section we describe the single-band Hubbard model used in this study to address modulation-doped Mott-insulator heterojunction properties. In Section III we discuss results obtained for the electronic properties of this model using HFT, TFT, and DMFT. In section IV we discuss materials which might be suitable for modulation doping of Mott insulator heterojunctions. Finally in Section V we summarize our findings and speculate on the potential of modulation doped Mott insulators.

5.2 Model Hamiltonian

The model system we focus on for the modulation doping is sketched in Fig. 5.1. The heterostructure is composed of two different $3d^1$ perovskites, AMO_3 and $A'M'O_3$, where both A and A' are group III elements and M and M' are group IV elements which have nominal $3d^1$ electronic structure in this structure. Since the total number

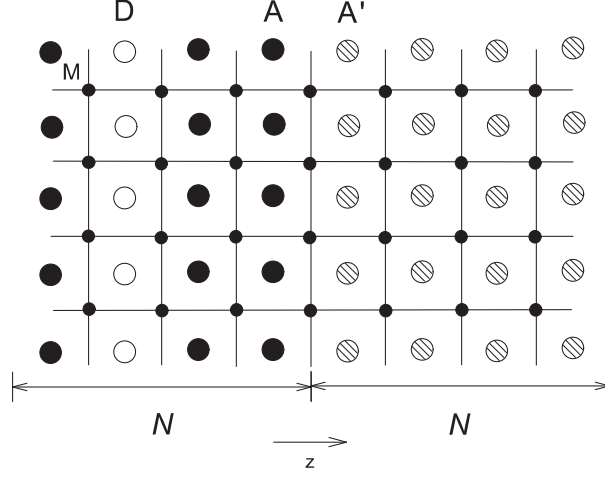


Figure 5.1: Schematic representation of the heterostructure studied for the modulation doping. We choose the $x - y$ plane as the interface plane and z as the layer-by-layer growth direction. The symbol D (white circle) denotes a dopant layer containing a fraction δ_D of dopant atoms with a valence larger than or smaller than the A (black circle) and A' (shaded circle) atoms. Our calculations are performed for a finite thickness film with N layers of transition metal M atoms (black dots) on each side of the heterostructure. In the one-band Hubbard model electrons hop between M sites only and are influenced by the space-charge field caused by the spatial separation between the dopant atoms and carriers in the upper Hubbard band.

of electrons per unit cell is odd, compounds of this type must be Mott-type when they are insulators, unless translational symmetries are broken. Modulation doping is achieved by replacing some of the A atoms in the larger gap insulator by elements with a different valence. We assume electron doping for convenience, although the hole doping case is completely equivalent, apart from (important!) materials specific details which we don't attempt to model in this qualitative study. If we assume that a fraction δ_D of the A atoms in a single layer of the larger gap material is replaced by donor atoms then the sum over all M atom layers of the upper Hubbard band fractional occupancy must be δ_D in order to accommodate the extra electrons. When modulation doping is successful the added electrons reside in the lower gap material, placing them some distance from the ionized donor atoms and reducing the importance of the chemical disorder normally associated with doping.

For this qualitative study we use a single-band Hubbard model that ignores any orbital degeneracies that might be present. Modulation-doping depends critically on the long-range Coulomb interactions so these must be realistically represented in the model. Our model Hamiltonian includes hopping, short-range repulsion, and long-range Coulomb interaction terms $H = H_t + H_U + H_{Coul}$, where

$$\begin{aligned}
H_t &= -t \sum_{\langle i,j \rangle, \sigma} (d_{i\sigma}^\dagger d_{j\sigma} + h.c.), \\
H_U &= \sum_i U(z_i) \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \\
H_{Coul} &= \frac{1}{2} \sum_{i \neq j, \sigma, \sigma'} \frac{e^2 \hat{n}_{i\sigma} \hat{n}_{j\sigma'}}{\epsilon |\vec{R}_i - \vec{R}_j|} - \sum_{i,j,\sigma,I} \frac{Z_I e^2 \hat{n}_{i\sigma}}{\epsilon |\vec{R}_i - \vec{R}_j^I|},
\end{aligned} \tag{5.1}$$

$Z_I = 1$ for $I = A, A'$ and $(1 + \delta_D)$ for $I = D$. Note that we do not account for randomness in the dopant layer. The index i denotes the position of a transition metal ion (M) so that $\vec{R}_i = a(n_i, m_i, z_i)$ and $\vec{R}_i^A = a(n_i + 1/2, m_i + 1/2, z_i + 1/2)$ respectively in a perovskite unit cell with lattice constant a . For the sake of definiteness, we ignore the possibility of a d-band offset between the two materials,

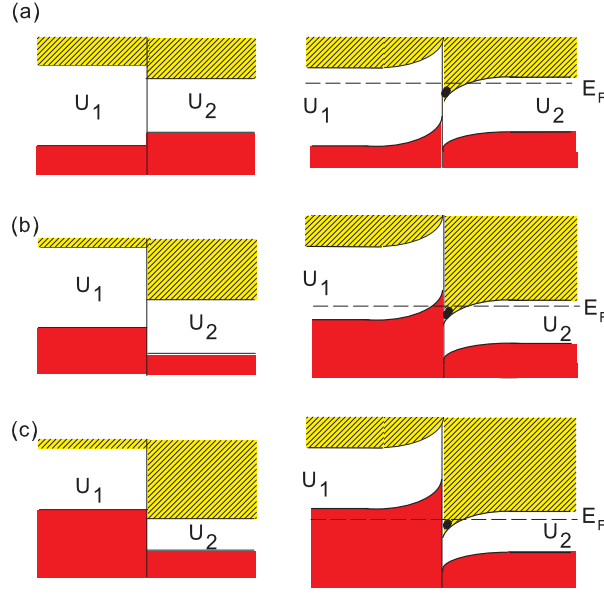


Figure 5.2: Modulation doping properties of different Mott-insulator Mott-insulator (MIMI) heterojunction classes. The figure illustrates the local electronic spectral function near the interface both before (left) and after (right) modulation doping. The upper Hubbard band spectral weight (yellow) is plotted with shading while the lower Hubbard band (red) is solid. Mott-Hubbard band bending near the interface is due to the electrostatic potential induced by the spatial separation of dopants and carriers. The discontinuity in bands at the interface is determined by atomic scale physics particular to an individual MIMI heterojunction. In analogy with semiconductor heterostructure terminology we define the following classes of MIMI heterojunctions: (a) Type I: The Hubbard gap of the smaller gap material is completely inside that of larger gap material. Both electrons and holes can then be trapped near the heterojunction, depending on doping. (b) Type II: The top of the lower Hubbard band or the bottom of the upper Hubbard band of the larger-gap material lies inside the Hubbard gap of the smaller-gap material. Only one sign of carrier can be trapped near the heterojunction in this case. (c) Type III: The top of the lower Hubbard band or the bottom of the upper Hubbard band of the larger-gap material lies in the opposite band of the smaller-gap material. In this case charge transfer across the heterojunction occurs even in the absence of doping. Experimental determination of how a particular MIMI heterojunction system fits in this classification scheme is a key element of its characterization. Here we study only Type I MIMI heterojunctions.

although these will certainly occur in practice. Given this assumption, a Type-I MIMI heterojunction will occur whenever the Hubbard U parameter is large enough to produce insulating behavior in both materials. We consider a system with a finite number $2N$ of layers labeled sequentially from left to right and define $U(z_i) = U_1$ for $z_i = 1$ to N and U_2 for $z_i = N$ to $2N$ with $U_1 > U_2$ so that the larger gap material is on the left. We treat the Coulomb part of the interactions in a mean-field Hartree approximation. Since Coulomb potentials in the absence of doping are implicitly included in the model band Hamiltonian, in evaluating this potential we include only the extra charges in the dopant layer and charges due to occupancy of lower or upper Hubbard bands. To be specific, the reference background has charge per atom equal to -1 for each M site and $+1$ for each A , A' , and D site. As a result, the mean-field long-ranged Coulomb interaction is:

$$H_{Coul}^{eff} = \sum_{i \neq j, \sigma} \frac{e^2(\rho_j - 1)\hat{n}_{i\sigma}}{\epsilon|\vec{R}_i - \vec{R}_j|} - \sum_{i, j, \sigma} \frac{\delta_D e^2 \hat{n}_{i\sigma}}{\epsilon|\vec{R}_i - \vec{R}_j^D|} \quad (5.2)$$

where $\rho_j = \sum_{\sigma} \langle \hat{n}_{j\sigma} \rangle$ is the electron density on site j .

5.3 Hartree-Fock theory

Following the formalism of HFT, the strong on-site Coulomb interactions is treated by replacing

$$\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \rightarrow \sum_{\sigma} \langle \hat{n}_{i,-\sigma} \rangle \hat{n}_{i\sigma}. \quad (5.3)$$

As noted[15] previously there are typically a number of self-consistent solutions of the HF equations, corresponding to a number of local minima of the Hartree-Fock energy functional. The various minima usually are distinguished by different types of magnetic order. Our philosophy in examining several different solutions without strong emphasis on their relative HF energies is that different types of order will

occur near different interfaces but neither the single-band Hubbard model nor any of the electronic structure approximations we consider (or indeed any known electronic structure approximation) is sufficiently reliable to confidently select between them. Indeed phase transitions between Mott insulator states with magnetic order and paramagnetic metallic phases, corresponding to magnetic and non-magnetic extrema of the Hartree-Fock energy functional, are often first order. (We will however make some conclusions of a more qualitative nature concerning trends and tendencies related to modulation doping.) As explained more fully below, we find that the HFT electron density distribution near a MIMI heterostructure is sensitive mainly to the relative orientations of electron spins on neighbouring metal sites on adjacent layers. Consequently, we present results only for usual bipartite antiferromagnetic (AFM) and ferromagnetic (FM) states, which in this respect cover the two possibilities. These two ordered states are metastable in both undoped and modulation doped regimes for the range of parameters we have studied.

The results of our HFT calculations are summarized in Fig. 5.3. We have chosen typical parameters for a one-band Hubbard model of perovskite transition metal oxides, taking $U_1/t = 24$, $U_2/t = 15$, and $U_c = e^2/\epsilon at = 0.8$. [15, 27] We can see from Fig. 5.3 that the modulation doping effect occurs for both AFM and FM states, although the details of the electron density distributions are quite different in the two cases. Short-range correlations therefore appear to play a relatively strong role in determining the charge distribution near MIMI heterostructures, in contrast to the MIBI heterojunction case in which they play [15] a relatively minor role. The upper Hubbard band electrons are noticeably more confined to the interface in the AFM state case and spread further into the smaller- U layer in the FM state case. This difference in density-distribution follows from a corresponding difference in the compromise between band-energy minimization and interaction energy minimization in the two-cases. The ferromagnetic state which has all spins parallel maximizes the

hopping amplitudes between sites, doing a better job of minimizing band energy at a cost in interaction energy. The bandwidth of the mean-field quasiparticle states is $\sim t$ for FM states and $\sim t^2/U$ for AFM states. Increased doping should favor FM states over AFM states, at least within HF theory. From a real-space point of view, doping frustrates the staggered moment order of the AFM state more strongly than it frustrates the FM order because of the nearest-neighbor hopping term H_t . In other words, doping favors the FM state over the AFM state.

The doped electrons have a strong tendency to accumulate nearly completely in one layer in the AFM state case. Larger setback distances for the dopant layer should result in larger space-charge fields at the heterojunction and less opportunity for electrons to spread out away from the interface, robbing the ferromagnetic state of the extra stability that it gains from the third dimension. We expect therefore that for a given doping level δ_D , antiferromagnetism will be favored by a larger setback distance for the dopants. A larger setback distance also favors the development of parallel conduction channel. These trends can be seen in the ground-state phase diagram plotted in Fig. 5.4. In summary, modulation doping in MIMI heterostructures may make it possible not only to create weakly-disordered low-dimensional strongly correlated electron systems, but also to engineer the compromises that occur in these systems between different types of magnetic order.

We note in Fig. 5.3 that for the FM state, a parallel conduction channel starts to appear adjacent to the doping layer at $\delta_D = 0.375$. For the parameters we have chosen modulation doping successfully places the carriers in a more remote layer up to this doping level.

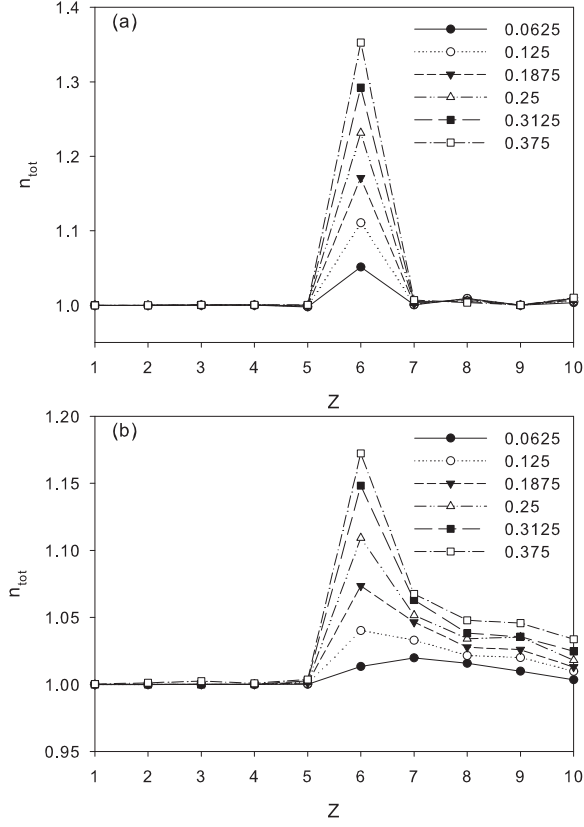


Figure 5.3: Electron density distributions from HFT for (a) AFM and (b) FM states as a function of δ_D . The parameters used are $U_1/t = 24$, $U_2/t = 15$, $U_c = 0.8$, and $N = 5$. z is the layer index for M site so that $U(z) = U_1$ for $z = 1 - 5$ and U_2 for $z = 6 - 10$. The dopant layer is at $z_D = 3.5$.

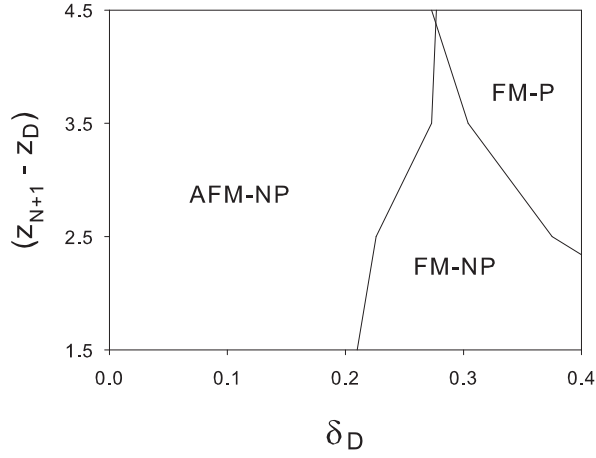


Figure 5.4: Ground state ($T = 0$) HFT phase diagram *vs.* doping concentration δ_D and setback distance $(z_{N+1} - z_D)$. AFM-NP denotes the antiferromagnetic state without a parallel conduction channel, and FM-NP (FM-P) denotes the ferromagnetic state without (with) a parallel conduction channel. Larger setback distances favor antiferromagnetism over ferromagnetism and strengthen the tendency toward development a of parallel conduction channel.

5.4 Thomas-Fermi theory

The HFT results can be understood using a Hubbard-model version of Thomas-Fermi theory. The TF equation for this system are:

$$\mu(\rho(z)) + v_H(z) = \text{const} \quad (5.4)$$

where $\mu(\rho)$ is the chemical potential at density ρ without long-ranged Coulomb interaction and $v_H(z)$ is the electrostatic potential for z th layer obtained from the charge density by solving the Poisson equation. In principle, $\mu(\rho)$ should be obtained from the exact solution of the three-dimensional Hubbard model. This input is unfortunately still unavailable. Instead, we can use HFT to obtain $\mu(\rho)$. In this way we have separate versions of the TF equations for AFM, FM, and PM states. As for $v_H(z)$, in the continuum limit each layer can be approximated by a 2-d uniformly-charged plane so that we have:

$$\frac{v_H(z)}{2\pi U_c} = \delta_D |z - z_D| - \sum_{z' \neq z} (\rho(z') - 1) |z - z'| \quad (5.5)$$

where z_D is the layer index for of the dopant layer and z' is summed over all electronic layers. Fig. 5.5 shows results calculated using this TFT for the same parameters as used in Fig. 5.3. The total electron density distributions are almost identical to those obtained from the full microscopic HFT. We do note that the parallel conduction channel in the FM state appears at lower doping in TF theory than in the microscopic theory.

The local-density approximation for correlations implicit in the Thomas-Fermi theory is obviously least reliable in judging the relative chemical potentials for adding carriers to spatially separate layers. The discrepancy also occurs partly because the long-ranged Coulomb interaction was evaluated using a three-dimensional

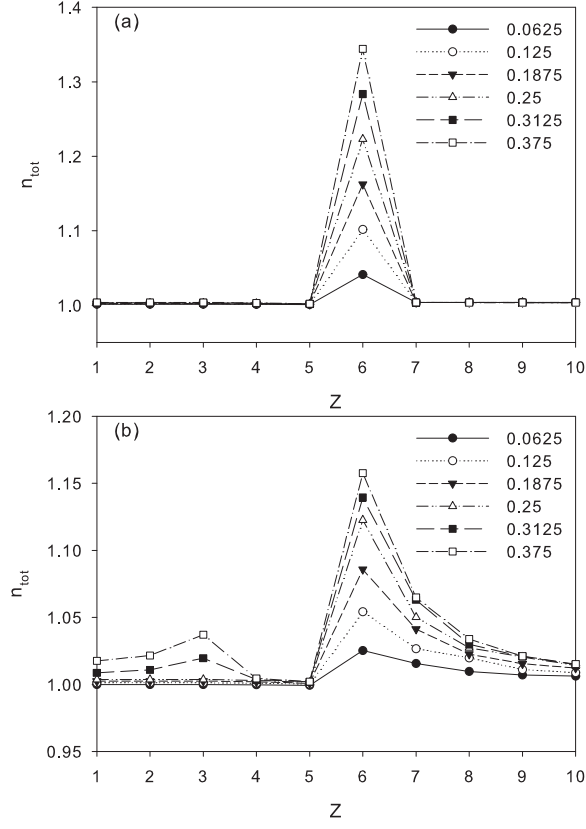


Figure 5.5: Total electron density distributions from TF theory for (a) AFM and (b) FM states with the same parameters as used in Fig 5.3. The results are close to those in Fig. 5.3, except for differences in the critical doping δ_c at which modulation doping starts to fail.

