Electronic and magnetic properties of strongly correlated systems

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by

Tsan-Chuen Leung

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CHAPTER 1. INTRODUCTION

Since the discovery of high $T_c$ superconductivity in the copper oxides materials, theoretical study of strongly correlated electron systems has been once again a focal point in condensed matter physics. The first breakthrough in high $T_c$ superconductivity was made by Bednorz and Müller[1], who won the Nobel prize because of their discovery in the $La_{2-x}Ba_xCuO_4$ system with $T_c$ between 30 and 40 K in 1986. In 1987 the $T_c$ was driven to nearly 50 K in the $La_{2-x}Sr_xCuO_4$ system by Tarascon et al. [2], and later 90 K in the $YBa_2CuO_7$ system by Wu et al. [3]. In the early 1988, soon after Maeda et al. [4] and Chu et al. [5] discovered the $Bi_2Sr_2CaCu_2O_{8+y}$ system with $T_c = 110$ K, Sheng et al. [6] found the $Tl_2Ba_2CaCu_2O_{8+y}$ system with $T_c = 115$ K. Then a series of structures of the form $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ were found, with $T_c$ increasing with the index $n$. In the limit of $n \to \infty$, we obtain their parent structure, $CaCuO_2$. A $Ca_{0.86}Cu_{0.14}O_2$ single crystal was grown, and reported to be an antiferromagnetic insulator with $T_N = 540 K$ [7]. There are certain features in common for these high $T_c$ materials, particularly the existence of the square $CuO_2$ layers, which contribute to most of the unusual features of the normal, the magnetic, and the superconducting state. The crystal structures of $La_2CuO_4$ and $YBa_2Cu_3O_7$
are shown in Figure 1.1, and the phase diagrams which describe the transition between normal-superconducting and paramagnetic-antiferromagnetic of the $La_2CuO_4$ and $YBa_2Cu_3O_7$ are shown in Figure 1.2. We see that $La_2CuO_4$ and $YBa_2Cu_3O_6$ are antiferromagnetic insulators, hence all the parent structures of high $T_c$ materials found are antiferromagnetic insulators.

Many calculations in the past decade have demonstrated that the local spin density functional approximation (LSDA) gives a good description of ground state properties of many moderately correlated systems [8]. LSDA has become the de facto tool of first-principles calculations in solid state physics, and has contributed significantly to the understanding of material properties at the microscopic level. For strongly correlated systems, the LSDA often fails. The failure of the LSDA is caused mainly by strong correlation effects. The valence electrons in the solid have a strong tendency to hop from atom to atom because this process will lower the kinetic energy due to the decreased spatial localization of the wave function. These kind of itinerant states are well described by the band picture. However, the Coulomb repulsion between electrons will oppose the hopping of the electrons between atoms. When the cost in potential energy arising from hopping outweighs the saving in kinetic energy, the electron becomes localized. Once the states are localized by strong intrasite Coulomb correlations, the magnetic interactions and tendency to integral occupation of such states strongly favors the antiferromagnetic ground state. Therefore antiferromagnetic materials are frequently strongly correlated systems. P. W. Anderson introduced a model [9] in order to understand why the majority of insulating magnetic materials were antiferromagnetic. Independently, John Hubbard studied the
magnetism and metal-insulator transitions by introducing a separate model [10], a
generalized version of the Anderson model, which gives the approximate solutions to
the many-body problem of a metal with strong intrasite Coulomb interactions.

Since the parent structures of high $T_c$ materials are antiferromagnetic insula-
tors, the wavefunctions responsible for the magnetism are very likely to be localized.
We believe that a detailed knowledge of the normal state electronic structure and
excitations will give important insight into the understanding of the nature of the
superconductivity in these materials. Therefore in this thesis we will first use the
LSDA to evaluate the electronic and magnetic properties of $La_2CuO_4$ and the re-
lated materials, and see what can be learned about high $T_c$ materials from the LSDA?
Then we will consider correlation effects. Since the treatment of strong intra-atomic
correlations in solids is difficult, it is appropriate at this stage to study model systems
which hopefully reveal the correct qualitative physics. Quantum Monte Carlo meth-
ods have recently been used to study finite two dimensional Hubbard models, and
have been extended to three band models to better study the $CuO_2$ interactions [11].
The quantum Monte Carlo methods are presently restricted to finite lattices, finite
temperatures, and very large computers. We have developed a mean field calculation
of the multi-band Hubbard model based on a projection operator scheme [12, 13, 14]
which is able to treat the correlations for such models in a much faster but approx-
imate fashion. The method also has the desirable feature that it can be generalized
all the way to many atoms per unit cell with $s, p, d$ orbitals included. We will apply
the method to study the ground state in the one and three band Hubbard models,
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CHAPTER 2. LOCAL SPIN-DENSITY FUNCTIONAL APPROXIMATION

$Sc_2CuO_4$

Introduction

The discovery of antiferromagnetism in slightly oxygen-deficient $La_2CuO_4-y$ [15, 16, 17, 18] has added to the developing school of thought which is considering antiferromagnetic spin interactions rather than phonons as a possible mechanism for superconductivity in the new copper-oxide based high-$T_c$ materials [19]. In most of these theories the starting point is a Hubbard-like Hamiltonian, with on-site Coulomb repulsion playing the key role. The difficulty in performing accurate analytical or numerical calculations for general versions of these model Hamiltonians has hindered a quantitative comparison with the growing amount of experimental information. Band-theoretical calculations have been criticized for such systems because of their inaccurate treatment of on-site Coulomb correlation. On the other hand, band-theoretical methods allow precise numerical calculations and have been very successful in the last ten years in the evaluation of the parameters governing conventional superconducting properties. Indeed, band-theoretical methods have recently been applied to the $La_{2-x}Sr_xCuO_4$ system to evaluate the electron-phonon coupling
and the transition temperature, with results in reasonable agreement with experiment [20]. It is therefore of interest to further test the band theoretical approach by evaluating the magnetic properties. To this end we have used a first-principles linear combination of atomic orbitals (LCAO) method to study both the ferromagnetic and antiferromagnetic response of Sc$_2$CuO$_4$. The Sc compound was chosen for the majority of the calculations in this calculation because of the fewer number of core electron (compared to La) which greatly facilitated calculations using the LCAO codes. As discussed below, the Sc and La potentials have a similar effect on the occupied band structure of these compounds, so that the conclusions we obtain with regard to the Cu – O interactions should be common to both materials.

Method

The self-consistent calculations were performed with an accurate first principles linear combination of atomic orbitals (LCAO) method [21]. In the LCAO method the trial wavefunctions are written in the linear combination of Bloch sums of localized orbitals centered at the atomic sites,

$$\Psi_k(\mathbf{r}) = \sum_{\nu nl m} b^{\nu nl m} \Phi_{\nu nl m}(\mathbf{r} - \mathbf{\tau}_\nu)$$ \hspace{1cm} (2.1)

$$\Phi_{\nu nl m}(\mathbf{r} - \mathbf{\tau}) = \frac{1}{N^{1/2}} \sum_{\mathbf{R}} e^{i \mathbf{k} \cdot \mathbf{R}} \phi_{\nu nl m}(\mathbf{r} - \mathbf{R} - \mathbf{\tau}_\nu)$$ \hspace{1cm} (2.2)

where the $\mathbf{R}$ sums run over the sites in the Bravais lattice, and the $\nu$ sums run over the basis of atoms in the unit cell. The $\phi_{\nu nl m}(\mathbf{r} - \mathbf{R} - \mathbf{\tau}_\nu)$ is the atomic orbital located at $\mathbf{R} + \mathbf{\tau}_\nu$. Each radial function $u_{nl}(r)$ is written as a linear combination of Gaussians.
\[ u_{nl}(r) = \sum_{i=1}^{i_{\text{max}}} C_{i}^{nl} r^l e^{-\alpha_{i} r^2} \] (2.3)

The coefficients \( C_{i}^{nl} \) are obtained from a converged self-consistent atomic calculation. In order to avoid the overcompleteness problem in the solid, we re-solve the Schrödinger equation of an isolated atom non-self-consistently using the self-consistent potential obtained before, but eliminating the longest-range Gaussian in the basis for the radial function. The expansion coefficients \( b_{\nu n l m}(k) \) in (2.1) are determined by minimizing the energy with respect to each coefficient with the constraint that the norm of the wavefunction is conserved.

\[ \frac{\partial}{\partial b_{\nu n l m}^*} <\Psi_{k}|H|\Psi_{k}> - E \frac{\partial}{\partial b_{\nu n l m}^*} <\Psi_{k}|\psi_{k}>= 0 \] (2.4)

Substituting (2.1) and (2.2) into (2.4), we obtain the secular equation

\[ \sum_{\nu n l m} [H_{\nu' n' l' m'};\nu n l m(k) - ES_{\nu' n' l' m';\nu n l m}(k)] b_{\nu n l m}(k) \] (2.5)

where

\[ H_{\nu' n' l' m';\nu n l m}(k) = \sum_{R} e^{ik\cdot R} \int u_{\nu' n' l' m'}(r - \tau_{n'}) H u_{\nu n l m}(r - R - \tau_{n'}) d^3r \] (2.6)

\[ S_{\nu' n' l' m';\nu n l m}(k) = \sum_{R} e^{ik\cdot R} \int u_{\nu' n' l' m'}(r - \tau_{n'}) u_{\nu n l m}(r - R - \tau_{n'}) d^3r \] (2.7)
The eigenvalues and the expansion coefficients of the wavefunctions can be calculated from equation (2.5) by using the subroutines in the EISPACK package of computer subroutines.

The charge (spin) density is written as a linear combination of Gaussian functions, the expansion coefficients are determined by a least squares fit to the exact charge (spin) density obtained from the occupied wave functions. In order to avoid overcompleteness of the charge density Gaussian basis functions, we have to monitor the eigenvalues of the basis overlap matrix carefully. When the smallest eigenvalue is very close to zero, we should reduce the number of Gaussian functions.

The potential is also expanded in a Gaussian basis, for convenience we use the same basis as we use in the charge density expansion. In order to make allowance for the singular nature of the screened nuclear potential at $r \to 0$, we add one additional term at each atomic site $\nu$ of the form $(Z_\nu/r)\exp(-\beta_0^\nu r^2)$, where $\beta_0^\nu$ is one of the Gaussians in the potential basis with value of $\sim 100$ a.u.. The exchange-correlation potential $V_{xc}$ is also expanded in the same Gaussian basis, and the expansion coefficients are determined by a least squares fit to the $V_{xc}(r_i)$ evaluated on a real space mesh. Since the radial part of the atomic basis functions, potentials, charge densities, and spin densities are expanded about atomic sites in a series of Gaussian functions, most integrations are handled analytically.

The frozen-core approximation was used in the calculation. In order to get a better result, we use a new set of basis functions obtained by orthogonalizing the noncore Bloch sums to all the core-state Bloch sums

$$\Phi_{nlm}^{\nu \text{eff}}(r - r\nu, k) = \Phi_{nlm}^{\nu}(r - r\nu, k)$$
\[
\sum_{\nu' n' l' m'} < \Phi_{\nu' n' l' m'}^c (r - \tau_{\nu'}, k) | \Phi_{\nu n l m}^v (r - \tau_{\nu}, k) > \Phi_{\nu' n' l' m'}^c (r - \tau_{\nu'}, k)
\] (2.8)

where the summation over \( \nu', n', l', \) and \( m' \) covers all the core states and all the atoms in the unit cell. Replacing the indices \( \{ \nu, n, l, m \} \) by \( i \), the secular equation now can be written as

\[
(H^{\text{eff}} - E S^{\text{eff}}) b = 0
\] (2.9)

where

\[
H_{ij}^{\text{eff}} = \langle \Phi_{i}^{\text{eff}} | H | \Phi_{j}^{\text{eff}} \rangle
\] (2.10)

\[
\langle \Phi_{i}^{\text{eff}} | H | \Phi_{j}^{\text{eff}} \rangle = H^{uvij} - \sum_{c} S^{uic} H^{cvj} - \sum_{c} H^{vjc} S^{cu} + \sum_{cc'} S^{uci} H^{cjc} S^{cvj}
\] (2.11)

\[
\langle \Phi_{i}^{\text{eff}} | \Phi_{j}^{\text{eff}} \rangle = S^{uvij} - 2 \sum_{c} S^{uic} S^{cvj} + \sum_{cc'} S^{uci} S^{cjc} S^{cvj}
\] (2.12)

We have used this method recently to successfully calculate the electronic structure and total energies of Si [22], Nb and Mo [23], and AlN [24]. In addition, we have tested the spin polarized version of the codes and obtained results in excellent agreement with calculations on Ni [25] and Cr [26]. For the spin-dependent local-density approximation to the exchange correlation potential we have used the von
Barth-Hedin form [27] as modified by Moruzzi et al. [28]. Besides the core states, the atomic basis consisted of $4s$, $4p$, and $3d$ functions on Sc; $2s$ and $2p$ functions on O; and $4s$, $4p$, and $3d$ functions on Cu. The lattice constants as measured by neutron scattering for $La_2CuO_4$ were taken from Jorgenson et al. [29]. With these lattice constants it was found that the lowest Sc 3d band remained unoccupied but dropped below the highest Cu – O antibonding band (at the X point in the tetragonal structure). This was the only significant difference with the band structure of $La_2CuO_4$. The lower Sc 3d band is related to the smaller ionic radius of the Sc atom compared to La. By decreasing the Sc – O distance along the axis perpendicular to the plane (this changed the lattice constant for the long axis from 25.045 to 24.00 a.u.) we found that the Sc – O interaction mimicked the La – O interaction. That is, the bottom Sc 3d band was raised so that the modified $Sc_2CuO_4$ bands closely resemble the $La_2CuO_4$ bands. The rest of the calculations on $Sc_2CuO_4$ were made with this modification of the lattice constants. The Cu – O in-plane separations were kept the same for both compounds.

Results

The band structure for $Sc_2CuO_4$ in the tetragonal phase (one formula unit per cell) is shown in Figure 2.1. The bands are very similar to those reported for $La_2CuO_4$ [30, 31]. The Fermi energy cuts a single band at the top of the Cu3d and O2p complex of 17 bands having a total width of about 10 eV. The Cu 3d-like character is spread throughout the bands in this energy range with the lowest band at the X-point consisting of bonding states between the Cu 3d$2x^2-y^2$ orbital and the nearest neighbor, in plane, O 2pz and 2py orbitals. The corresponding antibonding
band is at the top of the complex and is half occupied. The calculated Fermi surface is in good agreement with that reported by Xu [32] which differs only slightly from that of Mattheis [31]. An important quantity in the discussion of the magnetic properties is the generalized susceptibility

$$\chi^0(q) = \sum_k \frac{f(k)(1 - f(k + q))}{E(k + q) - E(k)},$$

(2.13)

which is shown in Figure 2.2 for q along the [110] direction. The wave vector corresponding to the observed antiferromagnetic ordering occurs in this direction at the zone boundary X point [16]. The calculated $\chi^0(q)$ for the partially occupied band is very similar to that reported for $La_2CuO_4$ by Xu et al. [32]. The magnitude of $\chi^0(q = 0) = \frac{1}{2} N(E_F) = 5.6\text{states}/(RyCell)$ is somewhat smaller than the $7.3\text{states}/(RyCell)$ of Xu et al. for $La_2CuO_4$ and our own value of $6\text{states}/(RyCell)$ for $La_2CuO_4$. The value of $\chi^0(q = X)$ is $11.7\text{states}/(RyCell)$ which is more than double the $\chi^0(q = 0)$ value.

We first consider the ferromagnetic response corresponding to $q = 0$. The unenhanced Pauli susceptibility is $\chi_{\text{B}} = 2.6 \times 10^{-5}\text{cm}^3/\text{mol}$. To calculate the enhancement we performed self-consistent spin-polarized calculations with an applied field created by shifting the spin-up (down) bands by $-2(+2)\text{mRy}$. These calculations were made for $Sc_2CuO_4$ in the tetragonal structure with $20k$ points sampled in the irreducible $1/16$ th of the Brillouin zone [33]. The band splitting, $\Delta E(k) = I(k)m$, was found to be nearly uniform near the Fermi level and gave an average for $I$ of about $0.030\text{Ry}$ cell. Thus the Stoner enhancement $S = [1 - IN(E_F)/2]^{-1} = 1.2$ is not very large, and indicates the ferromagnetic ground state is not stable. Indeed,
whenever we released the applied field during our calculations, the moment quickly decayed to zero in a few iterations. It is difficult to extract an experimental value for the Pauli susceptibility of $La_2CuO_4$ since many samples have some oxygen vacancies and order antiferromagnetically with $T_N$ as high as 290K [15]. Since the measured susceptibility above $T_N$ is not Curie-Weiss-like and seems to be similar for samples with various values of $T_N$, there may be some justification in making a comparison between our calculated value and the high temperature susceptibility. The measured $\chi$ at 500K is about $5 \times 10^{-5} cm^3/mol$ and rises gradually to about $7 \times 10^{-5} cm^3/mol$ and is a factor of 2 larger than our calculated $\chi_p = 3.0 \times 10^{-5} cm^3/mol$. The theoretical temperature dependence is small and amounts to less than 10% at 600K.

A potentially more informative measure of the ferromagnetic response would be the induced magnetic form factor as measured by neutron scattering. This is not the same as the form factor measured for the antiferromagnetic ordered state, but rather is a measure of the induced ferromagnetic spin density arising in response to an applied field. The applied field shifts the spin-up and spin-down bands only slightly, and the repopulation of states near the Fermi energy results in an induced spin density corresponding to the charge density for states on the Fermi surface:

$$S(r) = 2\mu^2_B \int_{E=E_F} \frac{dS}{|\nabla E|} |\psi_k(r)|^2.$$  \hspace{1cm} (2.14)

As discussed above, the states at $E_F$ are predominantly an antibonding combination of $d_{x^2-y^2}$ orbitals on Cu with $p_x$ an $p_y$ orbitals on O. This means that unlike the antiferromagnetic case described below, each in plane oxygen site has a fairly large moment (55% that of the Cu moment) and the contributes substantially to the form
factor. If band theory were incorrect and the moments were isolated on the Cu sites, the measured form factor would resemble an ionic Cu form factor. The calculated form factor is shown in Figure 2.3 and it differs from the Cu ionic form factor for reflections which involve destructive interference from the oxygen moment. Since the Fermi energy lies well above the center of the Cu $d$ and $O$ $p$ bands and below the Sc or La $d$ bands, we do not expect a significant van Vleck orbital contribution to the form factor. Likewise the spin-orbit coupling for Cu is not strong enough to add more than a few percent of orbital contributions. Thus, the calculated form factor in Figure 2.3 provides a clear theoretical prediction based on the itinerant model and it will be interesting to compare with forthcoming experiments [34].

We now consider the antiferromagnetic ordering. One might expect pure $La_2CuO_4$ to be very near an instability since less than 1% oxygen vacancies are required to stabilize the antiferromagnetic ground state. Within the itinerant model this state would be predicted to be stable if $I(q)x^0(q) > 1.0$. Assuming for the moment that $I(q = X) = I(q = 0) = I$ we find $Ix^0(q = X) = 0.3$, which is far from a magnetic instability. Before accepting this conclusion there are several factors to consider such as the magnitudes of $I(q = X)$ and $x^0(q = X)$ as well as the effect of the orthorhombic distortion.

It is possible to make an estimate of $I(q = X)$. First we consider the bands for the observed orthorhombic structure so that there are now two formula units per primitive unit cell. As pointed out by Kasowski et al. [35], this distortion leaves the two Cu atoms in the cell equivalent and results in a set of degenerate bands on the surface of the new Brillouin zone. This would indicate that $La_2CuO_4$ must remain metallic, contrary to experiments [15, 36]. Antiferromagnetic ordering does spit these
degenerate bands (see Figure 2.4) and, by applying a staggered field at the Cu sites and calculating the splitting and moment per Cu, we obtain an estimate for $I(q = X)$ of $0.022\text{Ry cell}$. This gives $I\chi^0 = 0.2$ at $q = X$ which is smaller than the previous estimate using the value of $I$ at $q = 0$. The main reason $I$ is smaller at $q = X$ is that there is now no moment allowed (by symmetry) on the in-plane oxygen, so that states at $E_F$ which have substantial in-plane oxygen character in their wave functions are missing this contribution (from an oxygen moment) to the splitting.

The magnitude of $\chi^0(q)$ is dominated by the states near the Fermi level separated by wave vector $q$. If there is a nesting feature in the Fermi surface so that two planar sections are exactly separated by wave vector $Q$, a logarithmic singularity occurs in $\chi^0(q)$ at $Q$ and the system is unstable. We do not find exact nesting; however it is fair to ask what would happen (i.e., what ground state properties would result) if $\chi^0(q = X)$ were much larger. We have been able to answer this question semiquantitatively by performing self-consistent, spin-polarized calculations for the room-temperature orthorhombic structure (this structure results from a distortion of the tetragonal phase corresponding to the same wave vector, $q = X$, that describes the magnetic ordering). We effectively raise $\chi^0(q = X)$ by including in our sampling mesh $k$ points along the zone boundary where, in the absence of a moment bands 33 and 34, which cut the Fermi level, are degenerate. For the $k$ points on the zone boundary we occupy the 33rd band but not the 34th band which is a way placing the Fermi level in the middle of the antiferromagnetically split bands. This is of course a device to maximize the tendency for the antiferromagnetic state. If the dispersion of these bands were smaller than the splitting, the Fermi level would fall in the gap naturally; however, the dispersion along the zone boundary shown in Figure 2.4 for bands 33 and
34 is 0.7eV while the splitting for any reasonable moment (without an applied field) is less than 0.1eV. The dispersion is smaller for $La_2CuO_4$ (0.43eV) and is reduced 10% further by including the full low temperature orthorhombic distortion, but is still too large relative to the splitting to give a semiconducting gap. Nevertheless, with a fictitious gap forced by constraining the occupation for the zone boundary states, the calculations did proceed to a self-consistent antiferromagnetic ground state which is quite informative.

The calculated moment on the $Cu$ sites was $0.136\mu_B$ with each out-of-plane oxygen site above and below the $Cu$ site having a moment of about 10% of that of $Cu$ and aligned in the direction opposite the copper moment. The average splitting of bands 33 and 34 along $MNSL$ on the Brillouin zone surface was 0.04eV. We also added staggered fields (corresponding to a moment per Cu of up to $0.8\mu_B$) to see if the system might sustain a larger self-consistent moment, but found the moment per $Cu$ to level off at about $0.16\mu_B$ as long as only physically reasonable fields were used so that bands 33 and 34 were the only ones involved. In a simple system one might expect a saturation of $1\mu_B/atom$, but here the bands at $E_F$ consist of states with a large amount of wave function character on the in-plane oxygen sites which have an equal amount of spin-up and spin-down density. We calculated the magnetic form factor for the self-consistent ground state and find that the small out-of-plane oxygen contribution interferes with the $Cu$ contribution so that the calculated form factor (shown in Figure 2.5) differs noticeably from a $Cu$ ionic form factor. The form factor has been measured experimentally for only four reflections with fairly large error bars (also shown in Figure 2.5) and has a shape similar to the theory which suggests a moment on the out-of-plane oxygen may be present [16]. The most important aspect
of the experimental measurement is the magnitude which would indicate a moment per \( Cu \) of about \( 0.6\mu_B \). This is well out of range that can be reached by an itinerant model, and is also far from the \( 1\mu_B \) one might expect for a localized model.

Calculations similar to those described above were made for the antiferromagnetic state with an 8% larger and an 8% smaller planar lattice area (we assume the effect of pressure on the states near \( E_F \) will be dominated by the change of the in-plane lattice constant). Surprisingly the increase in \( I \) with pressure was enough to overcome the decrease in \( \chi \) and a small (\( \sim 5\% \)) increase in the antiferromagnetic response in predicted with pressure.

We have subsequently calculated both the Van Vleck and diamagnetic susceptibility and find \( \chi_{VV} \sim 4 \times 10^{-5}\text{emu/mol} \), \( \chi_{\uparrow\downarrow} \sim 1.5 \times 10^{-5}\text{emu/mol} \), and \( \chi_D = -11 \times 10^{-5}\text{emu/mol} \); so that the total susceptibility within a standard band-theoretical treatment is negative.

Discussion

Although our calculations were made for \( Sc_2CuO_4 \), the copper-oxygen geometry was the same as for \( La_2CuO_4 \) and the occupied band structure of the two compounds are nearly identical. We therefore expect the calculated physical properties of the two materials to be similar. The spin-polarized calculations indicated little tendency toward ferromagnetic or antiferromagnetic ordering. This is somewhat surprising since less than 1% oxygen vacancies are needed to stabilize the antiferromagnetic state in \( La_2CuO_4 \). More significant is the observed semiconducting behavior of pure \( La_2CuO_4 \) at low temperature [15], while band theory has no energy gap at the Fermi level. A somewhat similar situation occurs in other transition metal oxides such as
NiO, FeO, and CoO which are frequently described as Mott insulators. These compounds, however, have the center of the oxygen bands well below the transition metal d bands and it is the d bands which occur at the Fermi level. The antiferromagnetic ground states of these compounds are obtained by band theory, but for FeO and CoO the observed semiconducting state is not obtained [37]. The bands for La₂CuO₄ are quite different in the sense that the center of the oxygen 2p and copper 3d bands is the same so the width of the band complex (~ 9eV) is determined essentially by the bonding and antibonding states from the Cu – O pσ interaction. This band width means the usual criterion for Mott insulators \( W/U \ll 1 \) is not well satisfied or is in need of modification for this type of bonding. We suspect the LSDA is not adequate here and some on-site or intersite (Cu – O) correlation beyond that of the LSDA is required for further progress.

If some symmetry breaking in the charge distribution arises so that local moments (ordered or not) can appear on the copper site then the induced magnetic form factor should look quite different than what we have predicted. On the other hand if localized states are present, one might have expected the measured moment in the antiferromagnetic state to be closer to \( 1 \mu_B/Cu \) rather than the 0.6\( \mu_B \) estimated from experiment [16].
Figure 2.1: The self consistent band structure of Sc$_2$Cu$_4$ in the tetragonal phase.
Figure 2.2: The generalized susceptibility for $Sc_2CuO_4$ along the (110) direction. Contributions only from band 17, which cut the Fermi level, are included.
Figure 2.3: The induced magnetic form factor normalized to the total moment. The reflections are labeled with respect to the orthorhombic structure and \( \sin \theta / \lambda \) values are for the \( La_2CuO_4 \) lattice constants (see Ref. 16). The ionic \( Cu^{2+} \) form factor is shown for comparison.
Figure 2.4: The bands near the Fermi level for $Sc_2CuO_4$ in the orthorhombic structure with an applied staggered field corresponding to 0.5 $\mu_B$ per Cu site. The splitting along MNSL on the zone boundary is entirely due to the antiferromagnetic field.
Figure 2.5: The magnetic form factor for the antiferromagnetic state as described in the text. The values have been normalized to $1 \mu_B$ on the Cu site. The values of $\sin \theta/\lambda$ correspond to the lattice constants of $La_2CuO_4$ in the orthorhombic structure (see Ref. 16 and Ref. 29). The experimental data is from Ref. 16 and has been normalized to 1.0 for the second reflection, with error bars from Ref. 34. The line is the $Cu^{2+}$ ionic form factor.
La$_2$CuO$_4$ with constrained $d^9$ configuration

Introduction

The difficulties encountered in calculating the ground state electronic structure of La$_2$CuO$_4$ are well-known [20, 38, 39]. The strong on-site Coulomb energy, $U_d$, for Cu is believed responsible for the breakdown of the usually successful local spin density functional approximation (LSDA) which predicts incorrectly that La$_2$CuO$_4$ should be a metal. Also, spin-polarized LSDA calculations fail to obtain the observed antiferromagnetic ground state [38]. This failure of the LSDA has helped focus attention on Hubbard-type models which can explicitly treat the correlations arising from the large $U_d$. In the extreme limit of large $U_d$, there would be no $d^{10}$ fluctuations allowed and La$_2$CuO$_4$ could perhaps be described as closer to the ionic picture consisting of La$^{3+}$, Cu$^{2+}$, and O$^{2-}$ ions. Here we consider this limit by constraining the Cu 3d orbitals in a first principles tight binding method to have a $d^9$ occupation, with the hole in the highest d state (the $d_{z^2}$ orbital). While the actual physical situation must include oxygen-Cu covalency effects [40], this simple procedure allows us to evaluate the average position in energy of the 3d-states with 9 electrons. To better understand the motivation for such a calculation, it is worth recalling the situation of the very strong correlation of the 4f levels in rare earth metals. Consider, for example, Erbium which has $\sim$ 11 4f electrons per atom in the solid. In an LSDA calculation for the metal one would start by overlapping atomic charge densities having exactly 11 4f electrons per site. On the first iteration the 4f "bands" would be extremely narrow (ignoring $L - S$ coupling and spin orbit effects) and lie about 7eV below $E_F$. Since the 4f bands can hold 14 electrons and
are well below $E_F$ the newly calculated charge density for the solid will have 14 4f electrons. In the usual procedure for iterating toward self consistency, a small percentage of this new density is mixed with the old and a new potential formed. The bands calculated for the next iteration using this new potential will have the 4f bands considerably raised because the additional occupancy of the 4f level means a larger Coulomb repulsion (essentially a larger $U_f < n_f >$) has been included in the potential. As the iterations proceed, the 4f occupancy will continue to increase until the 4f bands rise in energy to the Fermi level where partial occupancy of the 4f levels occurs and a self-consistent value of $< n_f >$ will result (perhaps $< n_f > \sim 11.2$). This is known to be a false picture and much better agreement with a variety of experiments is obtained by treating the 4f orbitals as core states and forcing an integral (partially filled) occupation. XPS spectra, for example, place the 4f levels in the rare earths well below $E_F$ (4 to 9 eV in going cross the series) [41]. We suspect the strong correlation in the Cu – O superconductors may cause similar but less extreme effects.

Method

The self-consistent calculations were performed with an accurate first principles LCAO method [21]. The basis states are atomic orbitals whose radial functions are expanded in Gaussian functions so that most integrations are handled analytically. The standard spin polarized LSDA band structure calculations do not yield an antiferromagnetic ground state [38]. The energy bands for the paramagnetic state are shown in Figure 2.6 and agree with numerous others reported [42]. We have plotted the bands in the Brillouin zone which correspond to the unit cell with the two
copper atoms in order to make comparison with the antiferromagnetic ground state results discussed below. The calculations were performed with the atomic core states frozen and the valence basis states orthogonalized to the core states. The valence states used were \( \text{La} - 6s, 6p, 5d; \text{Cu} - 4s, 4p, 3d; \text{O} - 2s, 2p \). It is relatively easy when using a LCAO code to treat the \( \text{Cu} - 3d \) states as core rather than valence states, and the resulting highest occupied energy bands will then have eigenfunctions consisting predominantly of \( \text{O} - 2p \) states orthogonalized to the neighboring \( \text{Cu} - 3d \) states. When performing these calculations we added \( \text{Cu} - 4d \) atomic functions to the valence basis, but they were high in energy and had little influence. Just recently Mattheiss and Hamann performed similar calculations (but nonself-consistent and non-spin-polarized) for \( \text{CaCuO}_2 \) using the LAPW method [43]. Their motivation was to study the symmetry of the highest states (those that become empty with doping) in the resulting oxygen bands.