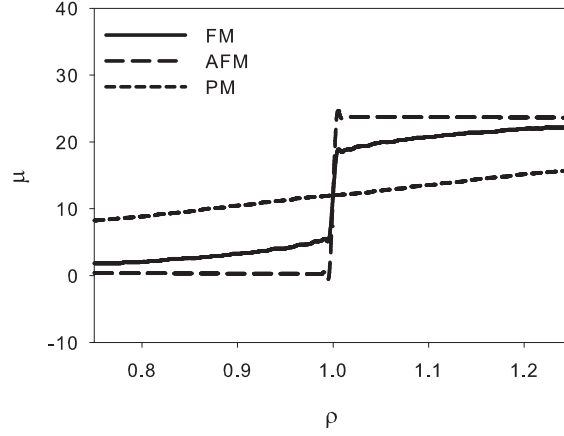


Figure 5.6: Chemical potential μ versus electron density ρ for AFM, FM and PM HFT states of the one band Hubbard model with $U/t = 24$. The jumps at $\rho = 1$ for AFM and FM states signal the opening of charge gap. The exact chemical potential is likely intermediate between the AFM and FM HFT values.

lattice version in the microscopic HFT whereas a continuum approximation for the layers was used in the TFT calculations. We expect that the TFT model is too simplified to determine the critical doping for parallel conduction δ_c accurately for any particular heterojunction, but it may be used to analyze trends.

The most important consequence of strong local interactions in the Hubbard model is the emergence of a jump in the chemical potential when the electron density per site crosses from less than one to more than one. As illustrated in Fig. 5.6, the opening of the Hubbard gap is accompanied by slower dependence of the chemical potential on density just above and just below $\rho(z) = 1$, *i.e.* by an increase in the thermodynamic density of states within the Hubbard bands. To capture these features we approximate the chemical potential in the upper Hubbard band near $\rho(z) = 1$, by $\mu(\rho(z)) \sim E_c(U(z)) + (\rho(z) - 1)/\mathcal{D}(U(z))$, where $E_c(U)$ is the bottom of the upper Hubbard band, and $\mathcal{D}(U)$ is the thermodynamic density of states averaged over the energy range of interest near the bottom of the band. This notation is

chosen to emphasize similarities to semiconductor heterojunction physics. Using this result in each layer we find that

$$\delta_c \sim \frac{E_c(U_1) - E_c(U_2)}{4\pi U_c(z_{N+1} - z_D)} + \mathcal{O}\left[\left(\frac{1}{\mathcal{D}(U_{1,2})}\right)\right] \quad (5.6)$$

where z_{N+1} is the index of the first metal layer on the small U side of the heterojunction. This simple and approximate expression emphasizes that δ_c increases with $E_c(U_1) - E_c(U_2)$, decreases with U_c and, as in the semiconductor case, decreases with the donor layer set-back distance. From HFT we estimate that $E_c(U) \approx U$ for AFM states while $E_c(U) \approx U - 6t$ for FM states. In both cases $E_c(U_1) - E_c(U_2)$ is approximately $U_1 - U_2$. As illustrated in Fig. 5.6, $\mathcal{D}$ tends to be larger for AFM states than for FM states. The precise form of the thermodynamic density of states near the band edge in any particular approximation can only be determined numerically. This simple expression does not fully capture the difference between AFM and FM states, but it does capture some simple but important properties. More effective modulation doping will occur materials combinations with larger U difference, and smaller U_c (*i.e.* larger dielectric constant ϵ) values. Additionally, because of stronger tendency to confine electrons in one layer in AFM state, δ_c is larger in AFM than in FM states in general. These features are confirmed by our numerical calculations.

TFT is successful because the dominating energy scales are the electrostatic energy and the correlation energy arising from local correlations. The ground state electron density distribution is a result of competition between these two energy scales, which is accurately captured by the TF approximation.

5.5 Dynamical mean-field theory

As discussed in Chapter 2, HFT provides a particularly poor description of paramagnetic (PM) strongly correlated states because it is unable to capture correlated

quantum fluctuations. In the limit of large U it is clear that the thermodynamic properties ($\mu(\rho)$ for example) of a paramagnetic state are much more similar to those of ordered states than suggested by Hartree-Fock theory. To obtain a better description of paramagnetic modulation-doped electron systems, we appeal to the two-site dynamical mean-field-theory[10] discussed in Chapter 2. Following the general framework of DMFT and the notation used by Okamoto *et al.*[15], the electron Green's function for each in-plane momentum $\vec{k}_{\parallel}$ can be written as:

$$G(z, z', \vec{k}_{\parallel}; \omega) = \left[\omega + \mu - H_t - H_{Coul}^{eff} - \Sigma(z, z', \omega) \right]^{-1} \quad (5.7)$$

where H_{Coul}^{eff} is given in Eq. 5.2. The self energy $\Sigma(z, z', \omega) = \delta_{z,z'} \Sigma(z, \omega)$ is obtained by solving a two-site quantum impurity model for each layer and satisfying a set of self-consistency equations[10, 15]. We note that the two-site method predicts that the critical value of U for the metal-insulator transition of a 3-d single band Hubbard model[28] to be $U^c \approx 14.7$. The U_1 and U_2 values we have chosen are both larger than U^c so that both perovskites are Mott insulators in the two-site method. Fig. 5.7 compares the results from DMFT and HFT for paramagnetic states. These results demonstrate that modulation doping is possible without magnetic order in DMFT. The failure of HFT in this respect is a well understood consequence of the importance of on-site correlation effects for MIMI heterostructure properties, and of the failure of HFT to capture these correlations.

In Fig. 5.8 we plot DMFT layer-dependent electronic spectral functions

$$A(z, \omega) = -(1/\pi) \int [d\vec{k}_{\parallel}/(2\pi)^2] \text{Im} G(z, z, \vec{k}_{\parallel}; \omega + i0^+). \quad (5.8)$$

Only the layer closest to the interface on the smaller- U side ($z = 6$ in the figure) develops finite spectral weight near the Fermi surface upon doping. The appearance of a peak in the spectral function near the Fermi energy in layers close to the interface

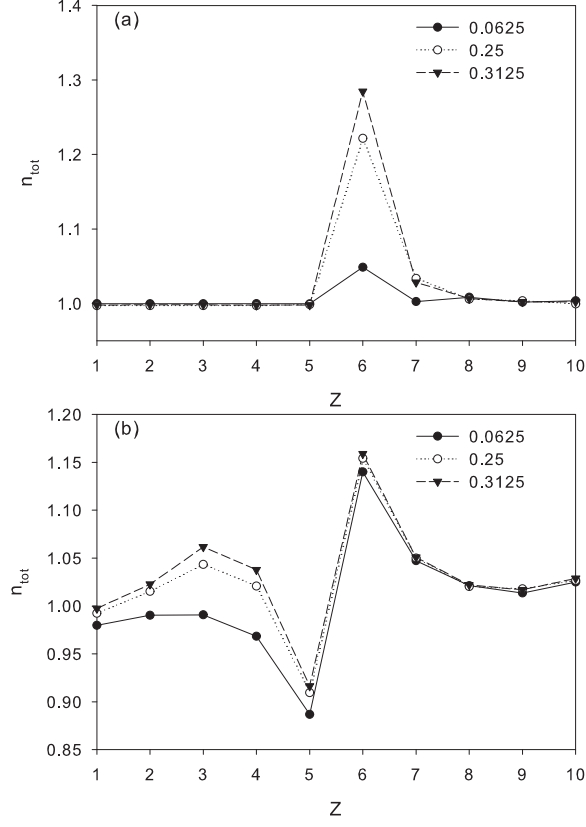


Figure 5.7: Total electron density distributions for the PM state calculated by (a) DMFT and (b) HFT. The DMFT results exhibit a modulation doping effect while those of HFT do not, implying that modulation doping near a MIMI heterojunction does not occur without on-site correlations. Note that Figure (b) can also be reproduced accurately by TF equation with the HFT $\mu(\rho)$ of the PM state.

is reminiscent of the findings of Okamoto *et al.*[15] for a MIBI heterojunction, who refer to this tendency as *electronic surface reconstruction*. The robustness of this phenomenon beyond the two-site method is not certain at present, nevertheless it is intriguing that it occurs in two quite different heterojunction systems. This finding has a natural interpretation in DMFT. In Eq. 5.7, $\mu - H_{Coul}^{eff}(z)$ acts like "layer-resolved chemical potential," which determines the total electron density in layer z . For each layer one must solve a separate quasi two-dimensional quantum impurity model whose solution shows insulating (metallic) behavior for electron density close to (away from) 1. The self-consistency equations ensure that all solutions are related. Consequently, DMFT generally predicts that a layers with electron density away from 1 (layer 6 in the present calculation) is metallic.

5.6 Discussions

All the results presented here suggest that it is possible to create a novel two-dimensional system using the modulation doping near the Mott-insulator heterojunctions. Because such a two-dimensional system inherits the feature of strongly correlation and its properties can be engineered by choosing appropriate value for the dopant density and the setback distances of the doping layers, this may be an ideal system to realize the doped Mott insulators. As for the possible material combinations that might exhibit the MIMI modulation doping, RMO_3 materials (R : Rare earth) appear to be an attractive possibility because of their relative simplicity. It has been shown that YMO_3 has stronger electronic correlation than $LaMO_3$ because of the smaller tolerance[29] factor f . Therefore $YMO_3/LaMO_3$ heterostructure appear to be a good candidate for realizing modulation doping. In particular $LaTiO_3$ and $YTiO_3$ are both Mott insulators with distorted perovskite structures ($GdFeO_3$ type) having gaps ≈ 0.2 eV and ≈ 1 eV respectively[30]. They might be used to realize a modulation doped heterostructure if $YTiO_3$ could be doped. We

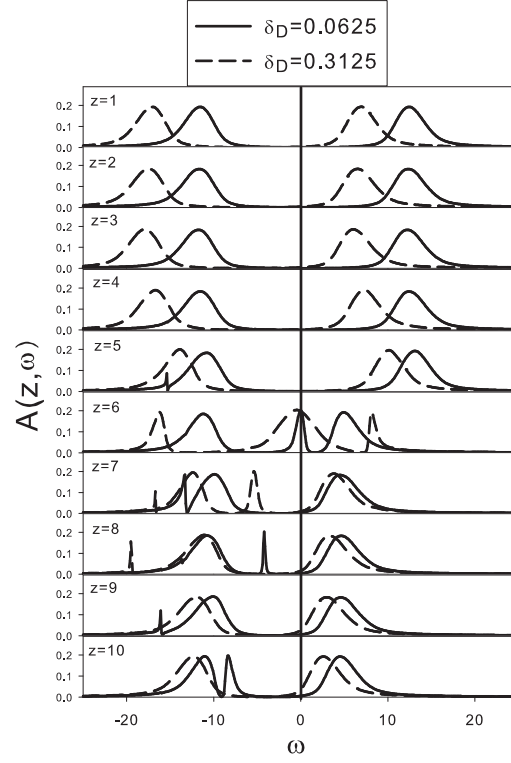


Figure 5.8: Local spectral functions for each layer calculated from DMFT for $\delta_D = 0.0625$ (solid line) and 0.3125 (dotted line). Only the layer closest to the interface on the smaller- U side ($z = 6$) becomes metallic upon doping.

emphasize that at present we do not know how the t_{2g} d-bands are aligned at a heterojunction between these two materials. Indeed, aside from the band-lineup issue, it is important to recognize that the simple model considered in this work is not sufficiently rich to capture all aspects of the interface physics that can be relevant to modulation doping and to magnetic order in the interface layer. For example orbital degeneracy plays a key role in the magnetic state of bulk YTiO_3 and in all likelihood would also play a role in determining the magnetic state of any two-dimensional metallic layer at the interface.

Although our one-band model is intended to qualitatively describe $3d^1$ systems with cubic perovskite structure, some of our results should be generalizable. As emphasized above, the modulation doping effect is a consequence of Coulomb space-charge fields and on-site correlations. We therefore do not expect that perfect affinity to the ideal perovskite structure to be of key importance. Other RMO_3 type Mott insulators with R =rare earth or alkaline earth and M =Mn,Cr might also be good candidates, although there will certainly be additional complications because of the larger d -valence that are not addressed at all in this work. Building up more realistic models for potential building block materials is an important challenge for theory.

Despite these additional complications of modeling the transition metal oxides, the simple toy model used in this chapter is still able to capture some important physics. Therefore it is interesting to think whether other types of MIMI heterostructures are possible based on this framework. In the next chapter we will study another MIMI heterostructure in which a similar two-dimensional system can also be created. This type of MIMI heterostructure echoes the $\text{LaAlO}_3/\text{SrTiO}_3$ in which the *polar catastrophe* makes the reconstructions of surface and interface states occur[19, 20, 21]. We will show that the similar physics can also be applied to the MIMI heterostructure. A wise combination of these different types of MIMI

heterostructures can help us explore more possibilities of novel two-dimensional systems.

Chapter 6

Electronic Interface Reconstruction at Polar-Nonpolar Heterojunctions

*Parts of this chapter have been published on Physical Review B **76**, 075339 (2007).*

6.1 Introduction

In this chapter we examine the electronic interface reconstruction (EIR) at a heterostructure between model polar and nonpolar Mott insulators, motivated by the $\text{LaAlO}_3/\text{SrTiO}_3$ superlattice described in Chapter 4. We will use the same theoretical approaches introduced in the study of the modulation doping effect presented in the last chapter, and we find that a minimum number of polar layers is required to induce an EIR because of strong local correlations, whereas the number of nonpolar layers does not play an essential role in determining the electron distribution.

6.2 Model Hamiltonian

Fig. 6.1 illustrates the model heterostructure we investigate in this chapter. We consider a thin film composed of N_p polar perovskite Mott insulator layers (AMO_3) and $N - N_p$ nonpolar perovskite Mott insulator layers ($A'M'O_3$), where A (A') is a group III (II) element with a valence of +3 (+2) in the $AO(A'O')$ layer. M (M') is a group IV (V) element which is a $3d^1$ Mott insulator because of strong local repulsion among the d-orbitals. In this study we disregard the interesting complications associated with orbital degeneracy and do not account directly for hybridization between the transition metal and oxygen ions. We therefore use a single band Hubbard model to describe the d valence electrons. Long-ranged Coulomb interactions are described realistically by accounting for charges at the oxygen sites and on the A , A' , and M , and M' ions. The resulting model Hamiltonian is:

$$\begin{aligned}
H &= H_d + H_U + H_{Coul} \\
H_d &= \sum_{i\sigma} \epsilon_d(z_i) d_{i\sigma}^\dagger d_{i\sigma} - \sum_{\langle i,j \rangle \sigma} t_{ij} (d_{i\sigma}^\dagger d_{j\sigma} + h.c.) \\
H_U &= \sum_i U(z_i) \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \\
H_{Coul} &= \frac{1}{2} \sum_{i \neq j, \sigma, \sigma'} \frac{e^2 \hat{n}_{i\sigma} \hat{n}_{j\sigma'}}{\epsilon |\vec{R}_i - \vec{R}_j|} \\
&\quad - \sum_{i, \sigma} \sum_{j(j_z \leq N_p)} \frac{Z^A e^2 \hat{n}_{i\sigma}}{\epsilon |\vec{R}_i - \vec{R}_j^A|} - \sum_{i, \sigma} \sum_{j(j_z > N_p)} \frac{e^2 \hat{n}_{i\sigma}}{\epsilon |\vec{R}_i - \vec{R}_j|}
\end{aligned} \tag{6.1}$$

where i labels a metal site and (grouping coplanar oxygen and A cation charges) $Z^A = 1$ in the present case. The d-orbital hopping term is expressed in Eq.(6.1) as a sum over links; most of our calculations have been performed for a model with nearest-neighbor hopping. Second nearest-neighbor hopping has little influence on our main results, but will impact the 2DSCES Fermi surfaces as discussed below. The sizes and alignments of the gaps in the two $3d^1$ Mott insulators are

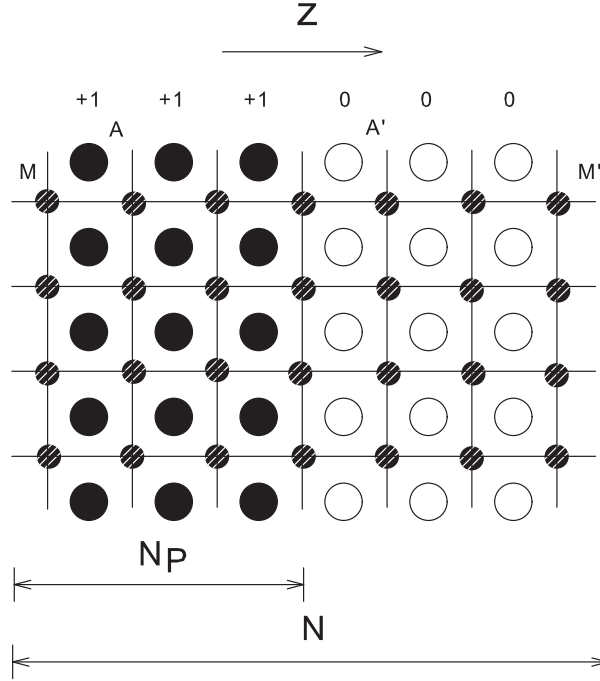


Figure 6.1: Schematic illustration of our model for a thin film containing a polar-nonpolar Mott insulator heterostructure. The model consists of N_p layers of a polar Mott insulator perovskite (AMO_3) and $N - N_p$ layers of a nonpolar Mott insulator perovskite ($A'M'O_3$). The $\hat{z}$ direction is chosen to be the layer-by-layer growth direction and the charge density is assumed to be uniform in each $x - y$ plane. The symbol A represents a group III element with nominal valence +3 in the AO layer while the symbol A' represents a group II element with nominal valence +2 in the $A'O$ plane. The AO layer therefore has a surface charge density of +1 per A atom while the $A'O$ layer is neutral. The symbols M and M' represent transition metal ions in group IV and V respectively. Both M and M' have $3d^1$ configuration before the electronic interface reconstruction (EIR).

fixed by the interaction and site energy parameters: $U(z_i) = U_P$ and $\epsilon_d(z_i) = \epsilon_{d1}$ for the polar layers and $U(z_i) = U_{NP}$ and $\epsilon_d(z_i) = \epsilon_{d2}$ for the nonpolar layers. In an ideal cubic perovskite unit cell with lattice constant a , $\vec{R}_i = a(n_i, m_i, z_i)$ and $\vec{R}_i^{A,A'} = a(n_i + 1/2, m_i + 1/2, z_i + 1/2)$ respectively. The third term in H_{Coul} accounts for a net effective charge per M' atom in the $M'O_2$ plane; this charge is the sum of the oxygen ion charges and the +5 charge of the M' ion when in a d^0 configuration. In this work we have neglected the uneven distribution of charge within each layer. In this calculation we for the most part assume that ϵ_d is constant, but emphasize that the difference between d-orbital energies on opposite sides of the heterojunction can be an important parameter. As in case of semiconductors, band lineups play a key role in determining heterojunction properties and are likely to be difficult to estimate with sufficient precision. Accurate values will most likely have to be determined experimentally for each heterojunction system considered. The requirement of overall electrical neutrality in the thin film implies that the d orbital occupancy, averaged over the thin film $\bar{\rho}$, satisfies $\bar{\rho} = 1$.