Results

Our results for \( \text{La}_2\text{CuO}_4 \) are shown in Figure 2.7. There is a gap of \( \sim 1.85 \, \text{eV} \), and the highest occupied states have the same \( \sigma(x, y) \) symmetry as the highest levels in the \( \text{Cu} - \text{O} \) set of bands in Figure 2.6. This is consistent with the results of reference 43. The oxygen bandwidth is \( \sim 7 \, \text{eV} \). In addition to the valence bands of Figure 2.7 we evaluated the energy of the \( \text{Cu} 3d \) states. There is some distribution of energies (\( \sim 2.0 \, \text{eV} \)) for these states because of crystal field and spin polarization effects. In Figure 2.8, we show the calculated density of \( \text{Cu} - 3d \) states convoluted with an 1.0 eV resolution function for both the itinerant and localized models. Also shown is the experimental XPS data (with a quoted resolution of \( \sim 1 \, \text{eV} \)) [44]. Because of
cross section dependence at the energies used, the XPS spectra are mainly due to Cu 3d states. Both the localized calculation and experiment place the 3d peak at about 3.5 eV below the top of the occupied states, while the standard LSDA Cu-DOS is shifted to higher energies and has a different shape. Recent x-ray emission spectra also place the Cu — 3d levels at ~ 3.5 eV binding energy with a much narrower width than expected from band theory [45].

Discussion

The position of the calculated 3d levels is in good agreement with experiment which suggests the actual 3d occupancy may be less than that obtained by band theory (in analogy with the 4f situation described above); although one should not assume < n_d > = 9 [46]. Also, quite noticeable from Figure 2.8 is that the width of the calculated 3d “core” levels is too narrow compared with experiment. In fact, the calculated width needs to be broadened by a Gaussian of FWHM of 3 eV to obtain agreement, and this can be taken as a measure of the Cu 3d — O p hybridization. It is smaller than calculated from band theory (as is expected for highly correlated systems); however, a quantitative analysis is not warranted for such an approximate model.
Figure 2.6: The self-consistent, paramagnetic electronic band structure for \( \text{La}_2\text{CuO}_4 \) for the Brillouin zone with two formula units per cell.
Figure 2.7: The self-consistent spin polarized band structure of $La_2CuO_4$. The Cu 3d states have been treated as core orbitals with a $d^9$ configuration, and the bands below $E_F$ are nearly pure oxygen 2p states.
Figure 2.8: The solid curve is the experimental XPS energy distribution curve from Ref. 44 with the low energy tail subtracted. The dotted curve is the Cu projected density of states from band theory. The short-long dashed curve is the resolution broadened Cu density of states from the self-consistent $d^9$ core calculation, and when broadened by 3 eV the dashed curve is obtained.
La$_2$NiO$_4$

Introduction

After the discovery of the high temperature superconductors, the electronic structure of transition metal monoxides, like CuO and NiO, has become once again a focal point in condensed matter physics. It is well known that LSDA does not give a correct ground state for these materials [37, 47, 48]. For NiO, the band gap and the magnetic moment are found to be 4.0 eV and 1.90 $\mu_B$ in experiment, and the corresponding results in LSDA are 0.2 eV and 1.04 $\mu_B$. The LSDA underestimates the band gap and the magnetic moment of NiO. For the case of CuO, the situation is even worse. Experimentally it is found to be an antiferromagnetic insulator with a band gap of 1.43 eV and a magnetic moment of 0.65 $\mu_B$, while the LSDA predicts that it is a paramagnetic metal [49].

The $d$ electrons of the transition metal monoxides and La$_2$CuO$_4$ are believed to be quite localized, so that correlation is strong in these materials. That is why the LSDA does not give the correct ground state. La$_2$NiO$_4$ has very similar properties compared with La$_2$CuO$_4$. They are both antiferromagnetic insulators, they have the same crystal structure (orthorhomic for low temperature and tetragonal for high temperature), their transition metal is surrounded by six oxygen atoms forming an octahedron. We believe that an understanding of the physical properties of La$_2$NiO$_4$ will give some insight the understanding of La$_2$CuO$_4$. There are two advantages to study the La$_2$NiO$_4$ system. Firstly, La$_2$NiO$_4$ is more stable than La$_2$CuO$_4$, thus it is easier to grow a large single crystal of La$_2$NiO$_4$ but not of La$_2$CuO$_4$. Then we can have more complete information from experiment. For example, all the
phonon branches were determined along the symmetry directions [100], [110], and [001] for $La_2NiO_4$ [50] while there are only a few branches measured for $La_2CuO_4$ [51]. The form factor for $La_2NiO_4$ has been measured for 15 different $Q$ vectors while there are only 7 $Q$ vectors available for $La_2CuO_4$ [52, 16]. Secondly, the $La_2NiO_4$ system is characterized approximatively by the $3d^8$ configuration of $Ni$, while the $Cu$ in the $La_2CuO_4$ system is characterized by $3d^9$. By analogy to the transition metal monoxides, where the transition metal is also surrounded by 6 oxygen atoms forming an octahedron, we may expect the magnetic moment of $Ni$ in the $La_2NiO_4$ system will be larger than that of $Cu$ in the $La_2CuO_4$ system. Then it is very likely that we can find an antiferromagnetic ground state for the $La_2NiO_4$ system by using LSDA, and maybe even obtain a gap at the Fermi level. Guo and Temmerman [53] have used the LMTO method to perform spin-polarized local-density band structure calculations on the $La_2NiO_4$ system, and find the ground state to be an antiferromagnetic metal. We have used the KKR method study the same system, which basically confirms their results.

Comparison of the calculated magnetic form factor with the experimental measurement will give information about the correctness of spin densities given by LSDA. Since it is not convenient to calculate the wavefunction outside the MT spheres for the KKR method, we use the LAPW method to calculate the spin density after we have obtained the KKR self-consistent potential. Then we use the spin densities to calculate the magnetic form factor and compare it to the experimental measurement.
Method

The calculations were performed using the scalar relativistic approximation which includes all the relativistic effects except spin-orbit coupling. This allows spin to be kept as a good quantum number and permits the straightforward application of spin-polarized techniques. We use the KKR method and the exchange-correlation local density functional of von Barth and Hedin as modified by Moruzzi et al. [27, 28] to perform a self-consistent calculation and then use the LAPW method to calculate the spin densities. The basis functions are expanded inside the spheres in lattice harmonics with \( l \) up to 4, and the number of plane waves used in the calculation is more than 950 for each \( k \) point. Here a brief description will be given of the LAPW method and the KKR method used in the calculations.

(a) LAPW method

The Linearized Augmented Plane Wave (LAPW) method [54, 55, 56, 57] is based on the Muffin-Tin (MT) approximation, in which the potential is assumed to be spherically symmetric inside the MT spheres around each atomic site, and is taken to be a constant outside these spheres. Then the Schrödinger equation is solved by use of the variational principle. The trial wavefunction is expanded as

\[
\Psi(r) = \sum_{i=1}^{N_{\text{v}}} C_i T_i(r),
\]

(2.15)

where the \( T_i(r) \) are the LAPW basis functions. We use a dual representation for our variational function. Outside the MT spheres the potential is constant, which can be
set equal to zero by shifting the energy, the basis functions are chosen to be of the form

$$\Phi_i(r) = \frac{1}{\sqrt{\Omega}} e^{ik_i \cdot r}. \quad (2.16)$$

Inside the $\nu$th MT sphere, the potential is spherically symmetric, and the solution of the Schrödinger equation is of the form

$$\Phi_{lm}(\rho \nu) = Y_{lm}(\rho \nu) u_l(\rho \nu) \quad (2.17)$$

where the $Y_{lm}(\rho)$ are the spherical harmonics, and the vector $\rho$ has its origin at the center of the sphere. The radial function $u_l(\rho)$ satisfies

$$h_l u_l - E u_l = 0, \quad (2.18)$$

$$h_l = -\frac{1}{\rho} \frac{d^2}{d\rho^2} \rho + \frac{l(l+1)}{\rho^2} + V(\rho). \quad (2.19)$$

Since each of the functions $\phi_{lm}(\rho)$ is a solution of the Schrödinger equation inside the MT sphere, it is a good candidate for the basis function used to expand the trial wavefunction. Then the basis function inside the MT sphere is chosen as follows

$$\Phi_i(\rho) = \sum_{lm} A_{lm}^i Y_{lm}(\rho) u_l(\rho, E), \quad (2.20)$$

where the $A_{lm}^i$'s are determined by the continuity of the $i$th basis function at the
MT sphere boundary. There are two major computational difficulties: one is the energy dependence of the basis function and the second is the derivatives of the trial wavefunction allowed to be discontinuous at the MT sphere boundary which may cause singular behaviour of the secular equation. These problems can be removed by including not only the radial solution but also its energy derivative in the basis functions inside the MT sphere. Then the basis functions inside the MT sphere are of the form

\[ Y_i(\rho) = \sum_{lm} [A_{lm}^i u_l(\rho, E_{l0}) + B_{lm}^i \dot{u}_l(\rho, E_{l0})] Y_{lm}(\rho), \]

(2.21)

where

\[ \dot{u}_l(\rho, E_{l0}) = \frac{d u_l(\rho, E)}{dE} \bigg|_{E=E_{l0}}. \]

(2.22)

The \( A_{lm}^i \)s and \( B_{lm}^i \)s are determined by the continuity of both the functions and their derivatives at the MT sphere boundary. Furthermore, if the energy parameter \( E_{l0}' \)s are chosen at the center of the band for that \( l \) character these basis functions work pretty well within a fairly wide energy range about \( E_{l0}' \).

For convenience, we require the radial function to be normalized inside the MT sphere

\[ \int_0^{r_{mt}} \rho^2 u_l^2(\rho) dr = 1. \]

(2.23)

By differentiating (2.18) with respect to \( E \), we obtain the differential equation for \( \dot{u}_l \)

\[ h_l(\rho) \dot{u}_l(\rho) - E \ddot{u}_l(\rho) = u_l(\rho). \]

(2.24)
When we differentiate (2.23) with respect to $E$, we find $u_l(\rho)$ and $\dot{u}_l(\rho)$ are orthogonal. By requiring $u_l(\rho)$ to have the correct expansion

$$u_l(E + \delta) = u_l(E) + \delta \dot{u}_l(E) + \cdots, \quad (2.25)$$

we find that the normalization constant of $\dot{u}_l(\rho)$ is given by the relation

$$r_{mt}^2 u_l'(r_{mt}) \dot{u}_l(r_{mt}) - u_l(r_{mt}) \dot{u}_l'(r_{mt}) = 1, \quad (2.26)$$

where

$$u_l' = \frac{\partial u_l}{\partial \rho}|_{\rho=r_{mt}}. \quad (2.27)$$

Using the Rayleigh expansion of the plane wave, we can write the basis function outside the MT sphere as

$$\Upsilon^i_r = \frac{1}{\sqrt{\Omega}} e^{ik_r r_r} \sum_{lm} i^l j_l(k_1 \rho) Y^*_{lm}(\hat{k}_1) Y_{lm}(\rho). \quad (2.28)$$

With the use of the continuity conditions at the MT sphere boundary, we obtain

$$A^i_{lm} = \frac{1}{\sqrt{\Omega}} 4\pi r_{mt}^2 j_l(k_{mt}) a_l(k_i), \quad (2.29)$$

$$a_l(k_i) = j_l(k_i r_{mt}) \dot{u}_l(r_{mt}) - j_l(k_i r_{mt}) \dot{u}_l'(r_{mt}) \quad (2.30)$$
We can now apply a standard variational procedure, like the one we used in LCAO method, to yield the secular equation:

\[ \mathbf{H} C = E S C \]  

(2.33)

where \( S_{ij} = \langle \Phi_i | \Phi_j \rangle \) and \( H_{ij} = \langle \Phi_i | h | \Phi_j \rangle \). By using (2.18), (2.21), (2.24), (2.26)-(2.33) together with the addition theorem

\[ \sum_{m=-l}^{l} Y_{lm}^*(\hat{k}_i)Y_{lm}(\hat{k}_j) = \frac{2l+1}{4\pi} P_l(\hat{k}_i \cdot \hat{k}_j) \]  

(2.34)

we find that the \( S_{ij} \) is given by the following expression

\[ S_{ij} = U(k_i - k_j) + \frac{1}{\Omega} 4\pi r_{mt}^4 \sum_l (2l+1)P_l(\hat{k}_i \cdot \hat{k}_j) \delta_{ij}^l \]  

(2.35)

where

\[ U(k) = \delta_k - \frac{1}{\Omega} 4\pi r_{mt}^2 \frac{j_1(kr_{mt})}{k}, \]  

(2.36)

\[ \delta_{ij}^l = a_l(k_i)a_l(k_j) + b_l(k_i)b_l(k_j)N_l, \]  

(2.37)
\[ N_l = \int_{r_m^l} \rho^2 \hat{u}_l(\rho) \hat{u}_l(\rho) dr, \] (2.38)

and the $H_{ij}$ have the following expression

\[ H_{ij} = k_i^2 U(k) + \frac{1}{\Omega} 4 \pi r^4_{mt} \sum_l P_l [ E_{l_0} s^l_{ij} + a_l(k_i) b_l(k_j) ] \] (2.39)

The $H_{ij}$ can be written in an explicitly Hermitian form as

\[ H_{ij} = \mathbf{k}_i \cdot \mathbf{k}_j U + \frac{1}{\Omega} 4 \pi r^4_{mt} \sum_l (2l + 1) P_l ( E_{l_0} s^l_{ij} + \gamma^l ), \] (2.40)

where

\[ \gamma^l = \hat{u}_l(r_{mt}) u^l_l(r_{mt}) [ j^l_l(k_i r_{mt}) j^l_l(k_j r_{mt}) + j^l_l(k_i r_{mt}) j^l_l(k_j r_{mt}) ] \] \[ - \hat{u}_l(r_{mt}) u^l_l(r_{mt}) j^l_l(k_i r_{mt}) j^l_l(k_j r_{mt}) ] \] (2.41)

To include relativity, we could solve the Dirac equation. However, there are two reasons for not using this full formalism. First, in order to handle the exchange interaction more easily, we want to keep the spin as a good quantum number. It is a reasonable approximation, because the valence electron exchange interaction usually dominates over its spin-orbit interaction. Secondly, the spin-orbit interaction breaks the symmetry of the system, then we have to consider both spins at once thereby doubling the size of the secular equations involved. D. D. Koelling and B. N. Harmon [56] developed a technique, in which the spin-orbit interaction is initially omitted, but
still retains all other relativistic kinematic effects. Then the spin-orbit interaction can be included as a perturbation after we obtain the "scalar-relativistic" spin-polarised bands and wavefunctions. For convenience, we will restrict our discussion to the MT approximation. Now let $M = m + \frac{1}{2c}(E + V)$, where the energies are measured relative to the rest mass. Then the Dirac equation can be written as a set of coupled linear differential equations of the form

\begin{align}
\dot{f}_\kappa &= \frac{1}{c}(V - E)g_\kappa + \left(\frac{\kappa - 1}{r}\right) f_\kappa \\
\dot{g}_\kappa &= -\frac{(\kappa + 1)}{r} g_\kappa + 2Mc f_\kappa
\end{align}

(2.43) (2.44)

where $\kappa$ is the relativistic quantum number, which is equal to $l (l - 1)$ when $j$ is equal to $l - \frac{1}{2} (l + \frac{1}{2})$. The solution inside the MT sphere is of the form

$$\Phi_{\kappa\nu} = \begin{pmatrix} g_\kappa \chi_{\kappa\mu} \\ -i f_\kappa \sigma_\tau \chi_{\kappa\mu} \end{pmatrix}$$

where

$$\chi_{\kappa\mu} = \sum_{s=\pm} C(l_{\frac{1}{2}}j; \mu - s, s) Y_l,_{(\mu - s)}(\rho) \chi_s$$

(2.45)