Throughout this study we use the Hartree approximation for the long-ranged Coulomb interaction and neglect the corresponding exchange term, since our goals in studying this toy model are purely qualitative. The self-consistently determined Hartree mean-field Hamiltonian is

$$H_{Coul}^{eff} = \sum_{i \neq j, \sigma} \frac{e^2(\rho_j - f)\hat{n}_{i\sigma}}{\epsilon|\vec{R}_i - \vec{R}_j|} - \sum_{i, \sigma} \sum_{j(j_z \leq N_p)} \frac{Z_A e^2 \hat{n}_{i\sigma}}{\epsilon|\vec{R}_i - \vec{R}_j^A|} \quad (6.2)$$

where $\rho_j = \sum_{\sigma} \langle \hat{n}_{j\sigma} \rangle$ is the electron density on site j , $f = 0$ for $j_z \leq N_p$, and $f = 1$ for $j_z > N_p$. In the continuum limit, H_{Coul}^{eff} becomes:

$$\frac{H_{Coul}^{eff}}{2\pi U_c} = \sum_{i\sigma} \left[\sum_{z_A} |i_z - z_A| - \sum_{z' \neq z} (\rho(z') - f)|z' - i_z| \right] \hat{n}_{i\sigma} \quad (6.3)$$

where $U_c = e^2/\epsilon a$.

6.3 Hartree-Fock theory

In HFT the Hubbard U term is replaced by its mean-field counterpart as the ones used in Chapter 5, and again there are almost always a number of distinct self-consistent solutions of the HF equations, corresponding to various local-minima and saddle-points of the HF energy functional. In the same spirit, here we present results for solutions with G -type antiferromagnetic (AFM) order, or (π, π, π) spin order, and ferromagnetic (FM) order. These solutions are representative of ordered states which occur frequently in complex transition metal oxides and are often global minima of the HF energy functional. The philosophy of following this procedure is that HFT can neither reliably judge the competition between different types of order, nor predict whether or not long-range order succumbs to fluctuations. The results nevertheless very often provides a reasonable description of local correlations in the strongly correlated regime.

Our HFT results for $N_p = 2$ and $N_p = 5$ are summarized in Fig. 6.2. For the calculations reported here, the total layer number $N = 10$ and typical values were chosen for the interaction parameters. ($U_P/t = U_{NP}/t = 20$ and $U_c/t = 0.8$.)[15] For both AFM and FM states EIR occurs only for the model thin film with the larger value of N_p . This feature is a result of the competition between the polar catastrophe[20] and strong local correlations. Although the polarity discontinuity at the interface favors a transfer of electrons from the outmost surface to the interface, this charge rearrangement is opposed by the Mott-Hubbard gap. It is instructive to consider space-charge induced band bending diagrams like the cartoon illustration of Fig. 6.3 which contrasts the $N_p = 2$ and $N_p = 5$ cases. For $N_p = 2$, the bending of the upper and lower Hubbard bands is not large enough to force the chemical potential μ at the heterojunction outside the gap region. When more polar layers

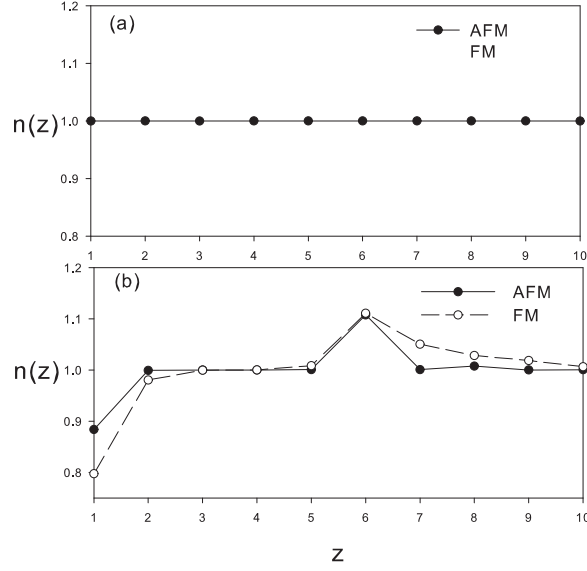


Figure 6.2: Electron charge distributions for AFM and FM Hartree-Fock states with $U_P/t = U_{NP}/t = 20$, $U_c/t = 0.8$, and ϵ_d constant for (a) $N_p = 2$ and (b) $N_p = 5$ cases. The total number of layers is $N = 10$. EIR occurs only in the model thin film with the larger number of polar layers. Confinement of the 2DSCES is stronger in the AFM state solution because of its stronger local correlations.

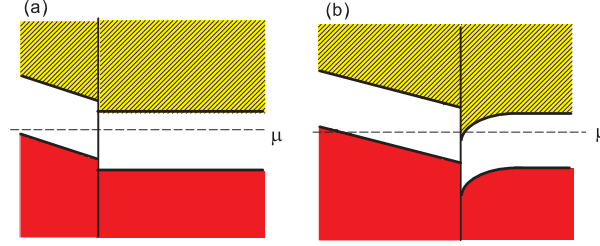


Figure 6.3: Cartoon illustration of band bending for (a) $N_p = 2$ (b) $N_p = 5$. The support of the upper Hubbard band's spectral weight is indicated by yellow shading while the support of the lower Hubbard band's spectral weight is indicated by solid red. These illustrations reflect the spectral weight only at the M and M' transition metal sites of $M(M')O_2$ layers with the end point on the polar side of the interface at the last MO_2 layer and the starting point on the nonpolar side of the interface at the first $M'O_2$ layer. Since the last MO_2 and the first $M'O_2$ layers are separated by a AO layer, the electrostatic potential reaches its minimum at the first $M'O_2$ layer. (The electrostatic potential is of course continuous along the growth direction, as required by the Poisson equation.) (a) μ lies in the gap region and no EIR occurs. (b) μ crosses the lower Hubbard band on the polar side and upper Hubbard band on the nonpolar side, indicating the appearance of EIR. If the top layer of the polar material was a positively charged AO layer rather than a negatively charged MO_2 layer, the charge transfer would occur from the lower Hubbard band near the heterojunction to the upper Hubbard band near the surface.

are grown, μ eventually crosses the lower Hubbard band of the outermost polar layer and the upper Hubbard band of the nonpolar layer nearest the interface, forcing the occurrence of an EIR. If the top layer of the polar material was a positively charged AO layer rather than a negatively charged MO_2 layer, the charge transfer would occur from the lower Hubbard band near the heterojunction to the upper Hubbard band near the surface.

An analogous competition has already been discussed and studied experimentally in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures [21]. In that case the energy which competes with the polar catastrophe is the energy difference between the top of oxygen p -bands in nonpolar SrTiO_3 and the bottom of aluminum d bands in LaAlO_3 , instead of the correlation gap in the example studied here. Since it always costs

the gap energy to add more electrons on any layer of the heterostructure, electrons accumulate initially near the interface to gain the most electrostatic energy, eventually spreading out through the heterostructure to minimize kinetic energy cost. Quantum confinement of the 2DSCES associated with EIR is stronger for states with stronger on-site correlations because the kinetic energy is then a smaller component of the overall energy budget. This is the reason that in Fig. 6.2(b) electrons are more confined to the interface in the AFM state than in the FM state. (The FM state has larger bandwidths and smaller correlation gaps, at least within HFT.) Based on the discussion above, we expect that for fixed U_P and U_{NP} , the minimum number of polar layers required to achieve reconstruction N_p^m will be smaller when U_c is larger. N_p^m will also tend to decrease when the Hubbard gap is reduced in either layer; in Fig. 6.4 we illustrate the dependence on U_{NP} when U_P is fixed. Note that a smaller value of U_{NP} favors ferromagnetic HF states.

A more microscopic view of EIR is provided in Fig.6.5 where we illustrate the electronic structure of the AFM solution of the Hartree-Fock equations for a thin film with $N_p = 5$. The parameters used to construct this illustration are the same as those used for the $N_p = 5$ case in Fig.6.2(b). The $N = 10$ thin film has 20 two-fold spin-degenerate 2D bands because of the reduced translational symmetry of the AFM state, and charge neutrality requires that 10 bands be occupied. In Fig. 6.5(a) we can identify 10 relatively widely spaced bands which correspond at high energies to the upper Hubbard band and at low energies to the lower Hubbard band in the polar material. The bands are widely spaced because of the average electric field in the polar material; for the same reason these bands are quite highly localized in individual atomic layers. The two groups of more narrowly spaced bands correspond respectively to the upper Hubbard band and the lower Hubbard band of the non-polar material. Because the space-charge electric fields are much either almost fully or at least partially screened out in the non-polar material by charge accumulation

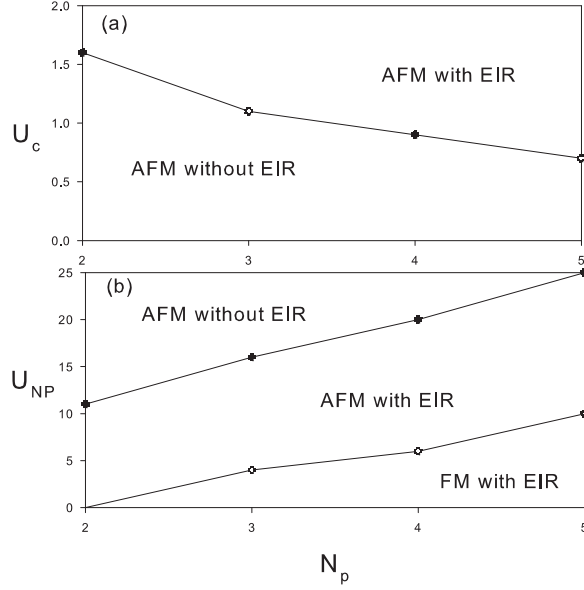


Figure 6.4: Ground-state phase diagram (a) *vs.* N_p and U_c/t for $U_P = U_{NP} = 20$ and (b) *vs.* N_p and U_{NP} for $U_P = 20$ and $U_c/t = 0.8$. The total number of layers is fixed at $N = 10$. (a) For fixed U_P and U_{NP} , EIR occurs for a smaller number of polar layers if U_c is larger. Note that the FM states always have higher ground-state energy than AFM states in these parameter regions. (b) For fixed U_P and U_c , EIR requires more number of polar layers when U_{NP} is larger. As indicated here, a smaller U_{NP} also favors FM states over AFM states in Hartree-Fock theory. For both (a) and (b) the phase boundary for the occurrence of EIR is accurately reproduced by the Thomas-Fermi approximation, Eq.6.7.

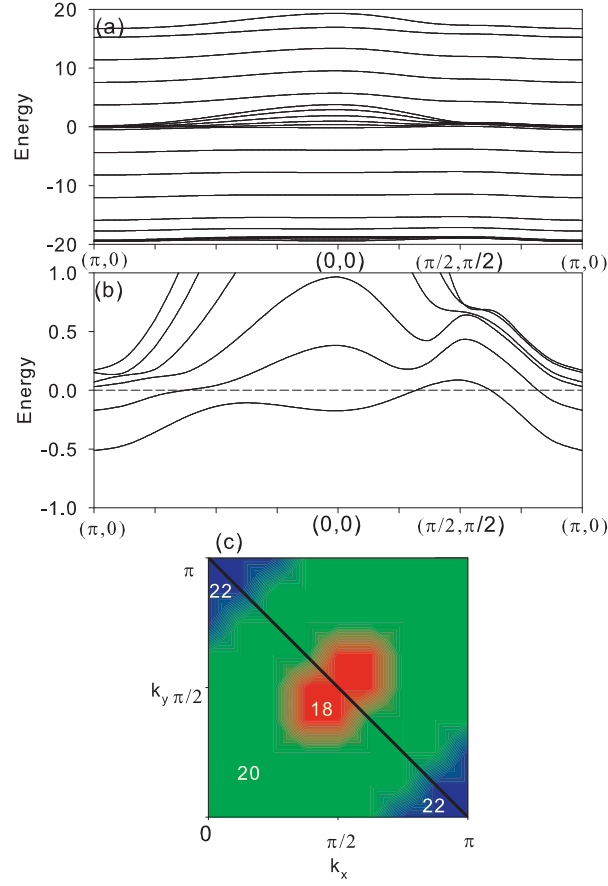


Figure 6.5: Electronic structure of the $N_p = 5$ AFM state whose charge distribution was illustrated in Fig.6.2(b). This plot was calculated with a non-zero second nearest-neighbor hopping parameter $t'/t = -0.15$. Energies are measured from the chemical potential of the thin film. (a) All 20 2D bands along high symmetry lines of the AFM Brillouin zone. (b) Crossing between the polar material surface layer lower Hubbard band and the five non-polar material upper Hubbard band layers. The space charge physics implies that these six bands will be close to the chemical potential. Note that only two bands are partially occupied. (c) Dependence of the total band occupancy on position in the Brillouin-zone on a color scale with occupancy 18 in red, 20 in green, and 22 and in blue.

at the interface, the bands are closely spaced and the corresponding eigenstates contain more inter-layer characters. When EIR occurs there is a weakly avoided anticrossing between the top-most lower Hubbard band state in the polar material and the upper Hubbard band states of the non-polar material. This anticrossing is apparent in Fig.6.5(b) which expands the region of the electronic structure close to the Fermi energy. In the ground state the polar lower-Hubbard band state is lower in energy at the Brillouin-zone center but higher in energy toward the Brillouin-zone edges. (For a model with only nearest-neighbor hopping the lower upper band has its maximum and the upper Hubbard band has its minimum along the line from $(\pi, 0)$ to $(0, \pi)$.)

For the parameters used in this calculation (with second nearest-neighbor hopping $t'/t = -0.15$) the EIR leads to two partially occupied 2D bands illustrated in Fig. 6.5(c), a nearly full lower-Hubbard band very localized on the surface and with two inequivalent hole pockets in the AFM Brillouin zone centered on $(\pi/2, \pi/2)$ and $(\pi/2, -\pi/2)$ and a nearly empty band concentrated on the first non-polar layer with an electron pocket centered on $(\pi, 0)$.

6.4 Thomas-Fermi theory

Layered oxide materials have a natural Thomas-Fermi approximation in which the total energy is expressed as the sum of the total electrostatic energy and a local-density-approximation for the band and correlation energies. For layered structures the contribution to the energy from each atomic layer is approximated by the energy per layer of an electrically neutral 3D system with the average site occupancy of that layer. Minimizing this energy with a fixed total density constraint leads to the following TF equation:

$$\mu(\rho(z)) + v_H(z) = \mu_0 \quad (6.4)$$

where $v_H(z)$ for this case is.

$$\frac{v_H(z)}{2\pi U_c} = \sum_{z_A} |z - z_A| - \sum_{z' \neq z} (\rho(z') - f) |z' - z| \quad (6.5)$$

and μ_0 is the overall chemical potential. Following the same approach described in Chapter 5, we can solve the TF equations for different ordered states using $\mu(\rho)$ calculated from HF solutions for the three-dimensional Hubbard model. We confirmed that TFT very accurately reproduces the results of HFT for the charge distribution between the layers, as in the case of modulation doping discussed in the last chapter.