Here $C(l_{\frac{1}{2}}j; \mu - s, s)$ are the Clebsh-Gordon coefficients, $\chi_s$ is a two-component spinor, and $\sigma_\tau$ is defined by $\sigma \cdot \hat{r}$ where $\sigma$ is the Pauli matrix. Combining (2.43) and (2.44), we obtain
The last term on the left hand side, which is the spin-orbit interaction, is the only term depending on $\kappa$. Therefore, by dropping the last term, we may obtain an equation for $g_\kappa$ which does not depend on spin, thus allowing spin to be maintained as a good quantum number. For reasons of mathematical simplicity, we define a new function $\phi_\kappa$ of the form

$$\phi_\kappa = \frac{1}{2Mc} g'_\kappa$$  \hspace{1cm} (2.47)

Using (2.46) without the spin-orbit term, we obtain

$$\phi'_\kappa = \frac{-2}{r} \phi_\kappa + \frac{l(l+1)}{2Mc^2r^2} + \frac{1}{c(V-E)} g_\kappa$$ \hspace{1cm} (2.48)

Since there is no longer any $\kappa$ dependence in the new coupled linear equations, (2.47) and (2.48), we can now replace all the $\kappa$ index in $g$ and $\phi$ by $l$, and rewrite the solution inside MT sphere as

$$\Phi_{\kappa\mu} = \begin{pmatrix} g[l\chi\kappa\mu] \\ -i[\phi_l + (\kappa+1)g_l]\sigma_\tau\chi\kappa\mu \end{pmatrix}$$

With the use of (2.47), the solution inside MT sphere can be written as
The first energy derivative of $\Phi_{lm,s}$ is given by

$$
\Phi_{lm,s} = \left( \begin{array}{c}
g_l Y_{lm} \chi_s \\
\frac{i}{2Mc} \sigma_r (-g_l' + \frac{1}{\tau} g_l \sigma \cdot L) Y_{lm} \chi_s
\end{array} \right)
$$

For reasons of convenience in numerical calculation, we introduce two new functions defined by

$$
P_l = r g_l
$$

$$
Q_l = r c \phi_l
$$

It can be shown that $P_l$ and $Q_l$ satisfy the radial equations

$$
\frac{dP_l}{dr} - \frac{P_l}{r} = 2Mc Q_l
$$

$$
\frac{dQ_l}{dr} + \frac{Q_l}{r} = \frac{l(l+1)}{2Mc c^2} + \frac{V - E}{c^2} P_l
$$

with the normalisation condition

$$
\int_0^{\tau_{mt}} dr (P_l^2 + Q_l^2) = 1
$$
and \( \dot{P}_l \) and \( \dot{Q}_l \) are given by

\[
\frac{d\dot{P}_l}{dr} - \frac{\dot{P}_l}{r} = 2Mc\dot{Q}_l + \frac{Q_l}{c}
\]

(2.54)

\[
\frac{d\dot{Q}_l}{dr} + \frac{\dot{Q}_l}{r} = \left[ \frac{l(l+1)}{2Mcr^2} + \frac{V - E}{c} \right] \dot{P}_l - \frac{P_l}{c}
\]

(2.55)

with the requirement that

\[
\int_0^{r_{mt}} dr (P_l \dot{P}_l + Q_l \dot{Q}_l) = 0
\]

(2.56)

Then we can choose our basis function of the form

\[
\Upsilon_{is}(r) = \begin{cases} 
\sum_{l,m} [A_{lms}^i \hat{\Phi}_{lms}(r) B_{lms}^i \hat{\Phi}_{lms}(r)] & \text{inside MT sphere} \\
\frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}_1 \cdot \mathbf{r}} \begin{bmatrix} \chi_s \\ \frac{(\sigma \cdot \mathbf{k}_1)}{W_i + mc^2} \chi_s \end{bmatrix} & \text{outside MT sphere}
\end{cases}
\]

where

\[
k_1 = k + G_1
\]

(2.57)

\[
W_i^2 = m^2 c^4 + k_i^2 c^2 \quad \text{and} \quad m^2 c^4
\]

(2.58)

By requiring the large component and its spatial derivative be continuous across the
MT sphere boundary, we obtain the $A_{lm}^i$ and $B_{lm}^i$ as follow

\begin{align}
A_{lm}^i &= \frac{1}{\sqrt{\Omega}} \frac{4\pi r_{mt}^2}{m} i Y_{lm}^*(\mathbf{k}_i) a_i(k_i) \tag{2.59} \\
B_{lm}^i &= \frac{1}{\sqrt{\Omega}} \frac{4\pi r_{mt}^2}{m} i Y_{lm}^*(\mathbf{k}_i) b_i(k_i) \tag{2.60} \\
a_i(k_i) &= [j''_l(k_i r_{mt}) \dot{g}_l(r_{mt}) - j'_l(k_i r_{mt}) \dot{g}'_l(r_{mt})]/Z_l \tag{2.61} \\
b_i(k_i) &= [j''_l(k_i r_{mt}) \dot{g}'_l(r_{mt}) - j'_l(k_i r_{mt}) \dot{g}_l(r_{mt})]/Z_l \tag{2.62}
\end{align}

where $Z_l = r_{mt}^2 \dot{g}_l(r_{mt}) \dot{g}'_l(r_{mt}) - g_l(r_{mt}) \dot{g}'_l(r_{mt})$. With the use of the properties of $\sigma$ matrix and $\kappa$, it is easily verify that the spin-orbit term can be written as

\[ H^{\sigma \sigma} = \frac{1}{4ME^2c^2} V'_{\sigma} \cdot \mathbf{L} \tag{2.63} \]

By omitting terms of order $(1/Mc)^3$, the MT Dirac Hamiltonian gives

\begin{align}
H_{MT} \Phi_{lms} &= e \Phi_{lms} + H_0^{\sigma \sigma} \Phi_{lms} \tag{2.64} \\
H_{MT} \dot{\Phi}_{lms} &= e \dot{\Phi}_{lms} + \Phi_{lms} + H_1^{\sigma \sigma} \Phi_{lms} \tag{2.65}
\end{align}

where

\[ H_0^{\sigma \sigma} \Phi_{lms} = \frac{1}{(2Mc)^2} \frac{dV_{MT}(r)}{dr} \left( \begin{array}{c} P_l \sigma \cdot \mathbf{L} Y_{lm} \chi_s \\ 0 \end{array} \right) \]
Since the basis functions are continuous in the large component and very nearly so in the small component, we can assume the basis functions are continuous, and use a standard variational procedure to yield the secular equation:

\[
HC = ESC.
\]  

The general procedure from this point is to temporarily ignore the matrix elements of \( H^0 \) and \( H^s \), then \( H_{ij} \) and \( S_{ij} \) can be calculated from (2.35) and (2.40) except that the radial solutions have been obtained from the "semi-relativistic" radial equations. Since the charge density is often affected little by the spin-orbit coupling, it is not necessary to include the spin-orbit term in each iteration. Therefore, at first we calculate the self-consistent eigenvalues and eigenfunctions in this spin-orbit-less problem, then include the spin-orbit effect in the final iteration. Including the spin-orbit effect, the matrix elements are given by

\[
H_{is,is'} \approx H^0_{is,is'} + H^s_{is,is'}
\]  

\[
S_{is,is'} \approx S^0_{is,is'}
\]
where

\[ H_{i,s,i',s'}^{so} \approx 4\pi \sum_{lmn'} R_{i,i'}^{l} \sum_{s} \langle \chi_s^+ | Y_{lm}^{*} \cdot \mathbf{L} Y_{lm'}^{*} | \chi_s' \rangle Y_{lm}^{*}(\mathbf{k}_i) Y_{lm'}^{*}(\mathbf{k}_{i'}) \]  

(2.69)

\[ R_{i,i'}^{l} = \frac{1}{\Omega} 4\pi \sum_{m} r m^{t} \{ a_{l}(k_{i}) a_{l}(k_{i'}) \xi_{l}^{t} + [a_{l}(k_{i}) b_{l}(k_{i'}) + b_{l}(k_{i}) a_{l}(k_{i'})] \xi_{l} + b_{l}(k_{i}) b_{l}(k_{i'}) \xi_{l} \}
\]

\[ \xi_{l} = \int_{0}^{r_{mt}} dr P_{l}^{2} \left( \frac{1}{2Mc} \right)^{2} \frac{1}{r} \frac{dVMT}{dr} \]

\[ \xi_{l} = \int_{0}^{r_{mt}} dr P_{l} \left( \frac{1}{2Mc} \right)^{2} \frac{1}{r} \frac{dVMT}{dr} \]

\[ \xi_{l} = \int_{0}^{r_{mt}} dr \dot{P}_{l} \left( \frac{1}{2Mc} \right)^{2} \frac{1}{r} \frac{dVMT}{dr} \]

The method outlined above is called the LAPW method, sometime we call it the SOLAPW method.

(b) KKR method

The Korringa-Kohn Rostocker (KKR) method of band structure calculation was developed by Korringa from the point of view of multiple scattering of waves [58], and independently by Kohn and Rostoker [59], using Green's function formulation, and generalized to the complex crystal, the system with more than one atom per unit cell, by Segall [60, 61]. In this section we shall follow the Kohn and Rostoker approach. For convenience, we will only consider the system with one atom per unit cell now.
We are seeking propagating solutions of the Schrödinger's equation

\[ [-\nabla^2 + V(r) - E] \Psi(r) = 0, \quad (2.70) \]

with the periodic potential

\[ V(r + r_N) = V(r). \quad (2.71) \]

The solution to (2.70) satisfies the Bloch condition, that is

\[ \Psi(r + r_N) = \exp(ik \cdot r_N) \Psi(r), \quad (2.72) \]

where \( k \) is the crystal momentum vector, and \( r_N \) is any translation vector of the lattice. If we introduce the Green function \( G(r, r') \) which is defined by

\[ (-\nabla^2 - E)G(r, r') = -\delta(r - r'), \quad (2.73) \]

and satisfies the same boundary condition as the wavefunction \( \Psi(r) \) does. By expanding the Green function in terms of the eigenfunctions of the homogeneous boundary value problem, one can easily verify that \( G \) satisfies

\[ G(r, r') = -\frac{1}{\Omega} \sum_n \frac{\exp[i(K_n + k) \cdot (r - r')]}{(K_n + k)^2 - E} \quad (2.74) \]
where $\Omega$ is the volume of the unit cell, $K_n$ is the reciprocal lattice vectors. Then the boundary value problem (2.70) and (2.71) can be replaced by an integral equation of the form

$$
\Psi(r) = \int_{\Omega} G(r, r') V(r') \Psi(r') d^3r'. 
$$
(2.75)

It is easily verified that (2.75) is equivalent to the variational principle:

$$
\delta \Lambda = 0, 
$$
(2.76)

where

$$
\Lambda = \int_{\Omega} \Psi^*(r) V(r) \Psi(r) d^3r 
- \int_{\Omega} \int_{\Omega'} \Psi^*(r) V(r) G(r, r') V(r') \Psi(r') d^3r d^3r'. 
$$
(2.77)

Using a trial wavefunction

$$
\Psi(r) = \sum_i C_i \Phi_i(r), 
$$
(2.78)

$$
C_i = a_i + ib_i, 
$$

where $a_i$ and $b_i$ are real numbers, and substituting (2.77) into (2.76), we obtain

$$
\Lambda = \sum_{i,j} C_i^* C_j \Lambda_{i;j}, 
$$
(2.79)
where $\Lambda_{ij}$ is defined by

$$
\Lambda_{ij} = \int_\Omega \Phi_i^*(r)V(r)\Phi_j(r)d^3r - \int_\Omega \int_{\Omega'} \Phi_i^*(r)V(r)G(r,r')V(r')\Phi_j(r')d^3rd^3r'.
$$

(2.80)

The conditions

$$
\frac{\partial \Lambda}{\partial a_i} = \frac{\partial \Lambda}{\partial b_i} = 0
$$

(2.81)

which follow from (2.76), give the linear equations

$$
\sum_{j=1}^{n} \Lambda_{ij} C_j = 0
$$

(2.82)

A necessary condition for a nontrivial solution of (2.81) is

$$
det\Lambda_{ij} = 0,
$$

(2.83)

which contains the required connection between $E$ and $k$.

In order to simplify the expression of $\Lambda_{ij}$, we use the MT approximation. Thus, it is natural to choose the trial wavefunction as a finite series of the form

$$
\Psi(r) = \sum_{l=0}^{lN} \sum_{m=-l}^{l} C_{lm} \Phi_{lm}(r),
$$

(2.84)
\[ \Phi_{lm}(r) = u_l(r)Y_{lm}(\theta, \varphi), \quad (2.85) \]

within the MT sphere. Here \( u_l(r) \) satisfies the radial differential equation

\[ \left[ -\frac{1}{r^2} \frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - E \right] u_l(r) = 0, \quad (2.86) \]

with a normalization \( u_l(r_{MT}) = 1 \). Since the potential outside the MT sphere is constant, which is set equal to zero now by shifting the energy, we can rewrite (2.78) as the following

\[ \Lambda_{lm;l'm'} = \int_{\Omega_{MT}} \Phi^*_{lm}(r)V(r)\Phi_{l'm'}(r) \, d^3r \]

\[ - \int_{\Omega_{MT}} \int_{\Omega_{MT}'} \Phi^*_{lm}(r)V(r)G(r, r')V(r')\Phi_{l'm'}(r') \, d^3r \, d^3r'. \quad (2.87) \]

To evaluate \( \Lambda_{lm;l'm'} \), we transform the expression for \( \Lambda_{lm;l'm'} \) from volume to surface integrals with the use of Green's Theorem

\[ \int U \nabla^2 V - V \nabla^2 U \, d^3r = \int (U \nabla V - V' \nabla U) \cdot dS. \quad (2.88) \]

Substituting \( U = G(r, r') \) and \( V = \Phi_{l'm'}(r) \) into (2.87), we obtain

\[ \int_{\Omega_{MT}} [G(r, r')\nabla'^2 \Phi_{l'm'}(r) - \Phi_{l'm'}(r')\nabla'^2 G(r, r')] \, d^3r' = \]
By utilizing the fact that \( \Phi_{l'm'}(r) \) is a solution to (2.70) and \( G(r, r') \) is a solution to (2.73), we can rewrite (2.89) as the following:

\[
\int_{r'=r'}^{r'}_{MT} [G(r, r') \nabla' \Phi_{l'm'}(r') - \Phi_{l'm'}(r') \nabla' G(r, r')] \cdot dS'.
\] (2.90)

With the use of Green's Theorem and (2.73), the expression

\[
\int_{\Omega_{MT}} \Phi_{l'm'}(r) V(r) G(r, r') d^3r = \int_{\Omega_{MT}} (\nabla_2 + E) \Phi_{l'm'}^*(r) G(r, r') d^3r,
\] (2.91)

can be rewritten as

\[
\int_{\Omega_{MT}} \Phi_{l'm'}(r) V(r) G(r, r') d^3r =
\int_{r'=r'}^{r'}_{MT} [G(r, r') \nabla \Phi_{l'm'}^*(r) - \Phi_{l'm'}(r) \nabla G(r, r')] \cdot dS.
\] (2.92)

Combining (2.90) and (2.92), we obtain the final expression for \( \Lambda_{lm;l'm'} \)

\[
\Lambda_{lm;l'm'} = \lim_{\epsilon \to 0} \int_{r'=r'}^{r'}_{MT} -2\epsilon dS \left[ \Phi_{l'm'}^*(r) \frac{\partial}{\partial n} \Phi_{l'm'}(r) - \frac{\partial}{\partial n} \Phi_{l'm'}^*(r) \right]
\]
\[
\int_{r=r_{MT}}\epsilon dS'(G(r, r') \frac{\partial}{\partial n} \Phi_{l'm'}(r') - \frac{\partial}{\partial n} G(r, r'))],
\]

where \( \frac{\partial}{\partial n} \) represents the derivative normal to the surface of the MT sphere and where \( \epsilon \) are used to avoid the singularity in the Green's function.

The Green's function can be expanded in spherical harmonics for \( r < r' < r_{mt} \) as

\[
G(r, r') = \sum_{l,m} \sum_{l',m'} [A_{lm;l'm'} j_l(\kappa r') j_{l'}(\kappa r') + \delta_{ll'} \delta_{mm'} j_l(\kappa r') n_l(\kappa r')] Y_{lm}(\hat{r}) Y_{l'm'}(\hat{r}'),
\]

where

\[
\kappa = \begin{cases} 
\sqrt{E} & \text{if } E > 0 \\
i\sqrt{-E} & \text{if } E < 0
\end{cases}
\]

Here \( j_l(x) \) and \( n_l(x) \) are the spherical Bessel and Neumann functions, which are related to the standard Bessel function \( J_\alpha(x) \) by

\[
\begin{align*}
\frac{\pi}{2x} j_l(x) &= \frac{1}{l+\frac{1}{2}} J_{l+\frac{1}{2}}(x), \\
-\frac{\pi}{2x} n_l(x) &= (-1)^{l+1} \frac{1}{l+\frac{1}{2}} J_{-l-\frac{1}{2}}(x),
\end{align*}
\]

For a detailed expression of \( A_{lm;l'm'} \) see Ref. 60. Substituting (2.85) and (2.94) into (2.93), we find the expression for the matrix element \( \Lambda_{lm;l'm'} \) as the following
\[ \Lambda_{l_{m; l'} m'} = (L_l j_{l'}) \left[ (A_{l_{m; l'} m'} j_{l'} + K \delta_{l l'} \delta_{m m'} n_{l'} - (A_{l_{m; l'} m'} j_{l'} + K \delta_{l l'} \delta_{m m'} n_{l'} L_{l'}) \right], \]

(2.97)

where

\[ L_l = \frac{1}{u_l(r)} \left. \frac{d u_l(r)}{d r} \right|_{r=r_{m t}}, \]

(2.98)

\[ j'_{l'} = \left. \frac{d j_l(K r)}{d r} \right|_{r=r_{m t}}. \]

(2.99)

Dividing each row of \( \Lambda \) by \((L_l j_{l} - j_{l'})\) and each column of \( \Lambda \) by \((L_l j_{l} - j_{l'})\) before we equate the determinant to zero, we can simplify the secular equation to the following form

\[ \det \left| A_{l_{m; l'} m'} + K \delta_{l l'} \delta_{m m'} \frac{n'_{l'} - n_{l} L_{l}}{j'_{l'} - j_{l} L_{l}} \right| = 0, \]

(2.100)

which gives the energy eigenvalues as a function of \( k \). Together with (2.84) one can obtain the wavefunctions from the following relations

\[ \sum_{l' m'} (A_{l_{m; l'} m'} + K \delta_{l l'} \delta_{m m'} \frac{n'_{l'} - n_{l} L_{l}}{j'_{l'} - j_{l} L_{l}}) C_{l' m'} = 0 \]

(2.101)

\[ C_{l m} = \frac{C_{l m}}{j'_{l} - j_{l} L_{l}} \]

(2.102)

The method outlined above is called the KKR method.
Results

La$_2$NiO$_4$ in the tetragonal structure has the space group $D_{4h}^{17}$ (I4/mmm), with atom positions (cf. Figure 1.1) for a unit cell given by $Ni$, (0,0,0); $La$, (0,0,$\pm Z_{La}$); $O(1)$, (0,$\frac{1}{2}$,0), ($\frac{1}{2}$,0,0); $O(2)$, (0,0,$\pm Z_{O}$). The lattice constants, $a = 7.2872 \text{a.u.}$ and $c = 23.9164 \text{a.u.}$ and position values $Z_{La} = 0.36$ and $Z_{O} = 0.17$, used in the present calculation are taken from Von A. Rabenau and P. Eckerlin [62]. In order to better approximate the potential between the atomic spheres, we added two auxiliary spheres at the position ($\frac{1}{2}$,0,0) and (0,$\frac{1}{2}$,0). The KKR basis functions are expanded inside the spheres in lattice harmonics with $l_{\text{max}}$ given by $La$, (3); $Ni$, (2); $O$, (1); and Aux, (1). The MT radii chosen as $La$, (2.806 a.u.); $Ni$, (1.9287 a.u.); $O$, (1.7021 a.u.); and Aux, (1.6497 a.u.). The self-consistent charge densities were evaluated on a uniform sampling of 30 $k$ points inside the $\frac{1}{16}$ irreducible Brillouin zone (IBZ). For K-space summations we used a Fermi surface broadening of 2 $mRy$ to improve $k$-point convergence.

Then we consider the antiferromagnetic ordering. Since the orthorhombic lattice distortion hardly affects the electronic band structure and antiferromagnetism [63], we neglect the distortion in our calculation. There are now two formula units, 14 atoms and 4 auxiliary spheres, per primitive unit cell in a base-centered tetragonal structure. The self-consistent charge densities were evaluated on a uniform sampling of 16 $k$ points inside the $\frac{1}{8}$ IBZ with a Fermi surface broadening of 2 $mRy$.

The band structure for La$_2$NiO$_4$ in the tetragonal phase is shown in Figure 2.9. We find the band structure is, in general, similar to that of La$_2$CuO$_4$. Since each La$_2$NiO$_4$ unit has one valence electron less than each La$_2$CuO$_4$ unit, the Fermi energy of La$_2$NiO$_4$ shifts downward and cuts 2 bands instead of one. The total
band width is 10 eV. Thus, there is a strong $Ni - O$ hybridization. The bands that cross the Fermi level along [011] are the anti-bonding bands of $Ni3d_{z^2} - O(2)2p_z$ and $Ni3d_{x^2-y^2} - O(1)p_z$, and the band that crosses the Fermi level along [100] is formed by the hybridization among $Ni3d_{z^2}, Ni3d_{x^2-y^2}, O(1)2p_z$, and $O(2)p_z$. The total charge inside each MT sphere is found to be $La$, (54.349e); $Ni$, (26.217e); $O(1)$, (7.530e); $O(2)$, (7.323e); and Aux, (0.082e).

We performed spin-polarized calculations for the orthorhombic $La_2NiO_4$ without including the low temperature orthorhombic distortion. The self-consistent spin-polarized band structure of $La_2NiO_4$ is shown in Figure 2.10. We find an antiferromagnetic solution with magnetic moment inside the MT spheres given by $Ni$, (+0.43$\mu_B$); $O(2)$, (+0.05$\mu_B$); and $La$, (+0.005$\mu_B$). About 60% of the magnetic moment inside $Ni$ sphere is contributed by $d_{z^2}$ while 40% of that is contributed by $d_{x^2-y^2}$. The total charge inside each MT sphere is given by $La$, (54.351e); $Ni$, (26.222e); $O(1)$, (7.535e); $O(2)$, (7.327e); and Aux, (0.082e). They are almost not changed as we expected.

Although the magnetic moments we obtained are smaller than those reported by experiment, one might expect the basic shape of the spin densities to be calculated reasonably. The best way to test it is to calculate the magnetic form factor and compare the result to the experimental measurement. Therefore, after we obtained the self-consistent potential, we calculated the wavefunction inside and outside the MT spheres using the LAPW method. The magnetic moment calculated using the LAPW method inside each MT sphere is given by $La$, (0.006$\mu_B$); $Ni$, (0.45$\mu_B$); $O(2)$, (0.046$\mu_B$). They are very close to the results calculated from the KKR method, we therefore expect the spin densities calculated with the use of the LAPW method are
reasonable.

The calculated magnetic form factor with the spin density scaled by a factor 2.9 together with the experimental measurement are shown in Figure 2.11. Most of the features agree fairly well, except for a few low Q reflections. There is a noticeable plateau in the measured form factor at low Q values while the calculated form factor shows a strong interference which is mostly due to the small out-of-plane oxygen contribution. The deviation of the total moment by roughly the 2.9 factor indicates the LSDA underestimates the on-site correlation in Ni and the shape difference in the form factors suggests the hybridization between Ni \(d^2\) and O(2) \(2p_z\) is too large. for the same reason.

Discussion

We have performed spin-polarized self-consistent calculations within the local density functional approximation. We find an antiferromagnetic solution with a magnetic moment of 0.49\(\mu_B\) /formula unit, more than 10% of which comes from the O(2) spheres. Comparison of the calculated form factor with the experimental measurement shows that the LSDA underestimates the total magnetic moment and overestimates the magnetic moment contributed by the out-of-plane oxygen. It is well known that LSDA usually underestimates the magnetic moment of a strongly correlated system such as transition metal monoxides, because it underestimates the effects of the intra-atomic Coulomb repulsion energy U of the local state. Therefore, we suspect the LSDA does not give an adequate description of \(La_2NiO_4\) and some approximation beyond the local approximation is needed to describe the observed antiferromagnetism. This is the topic of the next chapter.
Figure 2.9: The self-consistent paramagnetic electronic band structure for $La_2NiO_4$
La$_2$NiO$_4$ (AF)

Figure 2.10: The self-consistent spin polarized band structure of $La_2NiO_4$
Figure 2.11: The magnetic form factor for the antiferromagnetic state of $La_2NiO_4$. The black circles with error bars are the experimental values from Ref. 52, while the squares are from the LSDA calculations described in the text (and scaled by a factor of 2.9).
CHAPTER 3. BEYOND THE LOCAL SPIN DENSITY FUNCTIONAL APPROXIMATION

Introduction

Neutron scattering experiments have shown that the 3 dimensional long range antiferromagnetic order in $La_2CuO_4$ and $YBa_2Cu_3O_6$ is quickly suppressed by doping [16, 64, 65]. The antiferromagnetic correlations within the 2 dimensional $CuO_2$ planes persist over a large doping range, but the interactions among the local moments become weaker [65, 67, 68]. The degree to which these AF correlations extend into the same doping region of the crystal where superconductivity develops is still unclear. Since such correlations may enhance or suppress superconductivity (depending on the mechanism), they are of interest. NMR experiments on Cu and O sites indicate the pairing of spins occurs on both sites below $T_c$ [69], so the electrons on Cu do participate in the superconducting ground state and should not be considered as occupying an independent localized orbital with spin=$\frac{1}{2}$.

Analysis of magnetic neutron scattering data suggest that the net ordered moment in the undoped materials is on the order of $0.6 \mu_B$ [16, 64, 65]. It is believed that the 2 dimensional quantum fluctuations are partially responsible for reducing this from the 1.0 value. The quantum fluctuations reduce the magnetic moment by 39.3% and 15.6% in the 2D and 3D Heisenberg models in the spin wave theory, re-
respectively [66]. In fact, the spin wave spectrum for $YBa_2Cu_3O_6$ has been analyzed remarkably well by Rossat-Mignod et al. by using a 2 dimensional Heisenberg model with small XY-anisotropy [65]. These authors conclude that covalency effects of the $Cu$ orbitals with the neighboring oxygen orbitals could help reduce the ordered moment by 20% at the most. The rather small amount of oxygen 2p admixture into the $Cu$ 3d conduction bands is also found with electron energy-loss studies reported by Romberg et al. [70]. The same conclusion was reached based on the measurements of $La_2CuO_4$ by Stassis et al. [71]. All of these measurements are consistent with an oxygen admixture on the order of 15% ± 10%; a value in stark contrast to the one obtained by band structure calculations.

In chapter one, we have performed the spin polarized band structure calculations for the $Sc_2CuO_4$ system, and expected to find an antiferromagnetic insulator similar to the case of $NiO$. However the results revealed a rather small magnetic susceptibility which was far from an AF ground state [38]. A result which has since been confirmed by many other groups [72]. Furthermore, by applying a reasonably large staggered magnetic field to the $Cu$ sites in the band theory Hamiltonian, the induced magnetic moment on the $Cu$ sites saturated at about 0.3 $\mu_B$. The reason this is considerably less than the value of 1.0 one might expect, is because of the strong admixture of oxygen character into the conduction band. Near the Fermi level the conduction band is composed of antibonding $Cu-O$ orbitals with about 60% from the in-plane oxygen and only 40% from the $Cu$. The magnetic contribution from the oxygen (between two oppositely polarized $Cu$ sites) is zero by symmetry. The failure of the band theory approach to find a magnetic ground state and its prediction of too much oxygen admixture is believed to arise from an inadequate treatment of
the on-site Coulomb correlations among the tightly bound Cu 3d-state electrons. In the calculation of La$_2$CuO$_4$ with constrained $d^9$ configuration, we treated the 3d states as core-like and constrained their occupation to 9.0 electrons. This gave a Cu density of states in better agreement with XPS data than band theory where the d occupation is found to be closer to 9.5 [73]. In fact the calculated XPS peak was at a slightly larger binding energy than the experimental one, and a calculation with a constrained $d^{9.1}$ configuration would probably have yielded better agreement. When one then dopes these materials with holes, one certainly expects the 3d electron occupation to either remain the same or to slightly decrease [74]. On the other hand, standard band theory for the doped metallic phase seems to yield Fermi surface [75] and other properties (e.g. phonon frequencies [76]) in reasonably good agreement with experiment in spite of having a $3d^{9.5}$ configuration on Cu. We believe an explanation of these apparently contradictory viewpoints will require understanding of the strong correlations, and we have therefore retreated temporarily from the standard band structure approach and have been investigating models that allow a more precise treatment of correlations.