One advantage of using this TF equation is that we can derive some key properties analytically. For example, if we assume that the d-orbitals of polar and non-polar sides are both described by one-band Hubbard models and that the charge transfer occurs from a single surface layer to a single interface layer Eq.(6.4) reduces to

$$\epsilon_{d1} + \mu_P(1 - \delta n) + 2\pi U_c N_p(1 - 2\delta n) = \epsilon_{d2} + \mu_{NP}(1 + \delta n) \quad (6.6)$$

where the Hubbard model chemical potentials are expressed as function of density in units of electrons per atom, δn is the charge transfer, and the on-site energies which are usually set to zero in Hubbard models, restored on each side of the heterojunction. Since the left hand side is a monotonically decreasing function of δn and the right hand side is a monotonically increasing function of δn , this equation has a solution and EIR will occur if

$$2\pi U_c N_p \geq [\epsilon_{d2} + \mu_{NP}(1+)] - [\epsilon_{d1} + \mu_P(1-)] = E_{IG} \quad (6.7)$$

i.e. if the electric potential drop across the polar layer exceeds the spatially indirect gap E_{IG} between the bottom of the upper Hubbard band in the non-polar material and the top of the lower Hubbard band in the polar material. Since the

variation of chemical potential with density is strongly reduced outside of the gap in strongly correlated material, it follows that the amount of charge transferred once $U_c N_p$ exceeds the minimum value is given accurately by

$$\delta n \simeq \frac{2\pi U_c N_p - E_{IG}}{4\pi U_c N_p}. \quad (6.8)$$

As the right hand side of Eq. 6.8 becomes comparable to 0.5 at larger values of N_p , the fundamental assumption of our simple model (namely that the polar catastrophe is avoided by electronic rather than atomic reconstruction) becomes increasingly suspect. When EIR occurs it is likely to lead to relatively small 2D Fermi surface pockets, as illustrated in Fig. 6.5.

6.5 Dynamical mean-field theory

For the paramagnetic states, we adopt the two-site DMFT with the same reasons discussed in the last chapter. The results for $N_p = 2$ and $N_p = 5$ are presented in Fig. 6.6 with $U_P/t = U_{NP}/t = 20$ and $U_c/t = 0.8$. When a paramagnetic state is described by HFT, charge transfer from the surface to the interface occurs (incorrectly) even for $N_p = 2$. For $N_p = 5$, the screening of the surface layer electric field incorrectly begins immediately in the polar material. The DMFT calculations demonstrate that a larger value of N_p is required even if the spin-degree of freedom is not ordered in the Mott insulators. These results confirm that a minimum thickness of polar layers is required for EIR when on-site correlations are strong.

6.6 Discussions

From the experimental aspect, one may concern whether the polar-nonpolar MIMI heterostructures can possibly be made from existing materials. It is indeed not so easy to determine on purely theoretical grounds which material combinations

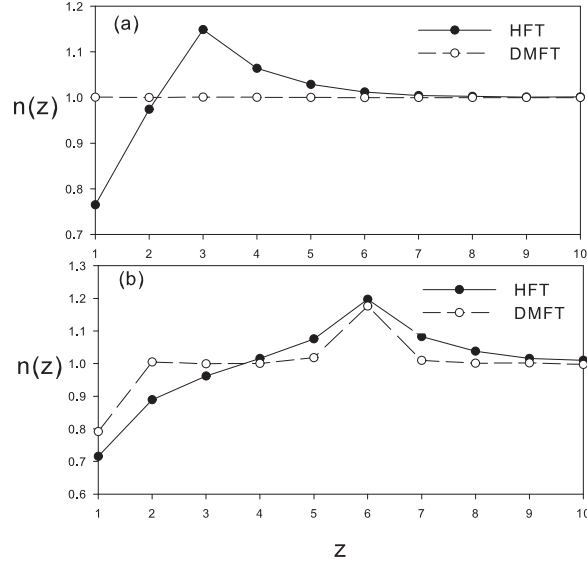


Figure 6.6: Electron distribution calculated by HFT and DMFT for PM state with (a) $N_p = 2$ and (b) $N_p = 5$. Other parameters are the same as those used in Fig 6.2. The comparison between HFT and DMFT for PM state demonstrates the role of on-site correlation in the EIR. The solutions of DMFT show that EIR only occurs with more polar layers and the confinement is stronger compared to HF solutions.

could be used to realize the EIR proposed here. In the family of cubic perovskites, candidate d^1 polar materials include LaTiO_3 and YTiO_3 and possible d^1 non-polar materials include SrVO_3 and CaVO_3 . The band offsets of the various possible materials combinations $\epsilon_{d1} - \epsilon_{d2}$ can be estimated from existing electronic structure calculations. LDA calculations based on Wannier functions[32] indicate that the t_{2g} bands tend to be higher in energy relative to the oxygen p levels in LaTiO_3 and YTiO_3 than in CaVO_3 and SrVO_3 . Assuming that the oxygen p levels are closely aligned across the heterostructure, we can expect that LaTiO_3 and YTiO_3 will have higher d orbital energies than CaVO_3 and SrVO_3 . Another interesting observation from the LDA calculations is that energy differences between different t_{2g} orbital associated with distortions of the ideal cubic perovskite structure tend to increase across the series SrVO_3 - CaVO_3 - LaTiO_3 - YTiO_3 . These additional features related to the t_{2g} orbital degree of freedom may bring in new physics which can not be explored in our single-band thin film model. Moreover, the tendency toward magnetic ordering may also be influenced by the presence or absence of t_{2g} orbital degeneracy, which will in turn be influenced by reduced symmetry near the heterojunction. The same calculations show that CaVO_3 and SrVO_3 are metallic in the bulk. Lower coordination and electric fields that reduce inter-layer hopping are likely to tip the balance toward the insulating state in thin films and especially near heterojunctions, so these materials are still candidates for realization of the physics studied here.

Although sophisticated first principle calculations can provide some insight and will help with the construction of realistic phenomenological models, the consequences of orbital degeneracy or near-degeneracy for complex oxide heterojunctions may depend on subtle issues of many-particle physics. Another aspect not captured realistically in this qualitative study is the dielectric constant which in general could be a very complicated function of positions throughout the heterostructures[33]. Experimental information when available will likely play an essential role in achieving

a full understanding.

One of the most important effect of the band lineups in our model is its influence on where the electrons accumulate when EIR occurs. We have shown that in the case of constant ϵ_d electron accumulation near the heterojunction appears on the first $M'O_2$ layer. This will change if ϵ_d for the polar materials is low enough so that the sum of ϵ_d and electrostatic potential is minimized at the last MO_2 layer, instead of the first $M'O_2$ layer.

6.7 Remarks on the two-dimensional strongly-correlated electronic systems - doped Mott insulators?

Two-dimensional (2D) electron systems have been a fertile source of interesting physics over the past few decades, playing host to the fractional and integer quantum Hall effects and cuprate superconductivity among other phenomena. The most widely studied and most thoroughly understood 2D electron systems are those that occur near semiconductor heterojunctions. In these systems carrier densities and disorder strengths can be adjusted using modulation doping and the electric field effect, and high sample quality can be achieved using lattice matched materials and epitaxial growth techniques. These 2D systems are well described by Fermi liquid theory, at least at magnetic field $B = 0$. Rapid recent progress in the epitaxial growth of complex transition-metal oxides foreshadows the birth of an entirely new class of 2D electron systems, one in which electronic correlations are strong even at $B = 0$ and non-Fermi-liquid behavior is common.

Although we have shown theoretically that it is possible to create novel 2D systems out of the MIMI heterostructures based on HFT, DMFT, and TFT, the effective theory to describe these 2D systems is still lacking. It would be expected that the orbital degeneracy, Jahn-Teller effect, and the spin properties due to the

magnetically ordered phases will all play important roles and couple to each other in the low energy theory. However, since the heterostructure in general have lower crystal symmetry, the orbitally ordered state would be more likely to occur at very low temperature. In this case, the single-band model with the spin degree of freedom may be appropriate for the 2D system near the heterojunction, and it could be an ideal candidate for the doped 2D Mott insulators.

Doped Mott insulators typically appear to have exotic properties when the doping is small and more conventional properties when the doping is large and the total band filling is well away from one, the value at which local correlations have maximum importance. In the case of the extremely heavily studied cuprate systems, for example, this crossover is interrupted, by high-temperature superconductivity. It is interesting to consider whether or not the two-dimensional electron systems considered here are Fermi liquids. Whereas bulk doping often leads eventually to a first order transitions between a doped Mott insulator and a relatively conventional metal, modulation doping in a single or several layers may make it possible to realize high-density, low-disorder, two-dimensional exotic metals which carry reflect the heritage of the three-dimensional Mott insulators from which they emerge. Since the very existence of these two-dimensional electronic systems depends on gaps that are entirely due to electron-electron interactions, it is clear that they cannot be adiabatically connected to non-interacting electron states. On the other hand, in the HFT description the doped state *is* a Fermi liquid with well defined quasiparticles. This approximation neglects quantum fluctuations of the magnetic state however, and its predictions for quasiparticle properties may not be reliable.

One of the most famous examples of the doped Mott insulators is the high- T_c cuprate superconductors. Debates on how much the Mott physics influences the properties of these material are still not fully resolved. In the rest parts of this thesis, we will investigate the excitation spectrum and superfluid density of the high-

T_c cuprates. We find that a number of the unusual properties of superconducting state in underdoped cuprates could be well understood by the weak coupling BCS theory implemented with the generalized random phase approximation calculations without the strong-coupling feature of the Mott physics. More detail comparisons of theories and experiments are required to do the final judgement, and we will expect the MIMI heterostructures proposed here to be a suitable testing platform.

Chapter 7

Introduction to Cuprates

7.1 Phase diagram

The fascinating and rich phenomenology of high temperature cuprate superconductors has been very thoroughly studied over the past 20 years. Although there is substantial variability in details from material to material, all cuprates exhibit robust Mott insulator antiferromagnetism when the hole-doping fraction x is very small, superconductivity which appears when x exceeds a minimum value ~ 0.1 , and a maximum T_c in optimally doped materials with $x \sim 0.2$. In the underdoped regime, the superconducting transition temperature is limited by phase fluctuations[34, 35, 36, 37], and experiments hint at a wide variety of (typically) short-range correlations associated with competing charge and spin orders. The underdoped regime poses a fundamental challenge to theory because its electronic properties are not fully consistent with any of the various well-understood *fixed-point* behaviors that often help us classify and predict the properties of complex materials.

The key to understand this universal phase diagram of the high- T_c cuprates is to find out the doping dependence of the superfluid density n_s . The phenomenological parameter ρ_s used to characterize phase-fluctuation stiffness in a superconductor

is normally expressed in terms of n_s by writing $\rho_s = \hbar^2 n_s / m^*$, an identification that is partly justified by BCS mean-field theory. The increase of ρ_s with x in cuprate superconductors is therefore readily accounted for by theories in which superconductivity is due to the condensation of Cooper pairs formed from holes in a doped Mott insulator first proposed by Anderson in his seminar paper in 1987[38]. This idea was later extensively elaborated by many authors[39] within the *slave-boson approach*. The basic idea of this approach is to rewrite the electron creation operator as: $C_{i\sigma}^\dagger = b_i f_{i\sigma}^\dagger$, where b_i is annihilation operator of *holon* carrying $+e$ charge but no spin and $f_{i\sigma}^\dagger$ is the creation operator of *spinon* carrying spin σ but no charge. In this framework, the superconductivity is characterized as holons Bose-Einstein condensed and spinons paired, and the increase of ρ_s with x can be easily realized because ρ_s must be limited by the holon condensate which is proportional to the holon density x . However, theories which start with this view must still explain the fact that ρ_s vanishes at a non-zero value of x , and deal with the property that cuprate superconductivity evolves smoothly from the underdoped regime to an overdoped regime in which it appears to be explainable in terms of conventional band-quasiparticle Cooper pair condensation. In addition, the spinons and holons interact strongly with an emergent gauge field associated with the awkward *non-doubly occupied constraint*, and an appropriate approach to handle such a strong coupling system is still unavailable. Therefore the debates on the physics in the underdoped region are still not fully settled down, and several alternative schemes have been proposed in the last decade[40, 41, 42].

7.2 Angle-resolved photoemission spectrum (ARPES)

The history of the photoemission spectrum can be traced back to as early as late nineteenth century when Hertz observed the photoelectric effect[43]. This effect was later understood by Einstein[44] in his Nobel-prize winning paper as a consequence

of the particle character of the light, the photons. Later it was realized that this effect can actually be a good tool to study the electronic structure in the materials if the energy of the incident photons and the final state of the escaped photoelectrons can be measured. The angle-resolved photoemission spectrum (ARPES) is just such spectroscopy which maps out the electronic structure of the materials. This mapping is achieved by measuring the energies and directions of the escaped photoelectrons and then applying the conservation laws for energy and momentum to obtain the initial state of the electrons when in the materials. In the past two decades, the energy and angle resolutions of ARPES have been improved tremendously, partly due to the huge interests of the science community on the high- T_c cuprates, and now ARPES has become one of the major tools to reveal the novel electronic structure of the high- T_c cuprates. A recent review on the ARPES data of the high- T_c cuprates can be found in Ref[45].

The quantum description of the photoemission process allows us to measure the *spectral function* $A(\vec{k}, \omega) = -1/\pi \text{Im}G(\vec{k}, \omega)$ which reveals a lot of information about the gap structure in the single particle spectrum of the cuprates. One of the most important discoveries due to ARPES is the observation of the *pseudogap*, which refers to the gap existing at temperatures between the superconducting transition temperature T_c and a new characteristic temperature T^* increasing as the doping decrease in the underdoped cuprates. Because early ARPES measurements suggested that the pseudogap was also *d-wave*, the same symmetry as the superconducting gap of the cuprates, it is naturally expected that the pseudogap is the *precursor* of the superconducting gap. This viewpoint is in fact consistent with the slave-boson theory very well. Since the superconducting state is characterized by holon condensate and spinon pairing within the slave-boson theory, the pseudogap can be understood as the state in which the holons are not condensed due to the phase fluctuations but the spinons are still paired. In addition, this proposal for the

pseudogap state can also account for the doping dependence of T^* since the strength of the spinon pairing is naturally enhanced with the increase of the electron density (thus the decrease of the hole density). This great success in explaining the pseudogap indeed provided a very strong support for the theories viewing the high- T_c superconductor as a remnant of its parent Mott insulator, although there are still many difficulties to make some quantitative comparisons with experiments due to some awkward properties of this kind of theories[39].

However, ARPES has never stopped surprising us. Very recently new ARPES measurements with further improved resolutions[74, 75] showed evidences for that the pseudogap is different from the superconducting gap. This finding challenges the slave-boson view point and arises a new debate on whether the 'two gap' structure is universal in the cuprates or not. Nevertheless, while these debates on the two gap structure are mostly at the temperature around T_c , it is no doubt that at very low temperature where the superconductivity is overwhelmingly dominant, the gap measured by ARPES is d -wave and closely associated with the superconductivity. This is a very important fact for our work, and in Chapter 9 we will explain how we can use ARPES data to make a realistic model to understand several unusual properties of the underdoped cuprates.

7.3 Inelastic neutron scattering measurements

In some senses, the inelastic neutron scattering (INS) measurement is pretty much similar to ARPES measurement. The difference is that it is the neutron, instead of photon, incident into the crystal under study. Since the neutron is a chargeless spin 1/2 particle and much massive compared to electrons, it interacts mostly with the ions and magnetic moments in the crystal. Therefore, by carefully subtracting the phonon contributions from the scattering cross section, the magnetic structure of the crystal can be revealed. Since the last decades, the INS measurements has

provided a number of important information about the spin fluctuations in the high- T_c cuprates.

Early INS measurements were mostly done on the LSCO family, although it was later realized that the spin responses seem to be fundamentally different in LSCO and in other families of the high- T_c cuprates. One unique feature of the LSCO family is the remarkable suppression of T_c near a magic doping concentration of $x = \frac{1}{8}$. The INS measurements showed that the spin response has peaks at the incommensurate momenta $\vec{q}_0 = (\pi, \pi) \pm 2\delta(\pi, 0)$ and $2\delta(0, \pi)$ [46]. Further analysis found a precise relation $\delta = x$ within a range of $x = 0.06$ to $x = 0.125$ [47]. A natural explanation for the incommensurate peak at $x = \frac{1}{8}$ is the stripe picture in which the charges form stripes with a period of 4 lattice constant in the antiferromagnetically-ordered background. This stripe picture had been discussed in the Hubbard model[4] even before the INS measurements were done, and was supported by the evidence of static spin and charge orders found by Tranquada *et al.*[48] Moreover, the stripe picture can also explain the anomalous suppression of T_c near $x = \frac{1}{8}$ since the charge density wave states compete with the superconductivity. However, although the stripe picture is consistent with these two unique features of LSCO, it inevitably predicts that the LSCO at $x = \frac{1}{8}$ is a charge insulator along the direction perpendicular to the stripes, which is obviously inconsistent with the experiment. This leads to the idea of fluctuating stripe picture which assumes that the charge stripes are fluctuating instead of static and is still under intensive study.

While spin response in LSCO family can be explained by fluctuations associated with the charge and spin density waves, the story for other families of cuprates seem to be quite different. In YBCO and Bi2212, the main feature of the INS measurements is the resonance mode (INSR) observed at $\vec{Q} \equiv (\pi, \pi)$ [49, 50]. Experimentally the INSR has been found to have several interesting doping dependences. First, the energy of the INSR is highest at the optimal doping and decreases with

both underdoping and overdoping, resembling the 'superconducting dome' in the famous cuprate phase diagram. For example, an empirical relationship between the INSR energy Ω^{res} and the superconducting transition temperature T_c is proposed for Bi2212: $\Omega^{res} \approx 5.4k_B T_c$ [51]. Second, while the INSR is only observed at temperature below T_c in optimally-doped cuprates, it survives in the pseudogap region as well in the underdoped region, and fraction of its spectral weight to the total spin sum rule increase significantly with underdoping[52, 53]. Third, further neutron scattering measurements observed the incommensurate peaks at momentum near $\vec{Q}$, appearing as a 'hourglass' dispersion of the collective excitations. Because all these features suggest their intimacy to the superconducting properties of the cuprates, a detail analysis of these INSRs will be helpful to a better understanding of the cuprates.