Model and Method

In this section we shall follow the Hubbard approach [10, 12]. For reasons of mathematical simplicity, we consider a partly-filled narrow s-band with n electrons per atom. The Bloch wave functions, $\psi_k$, and the corresponding energies, $\epsilon_k$, are assumed to have been calculated via the Hartree-Fock approximation. The Hamiltonian for such a system may be written as
63

\[ H = \sum_{k\sigma} \epsilon_k C_{k\sigma}^+ C_{k\sigma} + \frac{1}{2} \sum_{k_1 k_2 k_1' k_2'} \sum_{\sigma\sigma_1} < k_1 k_2 | \frac{1}{r} | k_1' k_2' > C_{k_1 \sigma_1}^+ C_{k_2 \sigma}^+ C_{k_2' \sigma'} C_{k_1' \sigma_1} \]

\[ - \sum_{kk'} \sum_{\sigma}(2 < kk' | \frac{1}{r} | kk' > - < kk' | \frac{1}{r} | k k' >) \nu_{k\sigma} C_{k\sigma}^+ C_{k'\sigma} \]  

(3.1)

where \( \sigma = \pm 1 \) is the spin label, the \( k \) sum runs over the first Brillouin zone, the \( \nu_{k\sigma} \) are the occupation numbers of the state, \( C_{k\sigma} \) and \( C_{k\sigma}^+ \) are respectively the destruction and creation operators for electrons in the Bloch state \((k, \sigma)\), and

\[ < k_1 k_2 | \frac{1}{r} | k_1' k_2' > e^2 \int \frac{\psi_{k_1}^*(r)\psi_{k_2}^*(r')}{\psi_{k_1'}(r)\psi_{k_2'}(r')} d^3r d^3r' \]  

(3.2)

Here the first term represents the Hartree-Fock energies, the second the electronic interaction, and the third subtracts off the average part of the interactions which has been already put into the Hartree-Fock term. Note that only electrons of identical spin contribute to the exchange energy. We can transform the previous expression to the Wannier representation by introducing the Fourier transforms:

\[ \psi_{k\sigma}(r) = \frac{1}{\sqrt{N}} \sum_i \exp(i k \cdot R_i) \phi_{\sigma}(r - R_i) \]  

(3.3)

\[ C_{k\sigma} = \frac{1}{\sqrt{N}} \sum_i \exp(i k \cdot R_i) C_{i\sigma} \]  

(3.4)
where \( N \) is the total number of sites, \( R_i \) is the translation vector of the lattice. The Hamiltonian can be rewritten as

\[
H = \sum_{ij} \sum_{\sigma} T_{ij} C_{i\sigma}^+ C_{j\sigma} + \frac{1}{2} \sum_{ijkl} \sum_{\sigma\sigma'} <ij|\frac{1}{r}|kl> C_{i\sigma}^+ C_{j\sigma}^+ C_{l\sigma} C_{k\sigma}
- \sum_{ijkl} \sum_{\sigma} [2 <ij|\frac{1}{r}|kl> - <ij|\frac{1}{r}|lk>] \nu_{ij} C_{i\sigma}^+ C_{k\sigma},
\]

where

\[
<ij|\frac{1}{r}|lk> = e^2 \int \frac{\phi^*(r - R_i)\phi^*(r' - R_j)\phi(r - R_i)\phi(r' - R_k)}{|r - r'|} \, d^3r \, d^3r'
\]

If we define \( U = <ii|\frac{1}{r}|ii> \) and neglect all of the Coulomb matrix elements between Wannier functions except \( U \), we can rewrite (3.7) as follow,

\[
H = \sum_{ij} \sum_{\sigma} T_{ij} C_{i\sigma}^+ C_{j\sigma} + \sum_{i} U_i n_i^\uparrow n_i^\downarrow - \frac{1}{2} N n^2 U,
\]

where \( n_{i\sigma} = C_{i\sigma}^+ C_{i\sigma} \), and \( n \) is the number of electrons per atom in the band. If we drop the constant term, the previous expression can be written as

\[
H = \sum_{ij} \sum_{\sigma} T_{ij} C_{i\sigma}^+ C_{j\sigma} + \sum_{i} U_i n_i^\uparrow n_i^\downarrow.
\]
This Hamiltonian, which was first discussed by Hubbard, is called the Hubbard Hamiltonian. The Hamiltonian of the system with more than one orbital per unit cell, which is called the extended Hubbard Hamiltonian, can be expressed in the form

\[ H = \sum_{i\nu\sigma} \varepsilon_{i\nu\sigma} n_{i\nu\sigma} + \sum_{\nu \neq \nu'} \sum_{\sigma} T_{ij}^{\nu\nu'} C_{i\nu\sigma}^+ C_{j\nu\sigma} + \sum_{i\nu} U_{i\nu} n_{i\nu\uparrow} n_{i\nu\downarrow} \tag{3.11} \]

where \( \varepsilon_{i\nu\sigma} \) is the atomic orbital energy for the \( \nu \text{th} \) orbital in the \( i \text{th} \) unit cell.

If \( A(t) = e^{iHt} A(0) e^{-iHt} \) (with units \( \hbar = 1 \)) and \( B(t') \) are any two Fermion operators, then the Green function can be defined by [77]

\[ \langle \langle A(t); B(t') \rangle \rangle = i\theta(t - t') \langle [A(t), B(t')]_+ \rangle, \tag{3.12} \]

where \([A, B]_+ = AB + BA \) and \( \theta(t) \) is the step function. These Green functions satisfy the equation of motion

\[ i\frac{d}{dt} \langle \langle A(t); B(t') \rangle \rangle = \delta(t - t') \langle [A(t), B(t')]_+ \rangle + \langle [A(t), H]; B(t') \rangle \tag{3.13} \]

Since \( \langle \langle A(t); B(t') \rangle \rangle \) is a function of \( t - t' \) only, we can define the Fourier transforms

\[ \langle \langle A; B \rangle \rangle_w = \int_{-\infty}^{\infty} \langle \langle A(t); B(0) \rangle \rangle e^{i\omega t} dt. \tag{3.14} \]
Using (3.13) and (3.14), we obtain the equation of motion

$$w << A; B >> w = << [A, B]_+ > + << [A, H]; B >> w.$$  \hspace{1cm} (3.15)

It can be shown [77] that

$$< BA >= \frac{1}{\pi} \int_{-\infty}^{\infty} dw \frac{Im << A; B >> w}{e^{\beta w} + 1}$$ \hspace{1cm} (3.16)

where $\beta = 1/kT$. Equations (3.15) and (3.16) together with methods of approximation, which will be described in the following sections, form the essential basis of our calculations.

(a) Hartree-Fock Approximation

Replacing the term $n_i\sigma n_i\bar{\sigma}$ by $\frac{1}{2}(n_i\sigma < n_i\bar{\sigma} > + n_i\bar{\sigma} < n_i\sigma >)$, we can obtain the effective Hartree-Fock Hamiltonian. Then (3.11) becomes

$$H = \sum_{\nu'k} \sum_{\nu} \sum_{\sigma} [t_{\nu'k}^{\nu} + \delta_{\nu'\nu} (\epsilon_{\nu\sigma} + U_{\nu} < n_{\nu\bar{\sigma}} >)] C_{k\nu\sigma}^+ C_{k\nu'\sigma} \hspace{1cm} (3.17)$$

The Fourier transformations now are defined by

$$T_{u_{\nu'1}}^{\nu\nu'1} = \frac{1}{N} \sum_k t_{k}^{\nu\nu'} e^{ik \cdot (R_{-R_1})}$$ \hspace{1cm} (3.18)

$$C_{l\nu\sigma} = \frac{1}{\sqrt{N}} \sum_k C_{k\nu\sigma} e^{ik \cdot R}.$$ \hspace{1cm} (3.19)
Now let $A = C_{k
u\sigma}^\dagger$ and $B = C_{k
u\sigma}^\dagger$. From (3.15) we obtain the equation of motion of the form

$$w << C_{k
u\sigma}^\dagger; C_{k
u\sigma}^\dagger >> w = << [C_{k
u\sigma}, C_{k
u\sigma}^\dagger]_+ >> + << [C_{k
u\sigma}, H]; C_{k
u\sigma}^\dagger >> w.$$ (3.20)

Using the following relations

$$[C_{k
u\sigma}, C_{k
u\sigma}^\dagger]_+ = \delta_{\nu\nu} I, \quad (3.21)$$

$$[C_{k
u\sigma}, H] = \sum_{\nu''} (t_{k\nu''}^{\nu''} + \delta_{\nu\nu} (\varepsilon_{\nu\sigma} + U_{\nu < n_{\nu\sigma}})) C_{k\nu\sigma}, \quad (3.22)$$

we obtain

$$w << C_{k
u\sigma}^\dagger; C_{k
u\sigma}^\dagger >> w =$$

$$\delta_{\nu\nu} I + \sum_{\nu''} (t_{k\nu''}^{\nu''} + \delta_{\nu\nu} (\varepsilon_{\nu\sigma} + U_{\nu < n_{\nu\sigma}})) << C_{k
u\sigma}^\dagger; C_{k
u\sigma}^\dagger >> w.$$ (3.23)

This equation can be rewritten in a matrix form as follows,

$$(wI - E)G = I,$$ (3.24)

where $I, E, G$ are $L \times L$ matrices defined by
\[ E_{\nu\nu'} = t^{\nu\nu'}_{kk'} + \delta_{\nu\nu'} (\epsilon_{\nu\sigma} + U_{\nu} < n_{\nu\sigma} >) \]  \hspace{1cm} (3.25)

\[ G_{\nu\nu'} = \langle\langle C_{k\nu\sigma}; C_{k\nu\sigma}^+ \rangle\rangle_w \]  \hspace{1cm} (3.26)

\[ I_{\nu\nu'} = \delta_{\nu\nu'} \]  \hspace{1cm} (3.27)

It can be shown that \( G \) satisfies the equation

\[ G = A(wI - \Lambda)A^+, \]  \hspace{1cm} (3.28)

where \( \Lambda \) is a diagonal matrix formed by the eigenvalues of \( E \), and \( A \) is an unitary matrix formed by the eigenvectors of \( E \). This equation can be rewritten as

\[ \langle\langle C_{k\nu\sigma}; C_{k\nu\sigma}^+ \rangle\rangle_w = \sum_{m} \frac{A_{\nu m}A_{\nu m}^*}{w - \Lambda_{mm}}. \]  \hspace{1cm} (3.29)

From (3.16), we find

\[ \langle C_{k\nu\sigma}^+ C_{k\nu\sigma} \rangle = \sum_{m(\Lambda_{mm} < \mu)} A_{\nu m}^* A_{\nu m}, \]  \hspace{1cm} (3.30)

where \( \mu \) is Fermi energy determined by requiring \( \frac{1}{N} \sum_{k\nu\sigma} < n_{k\nu\sigma} > \) equal to the total number of electrons inside the unit cell. The total energy of the system can be
calculated by

$$E_{tot} = \sum_{\nu \sigma} \epsilon_{\nu \sigma} <n_{\nu \sigma}> + \frac{1}{N} \sum_{k} \sum_{\nu \nu' \sigma} \sum_{\sigma} t_{k}^{\nu \nu' \sigma} <C_{k \nu \sigma}^{+} C_{k \nu' \sigma}>$$

$$+ \sum_{\nu} U_{\nu} <n_{\nu \uparrow}> <n_{\nu \downarrow}> .$$  \hspace{1cm} (3.31)

We can find the solution of the system by use of a standard self-consistent method. With the use of a set of reasonable starting parameters \(<n_{\nu \sigma}>>\), we can calculate the matrix elements of \(E\). After we find the eigenvalues and eigenvectors of \(E\), we can calculate the values of \(<n_{\nu \sigma}>>\). By mixing the new parameters with the old parameters, we obtain the parameters for the next iteration. The self-consistency procedure is continued until the total change of the parameters converges to within \(10^{-4}\) in successive iterations.

(b) Hubbard I Approximation

Let \(A = C_{i \nu \sigma}^{+}\) and \(B = C_{j \nu' \sigma}^{+}\). With the use of (3.15) and the relation

$$[C_{i \nu \sigma}, H] = \sum_{l \nu''} T_{il}^{\nu''} C_{l \nu'' \sigma}^{\rho} + \epsilon_{\nu \sigma} + U_{\nu} n_{i \nu},$$  \hspace{1cm} (3.32)

we find \(<C_{i \nu \sigma}; C_{j \nu' \sigma}^{+}>>w\) satisfies

$$w <C_{i \nu \sigma}; C_{j \nu' \sigma}^{+} >>w = \delta_{ij} \delta_{\nu \nu'} + \sum_{l \nu''} T_{il}^{\nu''} <C_{l \nu'' \sigma}; C_{j \nu' \sigma}^{+} >>w$$
By setting \( A = n_{i\nu\bar{\sigma}}C_{i\nu\sigma} \), \( B = C_{j\nu\sigma}^+ \) and using (3.15) together with the relation

\[
[n_{i\nu\bar{\sigma}}C_{i\nu\sigma}, H] = (\epsilon_{\nu\sigma} + U_{\nu})n_{i\nu\bar{\sigma}}C_{i\nu\sigma}
\]

we find \( \langle n_{i\nu\bar{\sigma}}C_{i\nu\sigma}; C_{j\nu\sigma}^+ \rangle \) satisfies

\[
\langle n_{i\nu\bar{\sigma}}C_{i\nu\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w = \delta_{ij} \delta_{\nu\bar{\nu}} \langle n_{\nu\bar{\sigma}} \rangle + (\epsilon_{\nu\sigma} + U_{\nu})
\]

\[
\langle n_{i\nu\bar{\sigma}}C_{i\nu\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w + \sum_{l\nu'' \neq l\nu'} T_{il}^{\nu''} \langle \langle n_{i\nu\bar{\sigma}}C_{i\nu''\sigma}; C_{j\nu''\sigma}^+ \rangle \rangle w
\]

\[
+ \langle C_{i\nu''\bar{\sigma}}^+ C_{l\nu''\bar{\sigma}} C_{i\nu\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w + \langle C_{l\nu''\bar{\sigma}}^+ C_{i\nu\bar{\sigma}} C_{i\nu\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w.
\]

In order to break off the sequence of Green function equations, we use the approximations which are given by

\[
\langle n_{i\nu\bar{\sigma}}C_{l\nu''\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w \approx \langle n_{i\nu\bar{\sigma}} \rangle \langle n_{i\nu\bar{\sigma}} \rangle \langle C_{l\nu''\sigma}; C_{j\nu\sigma}^+ \rangle \rangle w
\]

(3.36)
As a consequence of translational symmetry, the last two terms after the lattice sum will be canceled. Then (3.35) can be rewritten as

\[
[w - (\varepsilon_{\nu\sigma} + U_\nu)] \ll n_{\nu\bar{\sigma}} C_{\nu\sigma}; C_{j\nu\sigma}^+ >> w
\]

\[
-\ll n_{\nu\bar{\sigma}} \sum_{l'\neq\nu} T_{il'}^{\nu\nu} \ll C_{l'\sigma}; C_{j\nu\sigma}^+ >> w = \delta_{ij} \delta_{\nu\nu} \ll n_{\nu\bar{\sigma}} > (3.39)
\]

Equation (3.33) and (3.39) are the coupled equations used to solve the Green function of the system, we will present the method to solve it at the end of the next section.

(c) Projection Operator Mean Field (POMF) approximation [12, 13, 14]

We decouple the destruction operator \( C_{\nu\sigma} \) into two new operators \( f_{\nu\sigma} \) and \( F_{\nu\sigma} \) which are defined by

\[
f_{\nu\sigma} = (1 - n_{\nu\bar{\sigma}}) C_{\nu\sigma}
\]

\[
F_{\nu\sigma} = n_{\nu\bar{\sigma}} C_{\nu\sigma}
\]

The operator \( f_{\nu\sigma} \) is used to destroy an electron in \((\nu\sigma)\) when there is no electron in
(lνσ), so it acts on the single occupied state. On the other hand the operator \( F_{lνσ} \) is used to destroy an electron in \((lνσ)\) when \((lν\bar{σ})\) is occupied, so it acts on the double occupied state. Using the definition of \( f_{lνσ} \) and \( F_{lνσ} \), we find

\[
f_{lνσ}^+ F_{lνσ} = C_{lνσ}^+ (1 - n_{lν\bar{σ}}) n_{lνσ} C_{lνσ} = 0 \tag{3.42}
\]

\[
F_{lνσ}^+ f_{lνσ} = C_{lνσ}^+ n_{lν\bar{σ}} (1 - n_{lνσ}) C_{lνσ} = 0. \tag{3.43}
\]

Then we can express \( <n_{lνσ}> \) as the following

\[
n_{lνσ} = f_{lνσ}^+ f_{lνσ} + F_{lνσ}^+ F_{lνσ}, \tag{3.44}
\]

where the first term gives the occupation numbers for single occupation and the second term gives the occupation numbers for double occupation. It can be shown that they satisfy the following commutation relations

\[
[f_{lνσ}, f_{l'ν'?}^+] = 0 \tag{3.45}
\]

\[
[f_{lνσ}, F_{l'ν'?}^+] = \delta_\nu^\nu' \delta_\sigma^\sigma' \Phi_{lν} \tag{3.46}
\]

\[
[F_{lνσ}, f_{l'ν'?}^+] = \delta_\nu^\nu' \delta_\sigma^\sigma' \Phi_{lν} \tag{3.47}
\]

\[
[F_{lνσ}, F_{l'ν'?}^+] = 0 \tag{3.48}
\]

\[
[f_{lνσ}, f_{l'ν'?}^+] = \delta_\nu^\nu' \delta_\sigma^\sigma' \tag{3.49}
\]

\[
[f_{lνσ}, F_{l'ν'?}^+] = 0 \tag{3.50}
\]

\[
[F_{lνσ}, f_{l'ν'?}^+] = 0 \tag{3.51}
\]
\[ [F_{I
u\sigma}, F_{I
u'\sigma'}^+] = \delta_{\nu\nu'} \delta_{\sigma\sigma'} Q_{I
u\sigma'} \] (3.52)

where

\[ \Phi_{I\nu} = C_{I
u\sigma} C_{I\nu\bar{\sigma}} \] (3.53)
\[ q_{I\nu\sigma'} = -\sigma' C_{I\nu\bar{\sigma}} C_{I\nu\bar{\sigma}}' + \delta_{I\nu\sigma'} \] (3.54)
\[ Q_{I\nu\sigma'} = \sigma' C_{I\nu\bar{\sigma}} C_{I\nu\bar{\sigma}}' \] (3.55)