It is natural to seek for a theoretical explanation on the INSR by random phase approximation (RPA) calculation. Many efforts have been made following this track[54, 55, 56, 57, 58, 59]. A popular interpretation states that the INSR is an *exciton-like spin-triplet* excitation in the particle-hole channel[55, 57], which can be understood as following. The magnetic susceptibility in RPA calculations is given as:

$$\chi(\vec{q}, \omega) = \frac{\chi^{irr}(\vec{q}, \omega)}{1 - J(\vec{q})\chi^{irr}(\vec{q}, \omega)} \quad (7.1)$$

where $\chi^{irr}(\vec{q}, \omega)$ is the irreducible part of Feynman diagrams and $J(\vec{q})$ is the bare coupling constant. It is argued that the ladder diagrams do not produce important effects in $\chi^{rr}(\vec{q}, \omega)$ at energies below the particle-hole continuum[54], and therefore only the bubble diagrams are taken into account (we will challenge this statement later). Since summing over the bubble diagrams gives a function having poles at the energies of particle-hole excitations[55], the imaginary part of the irreducible bubble $\text{Im}\chi^{irr}(\vec{q}, \omega)$ is zero unless the frequency exceeds the particle-hole continuum threshold energy Ω_0 . Therefore $\text{Im}\chi^{irr}(\vec{q}, \omega)$ behaves like a step function near Ω_0 , and it

follows from the Kramers-Kronig relations that the real part of the irreducible bubble $\text{Re}\chi^{irr}(\vec{q}, \omega)$ has a logarithmic divergence at Ω_0 . Since INS experiment measures $\text{Im}\chi(\vec{q}, \omega)$, the resonance mode at $\vec{q} = \vec{Q}$ is the mode with the resonance frequency ω^{res} solving $1 - J(\vec{Q})\text{Re}\chi^{irr}(\vec{Q}, \omega^{\text{res}}) = 0$ and $\text{Im}\chi^{irr}(\vec{Q}, \omega^{\text{res}}) = 0$ simultaneously. Consequently, there exists only one solution of $\Omega^{\text{res}} = \hbar\omega^{\text{res}}$ which is always *slightly smaller* than Ω_0 . This explanation is just like a magnetic analog of the exciton in the semiconductor physics, hence it is sometimes referred as *spin exciton* in the literatures.

There is, however, still something unclear about the INSR. First, the earlier theories based on RPA calculation include the ladder diagrams via putting an effective reduction parameter α to the coupling constant, and the resonance mode is interpreted as a collective mode merely in the particle-hole channel. One exception is the alternative picture proposed by Demler and Zhang[60]. They concluded that the INSR is an antibonding collective mode in particle-particle channel, namely π resonance, and is observable in the INS measurement due to its coupling to the particle-hole channel in the superconducting ground state. However, it has been pointed out that this picture is not consistent with experiments because the predicted resonance energy is shown to be higher than two-particle continuum threshold[61, 62]. Nevertheless, in our viewpoints, since particle-hole and particle-particle channels could in principle couple to each other due to the particle-hole mixing of Cooper pairs in the superconducting state, a better treatment of summing both bubble and ladder diagrams should be employed to study this issue. The importance of ladder diagrams has been demonstrated in the Hubbard model[63]. A phenomenological approach has been proposed to include the ladder diagrams by using several fitting parameters to construct the bare Green's function and the response function which are consistent with several experimental measurements, in a hope to include more effects of the ladder diagrams[64].

These above mentioned approaches, however, still did not treat the summation of bubble and ladder diagrams rigorously. We will exploit the time-dependent mean-field theory (TDMFT) introduced in Chapter 3 to revisit the questions of the INSR. It will be seen that new interpretation for the INSR and profound new properties related to the INSR can be discovered after both the bubble and ladder diagrams are treated properly within the TDMFT.

Chapter 8

Superfluid Density in Underdoped Cuprates

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8.1 Introduction

As described in Chapter 7, there is a hidden inconsistency in choosing theoretical approaches to describe the physical properties of the underdoped cuprates. While the conventional weak coupling BCS theory is rejected due to its wrong prediction on doping dependence of the superfluid density, our current understanding of the INS is mostly based on the weak coupling RPA schemes. In the following two chapters, we will show that this inconsistency can be resolved as long as the correlation effects due to the quantum fluctuations are included within a rigorous GRPA scheme. Our argument accounts for the correlation energy of a d-wave superconductor in the presence of incipient antiferromagnetism and is based on the following general

expression for the phase stiffness of a superconductor:

$$\rho_s = \frac{1}{A} \frac{d^2 E}{dP^2}, \quad (8.1)$$

where $A = L^2$ is the area of the system, $\vec{P}$ the pairing wavevector, and E is the total energy including both mean-field and correlation contributions: $E = E^{MF} + E^{cor}$. The derivation of this expression will be given in the next section. We argue that because of the pairing-wavevector dependence of E^{cor} , the phase stiffness of a d-wave superconductors is suppressed when short-range antiferromagnetic correlations emerge. The relationship between pairing-wavevector and the correlation energy gained from short-range antiferromagnetism parallels a conjugate relationship[60] between pairing and antiferromagnetic fluctuations. In this picture of the underdoped state, the resonant magnetic mode (INSR) observed in inelastic neutron scattering[49, 50] experiments has a somewhat different interpretation from that in most earlier theories as discussed in Chapter 7, appearing as a kind of magnetic plasmon.

8.2 Relationship between superfluid density and the pairing wavevector

The expression for the superfluid density comes from an observation of the Ginzburg-Landau theory[69]. The microscopic free-energy of the superconducting state without magnetic field has the following form:

$$F^s = F^n + \int d\vec{r} a |\Phi(\vec{r})|^2 + \frac{b}{2} |\Phi(\vec{r})|^4 + \frac{1}{2m^*} |\hbar \vec{\nabla} \Phi(\vec{r})|^2 + \dots \quad (8.2)$$

where F^n is the free-energy of the normal state without magnetic field and $\Phi(\vec{r})$ is the space-dependent order parameter. For the BCS state with pairing wavevector

$\vec{P}$, $\Phi(\vec{r})$ can be written as:

$$\Phi(\vec{r}) = \sqrt{n_s} e^{i\vec{P} \cdot \vec{r}} \quad (8.3)$$

where n_s is the superfluid density. Substituting the above equation into the free-energy expression leads to

$$\begin{aligned} F^s &= F^n + A \left[a n_s + \frac{b}{2} n_s^2 + \frac{\hbar^2 n_s}{m^*} \frac{P^2}{2} + \dots \right] \\ &= F^n + A \left[a n_s + \frac{b}{2} n_s^2 + \rho_s \frac{P^2}{2} + \dots \right], \end{aligned} \quad (8.4)$$

where we have used $\rho_s = \frac{\hbar^2 n_s}{m^*}$. At zero temperature, $F = E$ so that we have:

$$\rho_s = \frac{1}{A} \frac{d^2 E}{dP^2} \Big|_{n, P=0}. \quad (8.5)$$

8.3 Effective Hamiltonian

The model we study has on-site repulsive interactions U which drive antiferromagnetism, near-neighbour spin independent interactions V and Heisenberg interaction J which drive d-wave superconductivity if $V < 0$ or $J > 0$:

$$\begin{aligned} H &= H_t + H_U + H_V \\ H_t &= -t \sum_{\langle i,j \rangle, \sigma} c_{i\sigma}^\dagger c_{j\sigma} + h.c. - t' \sum_{\langle i,j \rangle', \sigma} c_{i\sigma}^\dagger c_{j\sigma} + h.c. \\ H_U &= U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \quad H_J = J \sum_{\langle i,j \rangle} \hat{S}_i \cdot \hat{S}_j, \quad H_V = V \sum_{\langle i,j \rangle \sigma \sigma'} \hat{n}_{i\sigma} \hat{n}_{j\sigma'} \end{aligned} \quad (8.6)$$

where $\langle i, j \rangle$ means the nearest neighbor and $\langle i, j \rangle'$ means the next nearest neighbor. In Eq.(8.6) U , J , V , t and t' should all be thought of as effective parameters which apply at the energy scale of pairing. Values for V , t , and t' can be estimated from ARPES data, taking the view that the pseudogap can be identified

approximately with the mean-field theory gap[45]. Both interaction parameters are expected to increase with decreasing x , and the d -wave BCS state can be found for $U > 0$, $V < 0$, and $J > 0$ at the mean-field level in our convention. For demonstration purpose, the parameters of $t'/t = -0.3$, $U/t = -V/t = 2.0$, $J/t = 0$, $x = 0.12$ are chosen in this chapter. A more systematical fitting of these parameters for Bi2212 will be elaborated in Chapter 9.

8.4 d -wave BCS mean-field state

Since we are interested in the superconducting state, we choose H^{MF} describing a d -wave BCS state with pairing wavevector $\vec{P}$. The order parameters are:

$$\begin{aligned}
\langle c_{i\uparrow} c_{i\downarrow} \rangle &= \Delta_0 e^{-i\vec{P} \cdot \vec{R}_i} \\
\langle c_{i\uparrow} c_{j\downarrow} \rangle &= \Delta_\alpha e^{-i\vec{P} \cdot (\vec{R}_i + \frac{\alpha}{2})} \\
\sum_\sigma \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle &= \chi_\alpha \quad , \quad \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle = \frac{\chi_\alpha}{2} \\
\vec{R}_j &= \vec{R}_i + \alpha, \alpha = \hat{x}, \hat{y}
\end{aligned} \tag{8.7}$$

where $\vec{P}$ is the pairing wave vector and the d -wave BCS ground state is given by $\vec{P} = 0$. Then the mean-field Hamiltonian H^{MF} is:

$$\begin{aligned}
H^{MF} &= \sum_{\vec{k}} \epsilon(\vec{k} + \vec{P}/2) c_{\vec{k}+\vec{P}/2,\uparrow}^\dagger c_{\vec{k}+\vec{P}/2,\uparrow} + \epsilon(\vec{k} - \vec{P}/2) c_{-(\vec{k}-\vec{P}/2),\downarrow}^\dagger c_{-(\vec{k}-\vec{P}/2),\downarrow} \\
&\quad + \Omega(\vec{k}) (c_{-(\vec{k}-\vec{P}/2),\downarrow} c_{\vec{k}+\vec{P}/2,\uparrow} + h.c)
\end{aligned} \tag{8.8}$$

$$\Omega(\vec{k}) = -2V [\Delta_x \cos(k_x) + \Delta_y \cos(k_y)] - U\Delta_0$$

$$\epsilon(\vec{k}) = [(-2t - V\chi_x) \cos(k_x) + (-2t - V\chi_y) \cos(k_y)] - 4t' \cos(k_x) \cos(k_y) - \mu \tag{8.9}$$

and it is straightforward to obtain the eigenvalues and eigenvectors of the H^{MF} :

$$\begin{aligned}
E^\pm(k) &= \frac{\epsilon(\vec{k}+\vec{P}/2)-\epsilon(\vec{k}-\vec{P}/2)}{2} \pm \sqrt{\left(\frac{\epsilon(\vec{k}+\vec{P}/2)+\epsilon(\vec{k}-\vec{P}/2)}{2}\right)^2 + \Omega^2(k)} \\
c_{\vec{k}+\vec{P}/2,\uparrow} &= \cos \theta_{\vec{k}}/2\alpha_{\vec{k}} + \sin \theta_{\vec{k}}/2\beta_{\vec{k}}^\dagger \\
c_{-(\vec{k}-\vec{P}/2),\downarrow}^\dagger &= \sin \theta_{\vec{k}}/2\alpha_{\vec{k}} - \cos \theta_{\vec{k}}/2\beta_{\vec{k}}^\dagger \\
\cos \theta_{\vec{k}} &= \frac{\epsilon(\vec{k} + \vec{P}/2) + \epsilon(\vec{k} - \vec{P}/2)}{2\sqrt{\left(\frac{\epsilon(\vec{k}+\vec{P}/2)+\epsilon(\vec{k}-\vec{P}/2)}{2}\right)^2 + \Omega^2(\vec{k})}} \quad , \quad \sin \theta_{\vec{k}} = \frac{\Omega(\vec{k})}{\sqrt{\left(\frac{\epsilon(\vec{k}+\vec{P}/2)+\epsilon(\vec{k}-\vec{P}/2)}{2}\right)^2 + \Omega^2(\vec{k})}}
\end{aligned} \tag{8.10}$$

where $\alpha_{\vec{k}}$ is the eigen-vector for $E^+(\vec{k})$ and $\beta_{\vec{k}}$ is that for $-E^-(\vec{k})$ and the mean-field Hamiltonian can be written as:

$$H^{MF} = \sum_{\vec{k}} E^+(\vec{k})\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}} + (-E^-(\vec{k}))\beta_{\vec{k}}^\dagger\beta_{\vec{k}} + (\epsilon(\vec{k} - \vec{P}/2) + E^-(\vec{k})) \tag{8.11}$$

The ground state has the properties that $\langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle = 0(1)$ if $E^+(\vec{k}) > (<)0$ and $\langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle = 0(1)$ if $E^-(\vec{k}) < (>)0$. For $\vec{P} = 0$, $\langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle = \langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle = 0$. For $\vec{P} \neq 0$, however, some quasi-particle states may be occupied in the ground state.

The self-consistent equations for the order parameters are:

$$\begin{aligned}
\Delta_0 &= \frac{1}{2N} \sum_{\vec{k}} \sin \theta_{\vec{k}} \left[1 - \langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle - \langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle \right] \\
\Delta_\alpha &= \frac{1}{2N} \sum_{\vec{k}} \sin \theta_{\vec{k}} \cos(k_\alpha) \left[1 - \langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle - \langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle \right] \\
\chi_\alpha &= \frac{1}{N} \sum_{\vec{k}} \cos(k_\alpha + P_\alpha/2) \left[\frac{1 + \cos \theta_{\vec{k}}}{2} \langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle + \frac{1 - \cos \theta_{\vec{k}}}{2} (1 - \langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle) \right] \\
&\quad + \cos(k_\alpha - P_\alpha/2) \left[\frac{1 - \cos \theta_{\vec{k}}}{2} (1 - \langle\alpha_{\vec{k}}^\dagger\alpha_{\vec{k}}\rangle) + \frac{1 + \cos \theta_{\vec{k}}}{2} \langle\beta_{\vec{k}}^\dagger\beta_{\vec{k}}\rangle \right]
\end{aligned} \tag{8.12}$$

$$\alpha = \hat{x}, \hat{y}$$

and the chemical potential μ is determined by the doping x :

$$x = 1 - \sum_{\vec{k}, \sigma} \langle c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} \rangle = \frac{1}{N} \sum_{\vec{k}} \cos \theta_{\vec{k}} \left[1 - \langle \alpha_{\vec{k}}^\dagger \alpha_{\vec{k}} \rangle - \langle \beta_{\vec{k}}^\dagger \beta_{\vec{k}} \rangle \right] \quad (8.13)$$

The zero pairing wavevector BCS state is usually the lowest energy state within the realistic range of model parameters. The introduction of the finite pairing wavevector $\vec{P}$ is only for the purpose of the superfluid density calculation which will be discussed in the next section. For any other physical properties discussed, we will only be interested in the $\vec{P} = 0$ state with pure d -wave solution (i.e. $\Delta_0 = 0, \Delta_x = -\Delta_y = \Delta$). The mean-field theory presented here can cover all other non d -wave states in general, and we have confirmed that the d -wave BCS state with $\vec{P} = 0$ is always a solution of the self-consistent equations and usually the lowest energy state within the realistic range of model parameters. Therefore we will assume the zero pairing wavevector d -wave BCS state to be the ground state throughout Chapters 8 and 9.

8.5 Classification of the excitations based on symmetry considerations

We will apply the time-dependent mean-field theory described in Chapter 3 to treat the quantum fluctuations. The fluctuation Hamiltonian $H^{fluc}(t)$ contains terms

from both on-site and nearest-neighbor interactions:

$$\begin{aligned}
H_U^{fluc}(t) &= U \sum_i \left[\delta\langle c_{i\uparrow}^\dagger c_{i\uparrow} \rangle c_{i\downarrow}^\dagger c_{i\downarrow} + \delta\langle c_{i\downarrow}^\dagger c_{i\downarrow} \rangle c_{i\uparrow}^\dagger c_{i\uparrow} + \delta\langle c_{i\downarrow}^\dagger c_{i\uparrow}^\dagger \rangle c_{i\uparrow} c_{i\downarrow} + \delta\langle c_{i\uparrow} c_{i\downarrow} \rangle c_{i\downarrow}^\dagger c_{i\uparrow}^\dagger \right] \\
&\quad - \left[\delta\langle c_{i\uparrow}^\dagger c_{i\downarrow} \rangle c_{i\downarrow}^\dagger c_{i\uparrow} + \delta\langle c_{i\downarrow}^\dagger c_{i\uparrow} \rangle c_{i\uparrow}^\dagger c_{i\downarrow} \right] \\
H_V^{fluc}(t) &= -V \sum_{\langle i,j \rangle \sigma \sigma'} \left[\delta\langle c_{i\sigma}^\dagger c_{j\sigma'} \rangle c_{j\sigma'}^\dagger c_{i\sigma} + \delta\langle c_{j\sigma'}^\dagger c_{i\sigma} \rangle c_{i\sigma}^\dagger c_{j\sigma'} - \delta\langle c_{i\sigma}^\dagger c_{i\sigma} \rangle c_{j\sigma'}^\dagger c_{j\sigma'} - \delta\langle c_{j\sigma'}^\dagger c_{j\sigma'} \rangle c_{i\sigma}^\dagger c_{i\sigma} \right] \\
&\quad - \left[\delta\langle c_{j\sigma'}^\dagger c_{i\sigma}^\dagger \rangle c_{i\sigma} c_{j\sigma'} + \delta\langle c_{i\sigma} c_{j\sigma'} \rangle c_{j\sigma'}^\dagger c_{i\sigma}^\dagger \right]
\end{aligned} \tag{8.14}$$

where $\delta\langle \hat{O} \rangle$ means the fluctuation of $\langle \hat{O} \rangle$ around the mean-field state and thus is a function of time. We don't write out the time index just for convenience. Since H^{MF} is taken as the unperturbed Hamiltonian, it is better to Fourier transform $H^{fluc}(t)$ to momentum space and replace the creation and annihilation operators of the electrons by these of the quasi-particles of H^{MF} . It may look messy at the first sight since there are so many terms coupled to each other. Fortunately, we are still able to classify those terms into several independent groups from the symmetry considerations.