With the use of the commutation relations, we obtain

\[
\begin{align*}
[H, f_{I\nu\sigma}] &= \varepsilon_{\nu\sigma} f_{I\nu\sigma} + \sum_{l_1\nu_1\sigma_1} t_{l_1\nu_1}^{\nu\nu_1} q_{I\nu_1\sigma_1} C_{l_1\nu_1\sigma_1} + \sigma \sum_{l_1\nu_1} t_{l_1\nu_1}^{\nu\nu_1} C_{l_1\nu_1\bar{\sigma}} \Phi_{I\nu} \\
[H, F_{I\nu\sigma}] &= (\varepsilon_{\nu\sigma} + U_{\nu}) F_{I\nu\sigma} + \sum_{l_1\nu_1} t_{l_1\nu_1}^{\nu\nu_1} C_{l_1\nu_1\sigma_1} - \sigma \sum_{l_1\nu_1} t_{l_1\nu_1}^{\nu\nu_1} q_{I\nu_1\sigma_1} C_{l_1\nu_1\sigma_1} \\
&- \sigma \sum_{l_1\nu_1} t_{l_1\nu_1}^{\nu\nu_1} C_{l_1\nu_1\bar{\sigma}} \Phi_{I\nu} \] (3.56)
\]

In order to close our set of equations at the Mean field level, we use a projection operator \(\rho\) (defined explicitly in equation 3.67) to project every operator into the subspace formed by \(\{f_{I\nu\sigma}, f_{I\nu\sigma}^+, F_{I\nu\sigma}, F_{I\nu\sigma}^+\}\). To see how this is accomplished, let us define a set of orthogonal anticommutator projection operators as the following

\[ P_{I\nu\sigma}^1 X = \frac{f_{I\nu\sigma}}{M_{\nu\sigma}} \{<Q_{\nu\sigma}> <[f_{I\nu\sigma}^+, X]> \} \] (3.58)
\[ P_{I\nu\sigma}^2 X = \frac{F_{I\nu\sigma}}{M_{\nu\sigma}} \{<q_{\nu\sigma}> <[F_{I\nu\sigma}^+, X]> \} \] (3.59)
\[
\begin{align*}
    P_{l\nu_0}^3 X &= \frac{f_{l\nu_0}^+}{M_{\nu_0}} \{< Q\nu_\sigma > < [f_{l\nu_0}, X]^+ > \} \\
    P_{l\nu_0}^4 X &= \frac{f_{l\nu_0}^+}{M_{\nu_0}} \{< q\nu_\sigma > < [F_{l\nu_0}, X]^+ > \},
\end{align*}
\]

where
\[
\begin{align*}
    < q\nu_\sigma > &= < q_{\delta\sigma} > = 1 - < \nu\sigma > \\
    < Q\nu_\sigma > &= 1 - < q\nu_\sigma > = < \nu\sigma > \\
    < \Phi_\nu > &= < \Phi_{l\nu} > \\
    M\nu_\sigma &= < q\nu_\sigma > < Q\nu_\sigma > - < \Phi_\nu >^2
\end{align*}
\]

It is easily verified that they satisfy the orthogonal condition

\[
P_{l\nu_\sigma}^s P_{l'\nu'\sigma'}^t = \delta_{ll'} \delta_{\nu\nu'} \delta_{\sigma\sigma'} \delta_{ss'} P_{l'\nu'\sigma'}^s
\]

We choose the projection operator \( \varphi \) of the form

\[
\varphi = \sum_{s l \nu_\sigma} P_{l\nu_\sigma}^s,
\]

then it satisfies the basic projection operator condition \( (\varphi^2 = \varphi) \). It can be shown that

\[
p\{q_{l\nu_1\sigma_1} C_{l_1\nu_1\sigma_1} \} = f_{l_1\nu_1\sigma_1} Q_{\nu_1\sigma_1} q_{\nu_\sigma} q_{\nu_1\sigma_1} \delta_{\sigma_1\sigma}
\]
Let $A = f_{l
u \sigma}$ and $B = F_{l_2\nu \sigma}^+$. Using (3.15), (3.56), (3.68), and (3.69) we obtain

$$\begin{align*}
(w - \epsilon_{\nu \sigma}) << f_{l
u \sigma} ; F_{l_2\nu \sigma}^+ >> w &= \sum_{l_1 \nu_1} t_{l_1 l_1}^{\nu \nu_1} q_{\nu \sigma} << f_{l_1 \nu_1 \sigma_1} ; F_{l_2 \nu_2 \sigma}^+ >> w \\
+ \sum_{l_1 \nu_1} t_{l_1 l_1}^{\nu \nu_1} q_{\nu \sigma} \left(- < f_{l\nu \sigma} C_{l_1 \nu_1 \bar{\sigma}} > + < C_{l_1 \nu_1 \bar{\sigma}} F_{l\nu \sigma} > \right) << f_{l\nu \sigma} ; F_{l_2 \nu_2 \sigma}^+ >> w \\
+ \sum_{l_1 \nu_1} t_{l_1 l_1}^{\nu \nu_1} q_{\nu \sigma} << f_{l_1 \nu_1 \sigma_1} ; F_{l_2 \nu_2 \sigma}^+ >> w + \sum_{l_1 \nu_1} t_{l_1 l_1}^{\nu \nu_1} q_{\nu \sigma} \\
( < C_{l_1 \nu_1 \bar{\sigma}} F_{l\nu \sigma} > - < F_{l\nu \sigma} C_{l_1 \nu_1 \bar{\sigma}} > ) << f_{l\nu \sigma} ; F_{l_2 \nu_2 \sigma}^+ >> w \\
\end{align*}$$

(3.70)
\[ - \sum_{\nu_1} \gamma_{k\sigma}^{\nu_1} \ll F_{k\nu_1\sigma}^+; F_{k\nu_2\sigma}^+ \gg w = 0, \tag{3.71} \]

where

\[ \alpha_{k\sigma}^{\nu_1} = \frac{Q_{\nu\sigma}}{M_{\nu\sigma}} W_{\nu\sigma} \delta_{\nu_1} + q_{\nu\sigma} t_k^{\nu_1} \tag{3.72} \]

\[ \gamma_{k\sigma}^{\nu_1} = -\frac{q_{\nu\sigma}}{M_{\nu\sigma}} W_{\nu\sigma} \delta_{\nu_1} + q_{\nu\sigma} t_k^{\nu_1} \tag{3.73} \]

\[ W_{\nu\sigma} = \frac{1}{N} \sum_{\nu_1} t_i^{\nu_1} \langle F_{k_1\nu_2; C_{k_1\nu_2}} - C_{-k_1\nu_1; f_{-k_1\nu_1}} \rangle \tag{3.74} \]

Note that the \( W_{\nu\sigma} \) given by (3.74) are real. Similarly, by setting \((A, B)\) equal to \((f_{l\nu\sigma}, f_{l\nu\sigma}^+), (f_{l\nu\sigma}, f_{l\nu\sigma}^+), \) and \((F_{l\nu\sigma}, f_{l\nu\sigma}^+), \) we can get the other three equations of motion of the form

\[ - \sum_{\nu_1} (t_i^{\nu_1} - \alpha_{k\sigma}^{\nu_1}) \ll f_{k\nu_1\sigma}; F_{k\nu_2\sigma}^+ \gg w + \sum_{\nu_1} [\delta_{\nu_1}(w - \epsilon_{\nu\sigma} - U_{\nu\sigma}) \]

\[ - t_i^{\nu_1} + \gamma_{k\sigma}^{\nu_1} \ll F_{k\nu_1\sigma}; F_{k\nu_2\sigma}^+ \gg w = \delta_{\nu\sigma} Q_{\nu\sigma} \tag{3.75} \]

\[ \sum_{\nu_1} (\delta_{\nu_1}(w - [\delta_{\nu_1} \epsilon_{\nu\sigma} + \alpha_{k\sigma}^{\nu_1}]) \ll f_{k\nu_1\sigma}; f_{k\nu_2\sigma}^+ \gg w \]

\[ - \sum_{\nu_1} \gamma_{k\sigma}^{\nu_1} \ll F_{k\nu_1\sigma}; f_{k\nu_2\sigma}^+ \gg w = \delta_{\nu\sigma} Q_{\nu\sigma}, \tag{3.76} \]
\[
- \sum_{\nu_1} (t_k^{\nu_1} - \alpha_{k\sigma}^{\nu_1}) \langle \langle f_{k\nu_1 \sigma}^+ f_{k\nu_1 \sigma}^+ \rangle \rangle w
\]
\[
+ \sum_{\nu_1} [\delta_{\nu_1}(w - \epsilon_{\nu\sigma} - U_{\nu}) - t_k^{\nu_1} + \gamma_{k\sigma}^{\nu_1}] \langle \langle F_{k\nu_1 \sigma}^+ f_{k\nu_2 \sigma}^+ \rangle \rangle w = 0
\]  

(3.77)

If we define three \(2L \times 2L\) matrices \(E, G,\) and \(\Theta\) of the form

\[
E(k\sigma) = \begin{pmatrix} E^{ff}(k\sigma) & E^{fF}(k\sigma) \\ E^{Ff}(k\sigma) & E^{FF}(k\sigma) \end{pmatrix},
\]

\[
G(k\sigma) = \begin{pmatrix} G^{ff}(k\sigma) & G^{fF}(k\sigma) \\ G^{Ff}(k\sigma) & G^{FF}(k\sigma) \end{pmatrix},
\]

\[
\Theta_{ij} = \begin{cases} 
\delta_{ij}\delta_{ii} & \text{if } i \leq j \\
\delta_{ij}Q(i-L) & \text{if } i > j 
\end{cases}
\]

where \(E^{ff}(k\sigma), E^{fF}(k\sigma), E^{Ff}(k\sigma), E^{FF}(k\sigma), G^{ff}(k\sigma), G^{fF}(k\sigma), G^{Ff}(k\sigma), G^{FF}(k\sigma),\)

and \(G^{FF}(k\sigma)\) are \(L \times L\) matrices defined by

\[
E^{ff}(k\sigma) = (\epsilon_{\nu} + \frac{W_{\nu\sigma}}{Q_{\nu\sigma}}) \delta_{\nu\nu_1} + q_{\nu\sigma} t_k^{\nu_1}
\]  

(3.78)

\[
E^{fF}(k\sigma) = -\frac{W_{\nu\sigma}}{Q_{\nu\sigma}} \delta_{\nu\nu_1} + q_{\nu\sigma} t_k^{\nu_1}
\]  

(3.79)

\[
E^{FF}(k\sigma) = -\frac{W_{\nu\sigma}}{Q_{\nu\sigma}} \delta_{\nu\nu_1} + Q_{\nu\sigma} t_k^{\nu_1}
\]  

(3.80)
\[ E^{FF}_{\nu\nu_1}(k\sigma) = (\epsilon_\nu + U_\nu + \frac{W_{\nu\sigma}}{Q_{\nu\sigma}})\delta_{\nu\nu_1} + Q_{\nu\sigma}t_\nu^1 \] (3.81)

\[ G^{FF}_{\nu\nu_1}(k\sigma) = \langle\langle f_{k\nu\sigma}^+; f_{k\nu_1\sigma}^+ \rangle\rangle \] (3.82)

\[ G^{FF}_{\nu\nu_1}(k\sigma) = \langle\langle f_{k\nu\sigma}^+; F_{k\nu_1\sigma}^+ \rangle\rangle \] (3.83)

\[ G^{FF}_{\nu\nu_1}(k\sigma) = \langle\langle f_{k\nu\sigma}^+; f_{k\nu_1\sigma}^+ \rangle\rangle \] (3.84)

\[ G^{FF}_{\nu\nu_1}(k\sigma) = \langle\langle F_{k\nu\sigma}^+; F_{k\nu_1\sigma}^+ \rangle\rangle \] (3.85)

Then equation (3.71), (3.75), (3.76), and (3.77) can be combined into a matrix form as the following

\[ (wI - E)G = \Theta \] (3.86)

We find that \( E \) is not Hermitian, but \( S \), which is defined by \( S = \Theta - \frac{1}{2} E \Theta \frac{1}{2} \), is. It is easily verified that \( G \) satisfies

\[ G = (wI - E)^{-1}\Theta \]

\[ = \Theta \frac{1}{2} A (wI - \Lambda)^{-1} A^+ \Theta \frac{1}{2}, \] (3.87)

where \( \Lambda \) is an diagonal matrix formed by the eigenvalues of \( S \), and \( A \) is an unitary matrix formed by the eigenvectors of \( S \). This equation can be rewritten as follow

\[ G_{ji}(k\sigma) = \sum_{n=1}^{2L} \frac{\Theta^{\frac{1}{2}}_{jj} A_{jn} A_{in}^* \Theta^{\frac{1}{2}}_{ii}}{w - \Lambda_{nn}} \] (3.88)
Then we can calculate the expectation values of \( f_{k\nu\sigma}^+ f_{k\nu\sigma} \), \( f_{k\nu\sigma}^+ F_{k\nu\sigma} \), \( F_{k\nu\sigma}^+ f_{k\nu\sigma} \), and \( F_{k\nu\sigma}^+ F_{k\nu\sigma} \) by the following relation

\[
N_{ij}(k\sigma) = \langle O_i^+(k\sigma) O_j(k\sigma) \rangle
= -\frac{1}{\pi} \int_{-\infty}^{\infty} dw \frac{Im G_{ji}(k\sigma)}{e^{\beta w} + 1}
= \sum_{n(\Lambda nn \leq \mu)} \Theta_{jj} \frac{1}{2} A_{jn} A_{in}^* \Theta_{ii}^* \tag{3.89}
\]

where \( \mu \) is the Fermi energy, and

\[
O_i(k\sigma) = \begin{cases} 
  f_i(k\sigma) & \text{if } i \leq L \\
  F_{i-L}(k\sigma) & \text{if } i > L
\end{cases}
\]

The \( \langle n_{\nu\sigma} \rangle \) can be calculated by

\[
\langle n_{\nu\sigma} \rangle = \frac{1}{N} \sum_k \langle n_{k\sigma} \rangle, \tag{3.90}
\]

where

\[
\langle n_{k\sigma} \rangle = \langle f_{k\nu\sigma}^+ f_{k\nu\sigma} \rangle + \langle f_{k\nu\sigma}^+ F_{k\nu\sigma} \rangle + \langle F_{k\nu\sigma}^+ f_{k\nu\sigma} \rangle + \langle F_{k\nu\sigma}^+ F_{k\nu\sigma} \rangle \tag{3.91}
\]