The first symmetry we may use is the translational invariance. As mentioned in Chapter 3, the translational invariance makes the excitation momentum $\vec{q}$ a good quantum number so that we can reduce the matrix $\hat{M}$ given in Eq. 3.4 into isolated blocks characterized by $\vec{q}$. For the block of momentum $\vec{q}$, it can be further divided into two independent groups of $\Delta S_z = 0$ and $\Delta S_z = \pm 1$ excitations due to the spin rotational symmetry. To be specific, we can re-group the fluctuations as $H^{fluc}(t) =$

$$H^{f1}(t) + H^{f2}(t),$$

$$\begin{aligned}
H^{f1}(t) &= \frac{1}{A} \sum_{\vec{p}, \vec{k}, \vec{q}, \sigma} F(\vec{q}) \left[\delta \langle c_{\vec{p}+\vec{q}\bar{\sigma}}^\dagger c_{\vec{p}\bar{\sigma}} \rangle c_{\vec{k}-\vec{q}\sigma}^\dagger c_{\vec{k}\sigma} \right] + G(\vec{k}-\vec{p}, \vec{q}) \left[\delta \langle c_{\vec{p}+\vec{q}\sigma}^\dagger c_{\vec{p}\sigma} \rangle c_{\vec{k}-\vec{q}\sigma}^\dagger c_{\vec{k}\sigma} \right] \\
&\quad + H(\vec{k}-\vec{p}) \left[\delta \langle c_{\vec{q}-\vec{p}\bar{\sigma}}^\dagger c_{\vec{p}\bar{\sigma}} \rangle c_{\vec{k}\sigma} c_{\vec{q}-\vec{k}\bar{\sigma}} + h.c. \right], \\
H^{f2}(t) &= \frac{1}{A} \sum_{\vec{p}, \vec{k}, \vec{q}, \sigma} I(\vec{k}-\vec{p}) \left[\delta \langle c_{\vec{p}\sigma}^\dagger c_{\vec{p}-\vec{q}\bar{\sigma}} \rangle c_{\vec{k}-\vec{q}\bar{\sigma}}^\dagger c_{\vec{k}\sigma} \right] + J(\vec{k}-\vec{p}) \left[\delta \langle c_{\vec{q}-\vec{p}\sigma}^\dagger c_{\vec{p}\sigma} \rangle c_{\vec{k}\sigma} c_{\vec{q}-\vec{k}\sigma} + h.c. \right]
\end{aligned} \tag{8.15}$$

$F(\vec{q}) = U + 2V[\cos(q_x) + \cos(q_y)]$, $G(\vec{k}-\vec{p}, \vec{q}) = -2V[\cos(k_x - p_x - q_x) + \cos(k_y - p_y - q_y) - \cos(q_x) - \cos(q_y)]$, $H(\vec{k}-\vec{p}) = U/2 + V[\cos(k_x - p_x) + \cos(k_y - p_y)]$, $I(\vec{k}-\vec{p}) = [-U - 2V(\cos(k_x - p_x) + \cos(k_y - p_y))]$, $J(\vec{k}-\vec{p}) = V[\cos(k_x - p_x) + \cos(k_y - p_y)]$, $\bar{\sigma} = -\sigma$, and $A = L^2$ is the area of the system. The group I ($H^{f1}(t)$) contains the $\Delta S_z = 0$ fluctuations while the group II ($H^{f2}(t)$) contains the $\Delta S_z = \pm 1$ ones, and these two groups can be treated independently. Moreover, since the BCS states (with or without finite pairing wavevector $\vec{P}$) are spin singlet, the spin 1 excitations must have three fold degeneracy of which two modes will be found in the group II and one mode will be found in the group I. These reductions of $\hat{M}$ into small blocks greatly simplify the numerical calculations since we can perform the diagonalizations for each small block independently. In addition, the special structure of three-fold degeneracy for spin 1 excitations provides a realistic check of the correctness of the calculations.

Another advantage of this reduction reveals as we come to study the response functions which can be even reduced further to an integral matrix with finite size, a trick commonly used in the cuprate study[60, 61]. The reason why we can have this convenient form of integral matrix is that since we only consider on-site and nearest-neighbor interactions, the form factors of the interactions are either constants or functions of $\cos(k_x - p_x)$, $\cos(k_y - p_y)$, $\sin(k_x - p_x)$, and $\sin(k_y - p_y)$, all of which can be separated into multiples of $\cos k_x \cos p_x$, $\cos k_x \cos p_y$, $\cos k_y \cos p_y$ etc. We will

explain in more details in Chapter 9 as we discuss the response functions calculated from our theory.

8.6 Correlation contribution to the superfluid density

The expression for the superfluid density given in Eq. 8.5 is best suitable if the correlation energy can be obtained analytically. This is obviously not our case since our TDMFT approach to evaluate the correlation can only be done on a finite size system. Fortunately, because the free-energy F^s given in Chapter 8.2 depends only on the powers of P^2 , we can use an alternative expression for the ρ_s :

$$\rho_s = \frac{2}{A} \frac{dE}{d(P^2)} \Big|_{n, P^2=0} \approx \frac{2}{A} \frac{(E(\vec{P}_{min}) - E(0))}{P_{min}^2}. \quad (8.16)$$

where $\vec{P}_{min} = (2\pi/L, 0)$ is the finite pairing wavevector with minimal magnitude and $P_{min}^2 = |\vec{P}_{min}|^2 = 4\pi^2/L^2$, and L is the system size which is 34 in our calculations. The above expression is more convenient for numerical calculations since it requires only one derivative so that many numerical errors can be easily avoided. We will use it for both the mean-field ρ^{MF} and correlation ρ^{cor} contributions.

The mean-field energy E^{MF} is obtained by taking the expectation value of the *full Hamiltonian* H with respect to the mean-field state, and the correlation energy E^{cor} is calculated using the formalism given in Chapter 3. Fig.[8.1] illustrates the wavevector dependence of correlation contributions to ρ . We find that modes near $\vec{q} = \vec{Q}$ soften, making a negative contribution to ρ . As indicated in this figure we also find that for the model parameters chosen, collective modes at momenta near $(0, 0)$ have complex energies for both values of $\vec{P}$. This finding reflects the tendency of extended Hubbard models, and of real cuprate materials, to longer period density-wave instabilities[4]. In our picture these ubiquitous instabilities, which seem to be material specific, do not play an essential role in underdoped-cuprate superfluid

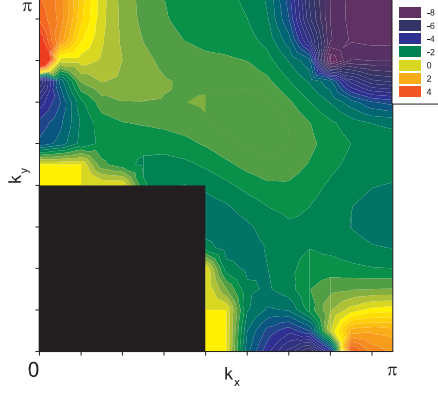


Figure 8.1: $\vec{q}$ -dependence of $\rho^{cor}(\vec{q})$ for model parameters given in the text. $\rho^{cor}(\vec{q})$ is plotted in dimensionless units normalized to average to ρ^{cor}/ρ^{MF} , which has the value -1.6 in this case. The GRPA excitation energies in the black area near $\vec{q} = (0, 0)$ are imaginary reflecting longer length scale instabilities[4] of the extended Hubbard model we use.

density suppression. Since the contributions to ρ^{cor} from $\vec{q}$ near zero are very small, as shown in Fig.[8.1], we do not believe that the inability of extended Hubbard models to describe small $\vec{q}$ excitations reliably influences our main conclusions.

We find that ρ^{cor}/ρ^{MF} is negative and of order -1 in the underdoped regime when extended Hubbard model parameters are in the range thought to represent underdoped cuprates. We conclude that a substantial suppression of the superfluid density due to the pairing wavevector dependence of the correlation energy occurs in underdoped cuprates and that it is responsible for the downturn in the critical temperature. Our weak-coupling theory is of course unable to describe physics very near the termination of the superconductivity on the underdoped side, although there is some indirect evidence from experiment[36, 37] (for example from the relatively weak temperature dependence of ρ) that critical fluctuations are important in a relatively narrow doping range.

Why does the correlation effect give this large suppression of superfluid den-

sity? Why are the suppressions much stronger near $\vec{q} = \vec{Q}$? In the next section we will answer these questions with the context of a Berry phase coupling existing in the fluctuations of this system. This hidden coupling has been overlooked in the earlier theories and we will see that it is important to explain several unusual properties of the INSR and the superfluid density in the underdoped cuprates.

8.7 Qualitative argument based on Berry phase coupling

In this section we give a qualitative argument for the suppression of the superfluid density due to the correlation energy. The basic ideas presented here are independent of most microscopic details, and most easily described in terms of the properties of a low-energy effective-field model for the collective fluctuations of a weak-coupling d-wave superconductor. We construct a quantum action by introducing a set of states which incorporate the coupled triplet pairing and spin-density fluctuations on which we focus. $|\Psi[\phi, V]\rangle$ is the Fock-space Slater determinant ground state of the quadratic Hamiltonian

$$\mathcal{H}^{fluc} = H^{MF} + \sum_{i\sigma} \sigma V_i c_{i\sigma}^\dagger c_{i\sigma} + \Delta_m \left[\sum_{i\tau} (-)^\tau [\exp(i\phi_i) - 1] c_{i\uparrow}^\dagger c_{i+\tau\downarrow}^\dagger + h.c. \right]. \quad (8.17)$$

where $\Delta_m = -2V\Delta$ in the convention used in previous sections. (For notational simplicity we have exhibited here only fluctuations with zero spin projection along the quantization direction.) In Eq.[8.17], τ labels the four neighbours of each site on a two-dimensional square lattice, and $(-)^\tau$ represents the d-wave variation of mean-field near-neighbor pair potentials. Using these states as an approximate identity resolution leads to the following low-energy imaginary-time action for the collective

variables ϕ_i and V_i :

$$\mathcal{S} = \int_0^\infty d\tau \left[\hbar \langle \Psi[\phi, V] | \partial_\tau | \Psi[\phi, V] \rangle + E[\phi, V] \right], \quad (8.18)$$

where $E[\phi, V] = \langle \Psi[\phi, V] | H | \Psi[\phi, V] \rangle$ and H is the full microscopic Hamiltonian. Mean-field theory states are obtained by minimizing $E[\phi, V]$. The first term in the action captures a Berry phase coupling between pairing and spin-density fluctuations on which we now elaborate.

Our proposal is motivated in part by the observation that Berry phase coupling is strong at wavevectors near $\vec{Q} = (\pi/a, \pi/a)$. (Demler and Zhang[60] have demonstrated a closely related conjugate relationship between triplet pair and spin excitations.) The potentials associated with the two types of fluctuations are:

$$\begin{aligned} \partial \mathcal{H}^{(fluc)} / \partial V_{\vec{k}} &= \sum_{\sigma, \vec{p}} \sigma c_{\vec{p}-\vec{k}, \sigma}^\dagger c_{\vec{p}, \sigma} \\ \partial \mathcal{H}^{(fluc)} / \partial \phi_{\vec{k}} &= i \sum_{\vec{p}} \Delta_{\vec{p}} [c_{\vec{p}-\vec{k}, \uparrow}^\dagger c_{-\vec{p}, \downarrow}^\dagger - h.c.]. \end{aligned} \quad (8.19)$$

Pairing phase fluctuations are conjugated to spin-density fluctuations for $\vec{k}$ near $\vec{Q} = (\pi/a, \pi/a)$, just as they are conjugated to charge-density fluctuations for $\vec{k}$ near 0, because the d-wave property $\Delta_{\vec{p}+\vec{Q}} = -\Delta_{\vec{p}}$ implies that their commutator is proportional to the d-wave order parameter.

The Berry phase term can be evaluated explicitly for small fluctuations by using perturbation theory expressions for the wavefunctions which appear in the Slater determinant $|\Psi[\phi, V]\rangle$:

$$\mathcal{S}_{Berry} = \int_0^\infty d\tau \sum_{\vec{k}} C_{\vec{k}} \phi_{-\vec{k}} \partial_\tau V_{\vec{k}}, \quad (8.20)$$

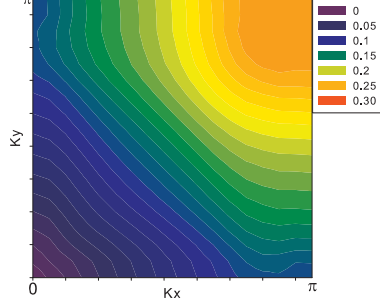


Figure 8.2: Berry's curvature $C_{\vec{k}}$ vs. $\vec{k}$ for the d -wave mean-field state of a generalized Hubbard model with parameters given in the text. $\Delta_m = 0.58$ in this case.

where

$$C_{\vec{k}} = 2 \sum_{\vec{p}} \frac{\text{Im} \left[\langle \chi_{\vec{p},-} | \frac{\partial \mathcal{H}^{fluc}}{\partial V_{\vec{k}}} | \chi_{\vec{p}+\vec{k},+} \rangle \langle \chi_{\vec{p}+\vec{k},+} | \frac{\partial \mathcal{H}^{fluc}}{\partial \phi_{-\vec{k}}} | \chi_{\vec{p},-} \rangle \right]}{(E_{\vec{p}+\vec{k}} + E_{\vec{p}})^2}. \quad (8.21)$$

In Eq.(8.21) we have made the usual Nambu spin-down particle-hole transformation of the mean-field Hamiltonian so that it has two eigenstates at each wavevector in the square lattice Brillouin zone with eigenvalues $\pm E_{\vec{p}}$, one ($\chi_{\vec{p},-}$) occupied and one ($\chi_{\vec{p},+}$) unoccupied. In Fig.[8.2] we show Berry curvature values calculated from this expression as a function of $\vec{k}$ which confirm our expectation that a peak should occur near $\vec{k} = \vec{Q}$.

We now argue that there is competition between the correlation energy gain due to antiferromagnetic fluctuations and d -wave singlet Cooper pair formation. Strong evidence for this view is provided by the apparent enhancement[39, 70] of antiferromagnetic fluctuations in cuprates in vortex cores and in the presence of external magnetic fields. Changes which weaken superconductivity enhance antiferromagnetism. Here we explore consequences for the dependence of correlation energy on $\vec{P}$. In our model the quadratic fluctuation action of a d -wave supercon-

ductor is

$$\mathcal{L}_{fluc} = \frac{1}{2\beta} \sum_{\omega, \vec{k}} [-2\hbar\omega C_{\vec{k},\omega} V(-\vec{k}, -\omega) \phi(\vec{k}, \omega) + K_{\vec{k},\omega}^{sp} |V(\vec{k}, \omega)|^2 + K_{\vec{k},\omega}^{\phi} |\phi(\vec{k}, \omega)|^2]. \quad (8.22)$$

In Eq.[8.22], K^{ϕ} and K^{sp} are phase and spin-density stiffnesses. The onset of antiferromagnetism occurs when $K_{\vec{Q},\omega=0}^{sp} = 0$. Frequency dependence is indicated in $C_{\vec{k}}$, $K_{\vec{k}}^{sp}$, and $K_{\vec{k}}^{\phi}$ to recognize the existence of non-adiabatic effects accounted for below in a GRPA approximation but neglected here. The quadratic fluctuation action then describes a system with collective modes at energies

$$E_{\vec{k}}^{res} = \frac{\sqrt{K_{\vec{k}}^{sp} K_{\vec{k}}^{\phi}}}{C_{\vec{k}}}, \quad (8.23)$$

and a corresponding zero-point energy contribution $E^{zp} = \sum'_k E_{\vec{k}}/2$. This adiabatic theory of the INSR mode is accurate only when $E_{\vec{k}}^{res}$ lies well below the particle-hole continuum; the prime on the wavevector sum above recognizes that this condition is satisfied only in underdoped samples and only near $\vec{k} = \vec{Q}$. The fluctuation correction to ρ is related to the pairing-wavevector dependence of the zero-point energy. We expect $K^{sp}(\vec{Q})$ to decrease with $\vec{P}$ because suppressed pairing favors antiferromagnetism. The magnitude of this dependence can be estimated roughly from experiment by associating the magnetic length ℓ_B at the magnetic field strength required to induce antiferromagnetism in a cuprate superconductor with the value of P^{-1} at which $K^{sp}(\vec{Q})$ goes to zero. Taking a typical value for this field ~ 100 Tesla and assuming that the resonance mode is well defined over the portion of the BZ with large Berry curvature (say $\sim 10\%$), gives a negative correlation energy contribution to the phase stiffness per two-dimensional cuprate layer of $\rho^{cor} \sim -0.1n\ell_B^2 E^{res} \sim -E^{res} \sim 0.05\text{eV}$, comparable to the value of ρ inferred from penetration depth measurements in optimally doped samples. Although this estimate is clearly very

rough, it does establish that the correlation correction to ρ can be substantial in the underdoped regime as the GRPA calculations in the last section have shown.

The next important task is to investigate the nature of these resonance modes. We propose that these resonance modes are just the peaks observed in the inelastic neutron scattering measurements, i.e. the INSRs. In the next chapter, we will apply our theory to explore the properties of the INSRs in underdoped Bi2212. The Bi2212 is one of the most heavily studied cuprates so that there already have a lot of experimental data. Therefore it is a great candidate for demonstrating the ideas proposed here.

Chapter 9

Hints from ARPES and INS on High- T_c Mechanism - A Study of Bi2212

Parts of this chapter have been submitted to Physical Review B.

9.1 Introduction

In the last chapter we have shown that the weak coupling BCS theory can account for the small superfluid density in the underdoped cuprates if the correlation effects due to the low energy quantum fluctuations are included within the GRPA scheme. This success is remarkable and motivates us to use the weak coupling theory to perform a systematical analysis. It is evident from many experiments[45, 71, 72] that high- T_c superconductors can be described at low energies by a weak coupling theory with effective interactions between square-lattice quasiparticles that lead to short-coherence-length d -wave superconductivity. After many years of study, the source of this effective interaction has still not been established with certainty.

The d-wave property is naturally associated with near-neighbor interactions, but these could be spin-independent (V) and possibly lattice mediated or Heisenberg-like (J) and possibly antiferromagnetic spin-fluctuation mediated. As shown in the previous study[60, 54, 55, 61] and in the last chapter, the resonance feature in inelastic neutron scattering[71], which appears to be generic in cuprates but absent in conventional superconductors, can be explained if interaction parameters are chosen so that the system is close to an antiferromagnetic instability, possibly one driven by strong-on site repulsion U .

In this chapter we attempt to draw conclusions about these interactions from the numerical arcana of cuprate superconductivity by requiring quantitative consistency between weak-coupling descriptions of neutron and ARPES data in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$. From ARPES antinodal gap values we conclude that $3J/2 - 2V \sim 250\text{meV}$, while from the occurrence of the INSR phenomenon we conclude that $2J + U \sim 350\text{meV}$. The proximity of these two energy scales strongly suggests that the Heisenberg interaction J dominates and, as we discuss, this in turn suggests that superconductivity is mediated by short-range antiferromagnetic interactions which are a remnant of the parent Mott-insulator.

9.2 Effective model and pairing potential for Bi2212

Let's come back to study the Hamiltonian given in Eq. 8.6 more rigorously. Since this Hamiltonian mostly describes the energy scale for the pairing potential necessary for the superconductivity, we do not view this phenomenological Hamiltonian as microscopic, but as what remains after incoherent high-energy electronic fluctuations are integrated out. In view of the Luttinger theorem, the chemical potential μ is nevertheless fixed by the doping concentration $x = 1 - \sum_{\vec{k},\sigma} \langle c_{\vec{k}\sigma}^\dagger c_{\vec{k}\sigma} \rangle$. The effective interaction parameters U , V , and J are assumed to be at least weakly doping dependent.

The order parameter for the d -wave superconducting state is $\langle c_{i\uparrow}c_{i+\hat{\tau}\downarrow} \rangle = (-)^\tau \Delta$, where $(-)^\tau = +1$ for $\hat{\tau} = \pm\hat{x}$ and -1 for $\hat{\tau} = \pm\hat{y}$ accounting for the d -wave character. Applying BCS mean-field theory to Eq.(8.6) leads to a gap function $\Delta(\vec{k}) = V_p \Delta (\cos k_x - \cos k_y)$ and to band energies $\epsilon \rightarrow \epsilon'$ which are modified by interactions. Here $V_p = 3J/2 - 2V$ has contributions from both interactions which can induce d -wave superconductivity. Mean-field ground state properties are completely determined by $\epsilon'(\vec{k})$ and V_p . The BCS Hamiltonian yields quasiparticles energies $\pm E(\vec{k}) = \pm(\epsilon'^2(\vec{k}) + \Delta^2(\vec{k}))^{1/2}$ which are measured in ARPES experiments. For $\epsilon'(\vec{k})$ we use the experimental Bi2212 normal state quasiparticle band structure[73]. Given this, the pairing potential V_p of the d -wave superconductivity is fixed by setting the mean-field maximum gap $\Delta_0 = 2|V_p|\Delta$ equal to ARPES antinodal gap[74, 75]. Table 9.1 summarizes V_p values obtained in this way for several underdoped Bi2212 samples. For concreteness we focus our discussion of numerical consistency between ARPES and INSR on the case of doping $x = .144$, reserving a discussion of doping dependence to the end of the paper. For $x = .144$, $V_p \sim 250\text{meV}$; the central question of cuprate superconductivity is whether this pairing is due to spin-independent attraction or due to antiferromagnetic spin-dependent effective interactions.

9.3 Competing nature between AFM and SC

The conclusions reached in this chapter depend critically on using the same weak-coupling Hamiltonian to consistently describe ARPES quasiparticle data and the INSR feature in neutron scattering experiments. As we explain in more detail below, the emergence of the INSR well below[51] the particle-hole continuum signals an incipient instability in cuprates, almost certainly the instability toward the antiferromagnetic state. In a weak-coupling GRPA theory the energy cost of static antiferromagnetic fluctuations K^s is the sum of quasiparticle and interaction energy contributions. The quasiparticle contribution K_{qp}^s is a property of the mean-field

Table 9.1: Singlet-pairing potential V_p for several underdoped Bi2212 samples. The doping x is extracted from experimental T_c data, assuming the parabolic relation proposed by Presland *et al.*[76].

x	T_c (K)	V_p (meV)	μ (meV)
0.144	92	250	-116.467
0.126	85	256	-111.358
0.11	75	278	-105.584
0.099	65	284	-102.369

state and based on ARPES data is $\sim 400\text{meV}$. We find below that $K^s = K_{qp}^s - 2J - U$ and conclude from qualitative and quantitative aspects of the INSR phenomenon that $K^s \ll K_{qp}^s$; more quantitatively a value close to $\sim 50\text{meV}$ seems likely. It follows that $2J + U \sim 350\text{meV}$. This conclusion is consistent with many experiments which hint at a close competition[77] between spin and superconducting order in cuprates. To explain this assessment more completely, it is necessary to describe the weak-coupling theory of spin and superconducting fluctuations in d-wave superconductors in greater detail.

9.4 GRPA theory for the INSR

Because the interactions in our model Hamiltonian are either on-site or nearest-neighbor, fluctuations at wavevector $\vec{q} = \vec{Q}$ can be expressed in terms of a small number of coupled channels[60, 61]. Specializing to the $S_z = +1$ projection of the triplet fluctuation spectrum, we identify seven operators whose fluctuations are

influenced by interactions:

$$\begin{aligned}
\hat{A}_1 &= \frac{1}{\sqrt{N}} \sum_{\vec{p}} S_{\vec{p}}^+ & \hat{A}_2 &= \frac{1}{\sqrt{2N}} \sum_{\vec{p}} s_{\vec{p}} S_{\vec{p}}^+ \\
\hat{A}_3 &= \frac{1}{2\sqrt{N}} \sum_{\vec{p}} d_{\vec{p}} (D_{\vec{p}} + \bar{D}_{\vec{p}}) & \hat{A}_4 &= \frac{1}{2\sqrt{N}} \sum_{\vec{p}} d_{\vec{p}} (D_{\vec{p}} - \bar{D}_{\vec{p}}) \\
\hat{A}_5 &= \frac{1}{\sqrt{2N}} \sum_{\vec{p}} d_{\vec{p}} S_{\vec{p}}^+ & \hat{A}_6 &= \frac{1}{2\sqrt{N}} \sum_{\vec{p}} s_{\vec{p}} (D_{\vec{p}} + \bar{D}_{\vec{p}}) \\
\hat{A}_7 &= \frac{1}{2\sqrt{N}} \sum_{\vec{p}} s_{\vec{p}} (D_{\vec{p}} - \bar{D}_{\vec{p}})
\end{aligned} \tag{9.1}$$

where $S_{\vec{p}}^+ = c_{\vec{p}\uparrow}^\dagger c_{\vec{p}+\vec{Q}\downarrow}$ is a spin-flip operator and $D_{\vec{p}} = c_{\vec{Q}-\vec{p}\downarrow} c_{\vec{p}\downarrow}$ and $\bar{D}_{\vec{p}} = c_{\vec{Q}-\vec{p}\uparrow}^\dagger c_{\vec{p}\uparrow}^\dagger$ are pair annihilation and creation operators. In Eq.(9.1) $s_{\vec{k}} = \cos k_x + \cos k_y$ and $d_{\vec{k}} = \cos k_x - \cos k_y$ are extended-s and d-wave form factors. The two-particle Greens functions which capture the fluctuations of these operators are:

$$\hat{\chi}_{ab}(\vec{Q}, \omega) = -i \int dt e^{i\omega t} \theta(t) \langle [\hat{A}_a(t), \hat{A}_b^\dagger(0)] \rangle. \tag{9.2}$$

We focus on the s-wave spin and d-wave pair fields ($\hat{A}_{1-4}$), which decouple from the d-wave spin and s-wave pair fields ($\hat{A}_{5-7}$) and are responsible for the INSR. Note that the extended-s spin-flip channel was not included in Refs. [60] and [61] and the equation for the total spin response therefore involved three rather than four coupled channels. As we will explain shortly, omission of this channel is a good approximation.

The GRPA Greens functions can be derived by expanding the Hamiltonian to quadratic order around the mean-field state and solving the equation-of-motion for $\hat{\chi}_{ab}(\vec{Q}, \omega)$. We find that

$$\hat{\chi}^{-1}(\vec{Q}, \omega) = \hat{\chi}_{qp}^{-1}(\vec{Q}, \omega) - \hat{V} \tag{9.3}$$

where $\hat{V} = \text{diag}(-U - 2J, J/2 - 2V, V + J/4, V + J/4)$ is the interaction kernel and

$$\hat{\chi}_{qp,ab}(\vec{Q}, \omega) = \frac{1}{N} \sum_{\vec{k}} \left(\frac{f_a f_b}{\omega - E(\vec{k}) - E(\vec{k}')} - \frac{(-1)^{a+b} f_a f_b}{\omega + E(\vec{k}) + E(\vec{k}')} \right) \quad (9.4)$$

is the bare mean-field-quasiparticle response function. In Eq.(9.4) $\vec{k}' = \vec{Q} - \vec{k}$, the factor $(-1)^{a+b}$ specifies the simple relationship between quasiparticle pair-creation and pair-annihilation matrix-elements[61] at $\vec{q} = \vec{Q}$, and the form factors f_a are[61]:

$$\begin{aligned} f &= (p^-(\vec{k}, \vec{k}'), \frac{s_{\vec{k}}}{\sqrt{2}} p^+(\vec{k}, \vec{k}'), d_{\vec{k}} l^+(\vec{k}, \vec{k}'), d_{\vec{k}} l^-(\vec{k}, \vec{k}')) \\ p^\pm(\vec{k}, \vec{k}') &= \frac{(u_{\vec{k}} v_{\vec{k}'} \pm v_{\vec{k}} u_{\vec{k}'})}{\sqrt{2}}, \quad l^\pm(\vec{k}, \vec{k}') = \frac{(u_{\vec{k}} u_{\vec{k}'} \pm v_{\vec{k}} v_{\vec{k}'})}{\sqrt{2}}. \end{aligned} \quad (9.5)$$

In the GRPA the ω dependence of $\hat{\chi}^{-1}$ comes from the ω -dependence of $\hat{\chi}_{qp}^{-1}$, which depends only on the band-structure, on the doping x , and on V_p . Typical numerical results for $\hat{\chi}_{qp}^{-1}(\vec{Q})$ are summarized in Fig. [9.1].

Since the INSR frequency is well below the particle-hole continuum, it is useful to expand $\hat{\chi}_{qp,ab}(\vec{Q}, \omega)$ to leading order in ω :

$$\begin{aligned} \hat{\chi}_{qp,ab}(\vec{Q}, \omega) &\approx R_0(a, b) - R_1(a, b)\omega + O(\omega^2) \\ R_0(a, b) &= \sum_{\vec{k}} \frac{-f_a f_b [1 + (-1)^{a+b}]}{E(\vec{k}) + E(\vec{k}')} \\ R_1(a, b) &= \sum_{\vec{k}} \frac{f_a f_b [1 - (-1)^{a+b}]}{[E(\vec{k}) + E(\vec{k}')]^2} \end{aligned} \quad (9.6)$$

The leading coupling between even and odd a operators is the Berry-phase coupling which appears at first order in ω ; the most important of these is the coupling between spin ($a = 1$) and d-wave-pair phase ($a = 4$), which is similar to the coupling between spin density and superconducting order parameter phase fluctuations found in the

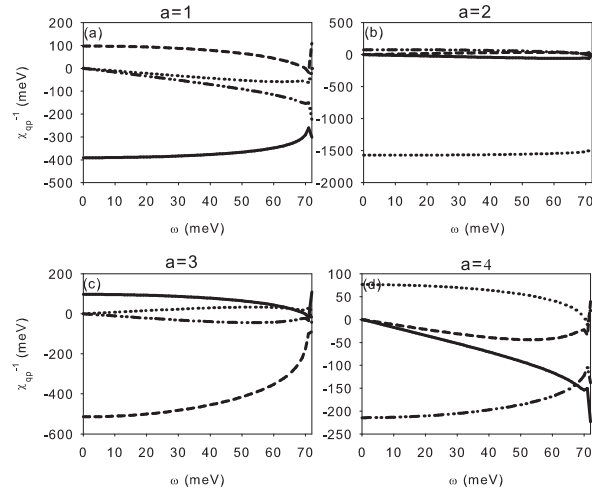


Figure 9.1: $\hat{\chi}_{qp,ab}^{-1}(\vec{Q}, \omega)$ for $\omega < \Omega_0$ where Ω_0 is the gap in the quasiparticle-pair excitation spectrum at $\vec{q} = \vec{Q}$ established by d -wave order. For each channel a , the solid, dotted, dashed, and dash-dotted lines represent respectively $\hat{\chi}_{qp,a1}^{-1}$, $\hat{\chi}_{qp,a2}^{-1}$, $\hat{\chi}_{qp,a3}^{-1}$, and $\hat{\chi}_{qp,a4}^{-1}$. ($\Omega_0 \approx 70\text{meV}$ for $x=0.144$ using the V_p value listed in Table 9.1.)

last chapter. Even-even and odd-odd fluctuations are coupled in the static limit. χ_{qp}^{-1} has a similar low-frequency expansion in which even-even and odd-odd fluctuations have little frequency-dependence until ω approaches the particle-hole continuum closely as seen in Fig.[9.1]. The even-even and odd-odd elements of $-\chi^{-1} \equiv K$ specify the energy cost of the corresponding density-fluctuations while the even-odd elements, approximately linear in frequency, specify how the collective fluctuation energy is quantized. The even-odd elements satisfy $\chi_{qp,ab}^{-1} \approx \omega C_{ab}$.

9.5 Magnetic plasmon and high- T_c pairing mechanism

The INSR energy E^{res} solves

$$\det|\hat{\chi}^{-1}| = \det|\hat{\chi}^{0-1} - \hat{V}| = 0. \quad (9.7)$$

To simplify our discussion of E^{res} we neglect the ($a = 2$) extended-s spin-density fluctuations which are much stiffer than other fluctuation modes, as shown in Fig.[9.1(b)], and the weak frequency dependence of the fluctuation energy contributions. With these approximations

$$E^{res} \approx \sqrt{\frac{K^s K^\phi K^{am} - K^\phi (K_{13}^{qp})^2}{K^{am} C_{14}^2 + K^s C_{34}^2 - 2K_{13}^{qp} C_{14} C_{34}}} \sim \frac{\sqrt{K^s K^\phi}}{C_{14}} \quad (9.8)$$

where $K^s = K_{11}^{qp} - U - 2J$, $K^{am} = K_{33}^{qp} + V + J/4$, and $K^\phi = K_{44}^{qp} + V + J/4$ are spin, π amplitude mode, and π phase mode stiffnesses respectively. Since $C_{14} \sim 2$ and the experimental value of $E^{res} \sim 40\text{meV}$ is small compared to $K_{11}^{qp} \approx 400\text{meV}$ and $K_{44}^{qp} \approx 200\text{meV}$, it is clear that interactions must substantially reduce the values of either K^s or K^ϕ , or both.

To understand the implications of this property more fully we start by discussing two extreme scenarios. We first assume that d-wave pairing is due entirely

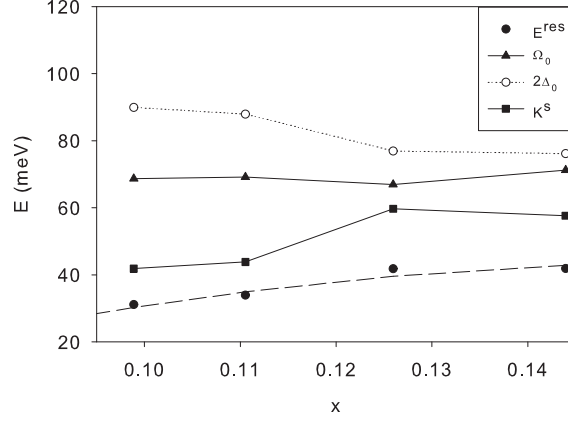


Figure 9.2: INSR energy E^{res} calculated from Eq. 9.7 (solid dots) with $U = V = 0$ and $J = \frac{2}{3}V_p$. The long-dashed line plots the empirical rule $E^{res} = 5.4k_B T_c$. The triangles, white dots, and the black squares show the doping dependencies of Ω_0 , $2\Delta_0$ calculated from V_p and the large-J model values for K^s .

to the Heisenberg near-neighbor interaction so that $J = 2V_p/3 \approx 180\text{meV}$. This choice is already consistent with the INSR experiments, even without invoking an additional on-site interactions, since it reduces $K_s \rightarrow 40\text{meV}$ and $E^{res} \rightarrow \sim 50\text{meV}$, in agreement with experiment. Near-neighbor Heisenberg interactions are therefore able to account simultaneously for pairing and for the INSR character. The dependence of the INSR position on doping obtained from the full GRPA theory after setting $J = 2V_p/3$ is shown in Fig.[9.2]. The good agreement across the full doping range strongly suggests that J is the only large coupling constant in the low-energy effective theory, with J ranging from ≈ 166 meV for $x=0.144$ to ≈ 190 meV for $x=0.099$.

What does this suggest about the character of the low-energy quasiparticles? First of all, the absence of a large repulsion U suggests that strong correlations between opposite spin-electrons have very substantially reduced the quantum amplitudes for double-occupation of the same lattice site. The picture which appears

appropriate is that of a single-particle Greens function which maintains Luttinger-theorem quasiparticle peaks near the Fermi energy, but has also developed incoherent lower and upper Hubbard band features in its spectral function. The interaction J would then seem to be the remanant of the parent Mott insulator's superexchange interactions. This picture is similar to the $t - J$ model[39], except that it does not start from rigid spin-charge separation. Indeed, even the size of the interaction J is reasonably consistent with antiferromagnetic-state exchange energies in cuprates. The reduction of the experimental band-width by approximately a factor of two compared to LDA estimates of bare bandwidths is also consistent with this scenario for the character of the quasiparticles in the weak-coupling theory. All this is just a picture and not a theory, of course - but it may suggest a direction for future work. It is remarkable that a single J can account simultaneously for both the the doping dependences of the antinodal gap and E^{res} .

The INSR position can also be accounted for of course by fine-tuning both U and V at fixed V_p . For example, if we first assume that d-wave pairing is due entirely to attractive spin-independent effective interactions $V = -V_p/2 \approx -130\text{meV}$. This value of V results in a small phase stiffness, $K^\phi \sim 70\text{meV}$ and would require that $U \sim 300\text{meV}$ in order to reduce E^{res} into the experimental range. This is a weaker correlation scenario in which the effective value of U is still fairly large. The INSR *magnetic plasmon* in this case has approximately equal pair-phase and spin character; in the large J scenario on the other hand the INSR mode has dominant spin character because $K^s \ll K^\phi$. More plausible is the choice $V = -J/4$, commonly used in $t - J$ model calculations and motivated by the theory of the superexchange mechanism. Compared to the J -only model, this choice shifts J slightly, from $J = 2V_p/3$ to $V_p/2$, resulting in slightly larger K^s and smaller K^ϕ without shifting the INSR position significantly.

9.6 Magnetic plasmon or spin exciton?

Finally we comment briefly on the interpretations of the magnetic plasmon and the spin exciton for the INSR. The key to distinguish these two interpretations is to identify the role of inter-channel Berry phase coupling, which has often been neglected in theoretical analyses, in determining the INSR position and character. When only the spin-channel is included (spin exciton), the equation for the resonance frequency is $K^s(E^{res}) = 0$. Because of the weak energy dependence of K_{qp}^s below the particle-hole continuum we see that when coupling is ignored, $U + 2J$ has to be adjusted to within $\sim 95\%$ of K_{qp}^s to explain the resonance position, placing the system even closer to the antiferromagnetic state instability point. For a given value of the interaction strength, mode coupling substantially lowers the resonance frequency. Mode coupling is therefore important in explaining the experimental relationship between the value of the resonance frequency and the proximity of the antiferromagnetic state, strongly suggesting that the magnetic plasmon is the better interpretation for the INSR than spin exciton.

Chapter 10

Conclusions

In this thesis we have explored several unusual properties of the two-dimensional systems with strong correlations.

Motivated by the rapid progress of the techniques for the layer-by-layer growth of the transition metal oxides, we have proposed two possible ways to create novel two-dimensional systems near the interfaces of the Mott-insulator-Mott-insulator (MIMI) heterostructures. In order to capture the effects of the on-site interaction U in strong coupling limit, in particular the Mott gap, we have adopted the Hartree-Fock theory for the magnetically ordered states and the dynamical mean-field theory for the paramagnetic states. While in the ferromagnetic state the Mott gap is corresponding to the gap between the bands of majority and the minority spins, in the antiferromagnetic state it is the gap produced by the nesting effect in the Brillouin zone between $\vec{k}$ and $\vec{k} + \vec{Q}$ where $\vec{Q} = (\pi/a, \pi/a)$. In the Hartree-Fock theory, the size of gap is $U - 6t$ for ferromagnetic state and approximately U for the antiferromagnetic state. For the paramagnetic state, the Hartree-Fock solutions incorrectly predict the metallic behavior because the only effect of U is to shift all the bands by a constant. To resolve this problem, the dynamical mean-field theory which includes *all* the local fluctuations is exploited. The two-site dynamical

ical mean-field theory predicts that the Mott transition occurs at $U^c \approx 14.7$ for a three-dimensional single-band Hubbard model, which seems to be realistic for the cubic perovskite Mott insulators AMO_3 . All these approaches have been described in details in chapter 2.

The ability to capture the Mott gap in the theoretical approaches is very important since we intend to propose the 'gap engineering' for the transition metal oxides in an analog of the semiconductors. In Chapter 5 the modulation doping in the MIMI heterostructures is discussed. We find that the modulation doping can occur in the MIMI heterostructure and the key factors for experimental controls of the two-dimensional system created near the interface can be estimated by a Thomas-Fermi theory complemented by the Hartree-Fock theory and the dynamical mean-field theory. In Chapter 6, the same theoretical framework is applied to another different type of MIMI heterostructure which consists of polar and nonpolar Mott insulators. We show that the two-dimensional system can be created near the interface and the surface of the polar material due to a mechanism driven by *polar catastrophe* in a similar way to the $\text{LaAlO}_3/\text{SrTiO}_3$ superlattices. This effect is unique in the transition metal oxides and does not occur in the semiconductors due to different characters of the conduction bands; more localized d conduction band in the transition metal oxides and more extended p conduction band in semiconductors. We believe that appropriate choices of the materials based on these two ideas will allow more possibilities for exploring new interesting systems and electronic devices.

Although we have shown the existence of the new two-dimensional system in the MIMI heterostructures, the low energy effective theory to describe the two-dimensional system is still lacking. It is inevitable that many realistic details, like orbital degeneracy, Jahn-Teller effect, etc. would have non-negligible influences in the low-energy theory. As we argued in the last section of Chapter 6, since an

orbital ordering is most likely to occur at the very low temperature, the single-band Hubbard model may be a reasonable starting point to investigate the interfacial two-dimensional system. In other word, the two-dimensional system created near the Mott insulator heterojunction may be an ideal candidate for the *doped Mott insulator* which has been intensively studied in the last few decades due to the high- T_c cuprate superconductors.

We devoted the second part of this thesis to study the resonance modes observed in the inelastic neutron scattering measurements and the superfluid density of the underdoped high- T_c cuprates. Motivated by the fact that the weak coupling BCS theory work relatively well in the overdoped region, we have managed to extend the same weak coupling theory to the underdoped region. We find that the weak coupling theory can account for various unusual properties in the underdoped cuprates if the correlation effects due to the quantum fluctuations are treated rigorously within the GRPA scheme. While the earlier theories did not imply any relationship between these two properties, in Chapter 8 we have proposed that they are closely related to each other via a Berry phase coupling between the spin fluctuation and phase fluctuation of the d -wave superconducting order parameter. In Chapter 9, we further concluded from our detail analysis on a realistic model for Bi2212 that the pairing mechanism of high- T_c superconductor is more likely anti-ferromagnetic fluctuations.

The superconductivity in the cuprates has been widely believed to be the remanence of its Mott-insulator parent compound. However, there are still debates on whether the influence of the Mott physics remains robust as the doping is introduced, providing the facts that the parent compound is actually a charge-transfer type Mott insulator, and that the antiferromagnetic phase, a hallmark of Mott insulator, vanishes rapidly with the presence of holes. A recent study of optical conductivity measurements on LSCO suggests the strength of the on-site interac-

tion is not that strong as required for being a Mott insulator[78]. Our fitted model for the underdoped Bi2212 also implies that small effective interaction parameters and standard GRPA calculations on the weak coupling BCS states are enough to describe a number of physical properties of the underdoped cuprates and none of these comes from the unusual strong-coupling feature of Mott insulators. Our work aims at proposing another viewpoint starting from the weak coupling theory rather than from the strong coupling theory of a doped Mott insulator. It will be a challenging task to investigate how these theories in two extreme limits merge at intermediate doping, and the progress will require more detail comparisons of theories and experiments.

Appendix A

Derivation of Self-Consistent Equations of Dynamical Mean-Field Theory

The derivation here closely followed the one given in Ref.[6]. Equating Eqs. 2.1 and 2.2 leads to:

$$e^{-S_{eff}} = \int \prod_{i \neq o} D[c_{i\sigma}^*] D[c_{i\sigma}] e^{-S} \quad (\text{A.1})$$

In order to see what S_{eff} looks like, it is convenient to divide the original action S in Eq. 2.1 into three terms:

$$\begin{aligned}
S &= S_o + \Delta S + S^{(o)} \\
S_o &= \int_0^\beta d\tau c_{o\sigma}^* (\partial_\tau - \mu) c_{o,\sigma} + U n_{o\uparrow} n_{o\downarrow} \\
\Delta S &= - \int_0^\beta d\tau \left\{ \sum_{i,\sigma} t_{io} (c_{i\sigma}^* c_{o,\sigma} + c.c) \right\} \\
&\equiv \int_0^\beta d\tau \left\{ \sum_{i,\sigma} \eta_i c_{i\sigma}^* + c_{i\sigma} \eta_i^* \right\}
\end{aligned} \tag{A.2}$$

where $\eta_i \equiv t_{io} c_{o\sigma}$ and $S^{(o)}$ is the remaining part of the original action without any terms related to site o . Substituting the above equations into Eq. A.1, we find:

$$e^{-S_{eff}-S_o} = \int \prod_{i \neq o} D[c_{i\sigma}^*] D[c_{i\sigma}] e^{-S^{(o)} - \Delta S} \tag{A.3}$$

It's clear that the right-hand side is just the generating functions of connected n -particle Green's function of the system with action $S^{(o)}$. Using the relation between the Generating function and the connected n -particle Green's function[8], S_{eff} can be written by:

$$\begin{aligned}
S_{eff} &= S_o + \sum_{n=1}^{\infty} \sum_{i_1, j_1 \dots i_n, j_n} \int_0^\beta d\tau_{i_1} d\tau_{j_1} \dots d\tau_{i_n} d\tau_{j_n} \eta_{i_1}^* \dots \eta_{i_n}^* \\
&\times \eta_{j_1} \dots \eta_{j_n} G_{i_1 \dots j_n}^{(o)}(\tau_{i_1} \dots \tau_{i_n}; \tau_{j_1} \dots \tau_{j_n})
\end{aligned} \tag{A.4}$$

where $G^{(o)}$ is the Green's function of the system *without* site o . We must try to relate $G^{(o)}$ to the Green's function of the original full Hubbard model (denoted as G). However, there is no general expression for this relation, except in the $d \rightarrow \infty$ limit.

Before discussing the $d \rightarrow \infty$ limit, it is essential to find out the appropriate scaling for parameters of the Hamiltonian. As the dimension increases, the U term is not affected since it is an on-site term. The kinetic term is, however, strongly affected. It becomes more clear if we write the kinetic term in k space for a d -dimensional simple cubic lattice:

$$\begin{aligned} H_k &= \sum_{k,\sigma} \epsilon_k n_{k,\sigma} \\ \epsilon_k &= -2t \sum_{j=1}^d \cos k_j \end{aligned} \tag{A.5}$$

The density of states (DOS) is simply:

$$D(E) = \frac{1}{V} \sum_k \delta(E - \epsilon_k) \tag{A.6}$$

It can be seen that for each k -point, ϵ_k involves a summation over d numbers ranging from -1 to 1 , which can be considered as a random walk. Therefore we can apply the central-limit theorem[9] to obtain DOS in $d \rightarrow \infty$ limit:

$$D(E) = \frac{1}{2t\sqrt{\pi d}} \exp[-(E/2t\sqrt{d})^2] \tag{A.7}$$

In order to have a non-trivial result, the DOS must remain finite in $d \rightarrow \infty$ limit so that t must scale as $t \propto t^*/\sqrt{d}$. This scaling behavior is quite important because it ensures the scaling of Green's function G_{ij} is at least $\propto 1/\sqrt{d}^{|i-j|}$. That implies in $d \rightarrow \infty$ limit, many Feymann diagrams will vanish so that only few diagrams need to be considered.

It has been concluded[6] that the only remaining term in Eq. A.4 in $d \rightarrow \infty$

is $n = 1$ term. Therefore the effective action reads:

$$S_{eff} = S_o + \sum_{i,j} \int_0^\beta d\tau_i d\tau_j t_{oi} t_{oj} G_{ij}^{(o)}(\tau_i, \tau_j) c_o^*(\tau_i) c_o(\tau_j) \quad (\text{A.8})$$

Substituting the definition of S_o in Eq. A.2, we can express S_{eff} in the form of quantum impurity model:

$$S_{eff} = - \int_0^\beta d\tau d\tau' \sum_\sigma c_{0\sigma}^\dagger(\tau) \mathcal{G}_0^{-1}(\tau - \tau') c_{0\sigma} + U \int_0^\beta d\tau n_{0\uparrow}(\tau) n_{0\downarrow}(\tau) \quad (\text{A.9})$$

where the free ($U = 0$) impurity Green's function is:

$$\mathcal{G}_0^{-1}(i\omega_n) = i\omega_n + \mu - \sum_{i,j} t_{oi} t_{oj} G_{ij}^{(o)}(i\omega_n) \quad (\text{A.10})$$

The last job is to relate $G^{(o)}$ to the full Green's function G . It can be shown[6] in a general lattice, the relation is:

$$G_{ij}^{(o)} = G_{ij} - \frac{G_{io} G_{oj}}{G_{oo}} \quad (\text{A.11})$$

After Substituting Eq. A.11 into Eq. A.9, we have two summations to perform. The first one is:

$$\sum_{i,j} t_{oi} t_{oj} G_{ij}(i\omega_n) \quad (\text{A.12})$$

For translational-invariant groundstate, the Fourier transform of the Green's function and t_{ij} can be simply expressed as: $G_{ij} = 1/V \sum_k G_k \exp[ik(R_i - R_j)]$ and

$t_{ij} = 1/V \sum_k \epsilon_k \exp[ik(R_i - R_j)]$ respectively, so that we have:

$$\begin{aligned}
& \sum_{i,j} t_{oi} t_{oj} G_{ij}(i\omega_n) \\
&= \frac{1}{V^3} \sum_{k,p,q} \sum_{i,j} \epsilon_k \epsilon_p G_q(i\omega_n) e^{ik(R_o - R_i)} e^{ip(R_o - R_j)} e^{iq(R_i - R_j)} \\
&= \frac{1}{V} \sum_q \epsilon_q \epsilon_{-q} G_q(i\omega) = \frac{1}{V} \sum_q \frac{\epsilon_q^2}{i\omega_n + \mu - \epsilon_q - \Sigma(i\omega_n)} \\
&= \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \frac{\epsilon^2}{\xi - \epsilon}
\end{aligned} \tag{A.13}$$

where $D(\epsilon)$ is the DOS for original full Hubbard model without U term defined in Eq. A.6, and ξ is defined as: $\xi \equiv i\omega_n + \mu - \Sigma(i\omega_n)$. Here the self-energy is independent of momentum due to the locality of the Green's function in $d \rightarrow \infty$ limit.

The remaining summation is:

$$\begin{aligned}
& \sum_{ij} t_{oi} t_{oj} G_{io}(i\omega_n) G_{oj}(i\omega_n) \\
&= \left(\sum_i t_{oi} G_{io}(i\omega_n) \right)^2 \\
&= \left(\frac{1}{V^2} \sum_{k,q} \sum_i \epsilon_k G_q(i\omega_n) e^{ik(R_o - R_i)} e^{iq(R_i - R_o)} \right)^2 \\
&= \left(\frac{1}{V} \sum_q \epsilon_{-q} G_q(i\omega_n) \right)^2 \\
&= \left(\int_{-\infty}^{\infty} d\epsilon D(\epsilon) \frac{\epsilon}{\xi - \epsilon} \right)^2
\end{aligned} \tag{A.14}$$

Special attention should be paid to the on-site Green's function $G_{oo}(i\omega_n)$. It is the on-site Green's function for the original full Hubbard model. However, it also equals to the on-site Green's function computed in the impurity model in Eq. A.9, as emphasized in section 2.3.1.

Now we have almost finished the derivation. The last job is to use the

following two identities:

(1)

$$\begin{aligned} \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \frac{\epsilon}{\xi - \epsilon} &= \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \left(\frac{\xi}{\xi - \epsilon} - 1 \right) \\ &= \xi G(i\omega) - 1 \end{aligned} \quad (\text{A.15})$$

(2)

$$\begin{aligned} \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \frac{\epsilon^2}{\xi - \epsilon} &= \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \epsilon \left(\frac{\xi}{\xi - \epsilon} - 1 \right) \\ &= \xi \int_{-\infty}^{\infty} d\epsilon D(\epsilon) \frac{\epsilon}{\xi - \epsilon} \\ &= \xi^2 G(i\omega_n) - \xi \end{aligned} \quad (\text{A.16})$$

where $\int d\epsilon D(\epsilon) = 1$ and $\int d\epsilon D(\epsilon) \epsilon = 0$ are used. After several substitutions, we finally obtain:

$$\begin{aligned} \mathcal{G}_0^{-1}(i\omega_n) &= i\omega_n + \mu - \sum_{i,j} t_{oi} t_{oj} G_{ij}^{(o)}(i\omega_n) \\ &= i\omega_n + \mu - \left[\xi^2 G(i\omega_n) - \xi - (\xi G(i\omega_n) - 1)^2 / G(i\omega_n) \right] \\ &= i\omega_n + \mu - \xi + G^{-1}(i\omega_n) \\ &= \Sigma(i\omega_n) + G^{-1}(i\omega_n) \end{aligned} \quad (\text{A.17})$$

It leads to the most important equation for DMFT:

$$\mathcal{G}_0^{-1}(i\omega_n) - G^{-1}(i\omega_n) = \Sigma(i\omega_n) \quad (\text{A.18})$$

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