The Fermi energy is determined by the follow relation

\[
N_t = \sum_{\nu\sigma} \langle n_{\nu\sigma} \rangle, \tag{3.92}
\]
where \( N_t \) is the total number of electrons per unit cell. At this point, we can use the self-consistent method to find the solution of the system. The iterating parameters now are \( \{ < n_{\nu \sigma} > \} \) and \( \{ W_{\nu \sigma} \} \). Because the dimension of \( S \) is \( 2L \times 2L \), we have \( 2L \) bands instead of \( L \) bands for a system with \( L \) orbitals per unit cell. When the hopping terms \( T_{ij}^{\nu \nu'} \) vanish, these bands can be classified into two groups - single occupied (lower) bands and double occupied (upper) bands. They are mixed up when the hopping terms are large. The \( W_{\nu \sigma} \) are the \( k \) and \( w \) independent self-energies. By setting \( W_{\nu \sigma} \) to be equal to zero, we can show that the coupled equations (3.71), (3.75), (3.76), and (3.77) are equivalent to the coupled equations (3.33) and (3.39) which were obtained using the Hubbard I approximation. So we can use the same method discussed in this section to study the solution of Hubbard Model within the Hubbard I Approximation. Now the iterating parameters are just \( \{ < n_{\nu \sigma} > \} \), since all \( \{ W_{\nu \sigma} \} \) are to be set equal to zero. We still have \( 2L \) bands for the system with \( L \) orbitals per unit cell. We will show the POMF Approximation gives better results than those calculated using Hubbard I Approximation. Unfortunately both approximations violate the basic on-site sum rule. To see this, we note that \( < f_{k \nu \sigma}^+ F_{k \nu \sigma} > \) is, in general, different from zero for arbitrary \( k \). However, if we sum this function over \( k \), we generate the on-site expression \( < f_{\nu \sigma}^+ F_{\nu \sigma} > \) which should be equal to zero, and which is not satisfied in both approximations. By comparing our results with the Monte-Carlo results, we find that in order to get the most reasonable results we have to include the \( < f_{\nu \sigma}^+ F_{\nu \sigma} > \) terms in our calculation. Therefore, in the calculation we use the following expressions.
\[
\begin{align*}
n_{\nu\sigma}n_{\nu\bar{\sigma}} &= \langle C^{+}_{\nu\sigma}F_{\nu\sigma} \rangle \quad (3.93) \\
Q_{\nu\sigma} &= \langle C^{+}_{\nu\bar{\sigma}}C_{\nu\sigma} \rangle \quad (3.94) \\
S_{2\nu}^{2} &= \langle C^{+}_{\nu\sigma}f_{\nu\sigma} \rangle - \langle C^{+}_{\nu\bar{\sigma}}f_{\nu\bar{\sigma}} \rangle \quad (3.95)
\end{align*}
\]

The total energy of the system can then be calculated by

\[
E_{tot} = \sum_{\nu\sigma} \varepsilon_{\nu\sigma} \langle n_{\nu\sigma} \rangle + \frac{1}{N} \sum_{k} \sum_{\nu\nu'1} \sum_{\sigma} l_{k}^{\nu\nu'1} \langle C^{+}_{k\nu\sigma}C_{k\nu'\sigma} \rangle + \sum_{\nu} U_{\nu} \langle C^{+}_{\nu\uparrow}F_{\nu\downarrow} \rangle.
\] (3.96)
Results

In order to demonstrate the capability of the POMF approximation, we present some test results before we study the \( \text{CuO}_2 \) plane. Since Quantum Monte Carlo (QMC) simulations are able to give an accurate description of the Hubbard model, we will compare the results calculated by the POMF approximation, the HF approximation, and the Hubbard I approximation to those of the QMC simulation. Then we will use parameters determined from calculations using the constrained local density functional approximation for the \( \text{CuO}_2 \) plane with the POMF approximation and compare the results to experimental measurements. Finally, we will study \( \text{CuO}_2 \) with various sets of parameters to examine the effect on the solution of each parameter. All the calculations were performed for finite temperature, therefore we can make a direct comparison with the QMC results.

A. One-band Hubbard model

We consider the one-band Hubbard model on a square lattice with

\[
H = -t \sum_{\langle i,j \rangle} \sum_{\sigma} (C_{i\sigma}^+ C_{j\sigma} + C_{j\sigma}^+ C_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.97)
\]

In the following the hopping parameter will be fixed at \( t = 1 \). The ground state of the half-filled two-dimensional Hubbard model is known to be an antiferromagnetic insulator for a wide range of the Coulomb repulsion \( U \) [79, 80]. The critical \( U \) is probably zero. When the system is doped away from half-filling, antiferromagnetism is depressed rapidly. We find the Hubbard I approximation does not give any magnetic
solution for any value of U and \( <n> \). Using the HF approximation, the ground state of the system at half-filled is found to be an antiferromagnetic insulator for any value of U. When the system is doped away from half-filling, antiferromagnetism is depressed slowly. Using the POMF approximation we can get an antiferromagnetic ground state solution only when U is greater than 14 and \( n \) is close to half-filled, and no ferromagnetic solution for any U and \( <n> \). We can extend the range of the antiferromagnetic solution by adding a small ad hoc self-energy correction into the W term, however since we do not know yet how to self-consistently evaluate this self-energy correction, we will not include this correction in the rest of the calculations described.

The average energy per site \( <E> \) and the squared magnetic moment \( <S_z^2> \) as a function of band filling calculated by the HF approximation, the Hubbard I approximation, and the POMF approximation together with the QMC [80] results are shown in Figures 3.1a and 3.1b. These results are calculated at U=4 and \( \beta = 10 \), where \( \beta \) is the inverse temperature. The HF approximation gives the average energy too high and squared magnetic moment too small. In this case the system exhibits antiferromagnetism for \( 0.8 < n < 1.2 \), and paramagnetism for \( n < 0.8 \) and \( n > 1.2 \). The results given by Hubbard I generally agree pretty well with the QMC results, but they are bad when the system is close to half-filled. Since the magnetic energy \( (E_{PM} - E_{AF}) \) is small for the system we considered, the average energy calculated by POMF agrees very well with the QMC result. On the other hand, the squared magnetic moment is very strongly dependent on the magnetic ordering of the system. Therefore the squared magnetic moment gets worse for \( <n> \) close to half-filled where the system is found to be antiferromagnetic by QMC. Here, the \( <S_z^2> \) in HF
is calculated by

\[ \langle S_z^2 \rangle = \langle n \uparrow \rangle + \langle n \downarrow \rangle - 2 \langle n \uparrow \rangle \langle n \downarrow \rangle \] (3.98)

The squared magnetic moment at half-filling given by HF agrees excellently with the QMC result. But it is just an accident.

The average energy per site and the squared magnetic moment, respectively, for values of \( U = 1, 2, \) and 4 as a function of band filling calculated by the POMF approximation and the QMC simulation are shown in figures 3.2a and 3.2b. They generally agree very well except for \( n \) close to half-filling. Although the value of \( \langle S_z^2 \rangle \) at half-filling with \( U = 4 \), calculated with the HF approximation is given by 0.74 \( \mu_B^2 \) which is in excellent agreement with QMC, the \( \langle S_z^2 \rangle \) calculated with the HF approximation for \( U = 2 \) and \( U = 1 \) are given by 0.52 \( \mu_B^2 \) and 0.5 \( \mu_B^2 \), respectively, which are quite different from the QMC results.

We have also calculated the reduction in effective hopping which is defined by

\[ \frac{t_{eff}}{t} = \frac{\langle C_i^\dagger C_j \sigma + C_j^\dagger C_i \sigma \rangle \neq 0}{\langle C_i^\dagger C_j \sigma + C_j^\dagger C_i \sigma \rangle \neq 0} \] (3.99)

The \( t_{eff}/t \) as a function of band filling for \( U = 4 \) and \( \beta = 6 \) calculated by Hubbard I and POMF together with QMC are shown in Figure 3.3. The effective hopping is depressed by the Coulomb repulsion. We can see that the results given by the POMF approximation are quite reasonable except for \( \langle n \rangle \) very close to 1. On the other hand, the HF approximation alway gives the value of \( t_{eff}/t \) equal to 1, no matter what values of \( U \) and \( \langle n \rangle \) are used.
Figure 3.1: The comparison of (a) the average energy per site and (b) the squared magnetic moment obtained using the POMF approximation, HF approximation, Hubbard I approximation, and QMC simulation (Ref. 80) for $U = 4$, $t = 1$, and $\beta = 10$. 
Figure 3.2: The comparison of (a) the average energy per site and (b) the squared magnetic moment obtained using the POMF approximation and QMC simulation (Ref. 80) for $U = 1, 2,$ and $4$, $t = 1$, and $\beta = 10$
Figure 3.3: The comparison of $t_{\text{eff}}/t$ obtained using the POMF approximation, Hubbard I approximation, and QMC simulation (Ref. 80) for $U = 4$, $t = 1$, and $\beta = 6$
B. Three-band Hubbard model

We now consider the three band Hubbard model, which consists of the hybridized binding band arising from the Cu \(d_{x^2-y^2}\) and O \(p_{x(y)}\) orbitals in the CuO\(_2\) plane as shown in Figure 3.4. Thus, we study the following Hamiltonian:

\[
H = \sum_{i} \epsilon d_{i\sigma}^+ d_{i\sigma} + \sum_{j} \epsilon p_{j\sigma}^+ p_{j\sigma} + \frac{1}{2} \sum_{i} U_d d_{i\sigma}^+ d_{i\bar{\sigma}}^+ d_{i\bar{\sigma}} + \frac{1}{2} \sum_{j} U_p p_{j\sigma}^+ p_{j\bar{\sigma}}^+ p_{j\sigma} p_{j\bar{\sigma}} + \sum_{<i,j>} U_{dp} d_{i\sigma}^+ d_{i\sigma} p_{j\sigma}^+ p_{j\sigma} + \sum_{<i,j>} t_{ij}(d_{i\sigma}^+ p_{j\sigma} + H.c.)
\]

\[
+ \sum_{<i,j>} \sum_{\sigma'\sigma} t_{ij}(p_{j\sigma'}^+ p_{j\sigma} + H.c.)
\]

where the index \(i(j)\) runs over the Cu(O) sites. Here \(d_{i\sigma}^+\) and \(p_{j\sigma}^+\) denote the creation operators of a hole in a Cu \(d_{x^2-y^2}\) state at site \(i\) and a hole in an O \(p_{x(y)}\) state at site \(j\), respectively. \(\sigma\) is the spin index, \(U_d\) and \(U_p\) are the on-site hole repulsion, and \(U_{dp}\) denotes the Coulomb repulsion between holes at neighboring Cu and O sites. The on-site energy is given by \(\epsilon_d\) and \(\epsilon_p\) and the charge-transfer energy is given by \(\Delta = \epsilon_p - \epsilon_d\). The strong hybridization between the Cu \(d_{x^2-y^2}\) and O \(p_{x(y)}\) orbitals is governed by the hopping parameters

\[
t_{ij} = t_{dp}(-1)^{\alpha_{ij}}
\]  

(3.100)

where \(\alpha_{ij} = 2\) if \(j = i + \hat{x}/2\) or \(i - \hat{y}/2\), and \(\alpha_{ij} = 1\) if \(j = i - \hat{x}/2\) or \(i + \hat{y}/2\). The O – O hopping matrix element is defined in a similar way:
where $\beta_{jj'} = 1$ if $j' = j - \hat{x}/2 - \hat{y}/2$ or $j + \hat{x}/2 + \hat{y}/2$, and $\beta_{jj'} = 2$ if $j' = j - \hat{x}/2 + \hat{y}/2$ or $j + \hat{x}/2 - \hat{y}/2$.

We use the hole notation in our calculation, so that the vacuum is the state in which all orbitals are fully occupied. At first, we examine the POMF solution for the three-band Hubbard model by calculating some physical quantities that have been studied using QMC [81]. Figure 3.5 shows the POMF and QMC results for the hole occupation on the Cu site, $< n_{Cu} >$, and the O site, $< n_{O} >$, for $\beta = 8$, $U_p = 0.0$, $t_{dp} = 1.0$, $t_{pp} = 0.0$, $U_d = 6$, and $\Delta = 2$. Both the AF solution and the PM solution calculated by POMF are included in Figure 3.5. We can see that the AF solution agrees better with the QMC results for $n = 0.8, 0.9, 1.0$, and $1.1$, where the total energy calculated using POMF for the AF solution is lower than that of the PM solution. For $n = 1.2$, we find the total energy of the PM solution is lower than that of the AF solution and the PM solution agrees better with the QMC result. We can also see that when holes are added to the system away from half-filling, $n = 1$, they go mainly to the oxygen site. On the other hand, if the electrons are added to the system, decreasing $n$, holes are mainly removed from the Cu sites. That is in agreement with experimental observation [82].

The squared magnetic moment $< S^2_z >$ and the hole occupation on Cu sites $< n_{Cu} >$, respectively, as a function of charge transfer energy $\Delta$ for $U_d = 6$, $t_{dp} = 1$, $U_p = U_{dp} = t_{pp} = 0$, and $\beta = 10$ at half-filling calculated by POMF and QMC are shown in Figures 3.6a and 3.6b. Again they agree quite well with each other. When
the charge transfer energy $\Delta$ increases, more holes go to the Cu sites and $<S_z^2>$ increases as expected.

We have presented several test cases, and the agreement with the QMC results gives clear evidence for the utility of the present POMF method to study the three-band Hubbard model. Now we go to the second part - study the solution of the three-band Hubbard model with parameters more suitable for the $CuO_2$ plane using the POMF approximation. Recently, the parameters of the three-band Hubbard model were determined, both theoretically, from LSDA calculations [83, 84, 85], and experimentally, by analyzing the photoemission experiments [86, 87, 88]. The values of the parameters determined by different groups are quite similar. The ranges for the values of the parameters are given by $\Delta$, (1.5eV ~ 4.0eV); $U_d$, (8.8eV ~ 10.5eV); $U_p$, (4.0eV ~ 6.0eV); $U_{dp}$, (0.0eV ~ 1.5eV); $t_{dp}$, (1.07eV ~ 1.6eV) and $t_{pp}$, (0.33eV ~ 0.65eV). McMahan, Annett, and Martin [85] included two more orbitals, Cu $d_{3z^2-r^2}$ and out of plane $Op_z$ in their calculation. In the calculations presented below, we will use the parameters determined by Hybertsen, Schlüter, and Christensen (HSC) [83] as shown in Table 3.1. HSC perform standard LMTO calculations with the use of the constrained local density functional approach to calculate the energy surface as a function of local orbital occupation in $La_2CuO_4$. Then they extract the parameters by matching the energy surface to the one obtained by a HF solution of the three-band Hubbard model.
Figure 3.4: A schematic representation of the orbitals. On the Cu sites we consider the $d_{x^2-y^2}$ orbitals and on the oxygen sites the $p_x$ and $p_y$ orbitals
Figure 3.5: The hole occupation numbers on the Cu site $<n_{Cu}>$ and the O site $<n_O>$ versus band filling $n$ for $U_d = 6, \Delta = 2, t_{dp} = 1.0, t_p = U_p = 0$, and $\beta = 8$ calculated using the POMF approximation and the QMC simulation (Ref. 81)
Figure 3.6: (a) The squared magnetic moment $< S_z^2 >$ and (b) the hole occupation on Cu site $< n_{Cu} >$ versus charge transfer energy $\Delta$ for $U_d = 6, t_{dp} = 1.0, t_p = U_p = U_{dp} = 0$, and $\beta = 10$ at half-filling calculated using the POMF approximation and the QMC simulation (Ref. 81)
Table 3.1: Parameter values for the CuO$_2$ plane used in the present calculation. All values are in eV

<table>
<thead>
<tr>
<th>$U_d$</th>
<th>$U_p$</th>
<th>$U_{dp}$</th>
<th>$\Delta$</th>
<th>$t_{dp}$</th>
<th>$t_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>4.0</td>
<td>1.2</td>
<td>3.6</td>
<td>1.3</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Note that all the parameters listed in Table 3.1 are evaluated in the hole picture. The corresponding parameters in the electron picture can be obtained by the following relations.

\[
U_d^{(e)} = U_d \quad (3.102)
\]
\[
U_p^{(e)} = U_p \quad (3.103)
\]
\[
U_{dp}^{(e)} = U_{dp} \quad (3.104)
\]
\[
t_{dp}^{(e)} = -t_{dp} \quad (3.105)
\]
\[
t_p^{(e)} = -t_p \quad (3.106)
\]
\[
\epsilon_p^{(e)} = -[\epsilon_p + U_p + 2U_{dp}] \quad (3.107)
\]
\[
\epsilon_d^{(e)} = -[\epsilon_d + U_d + 4U_{dp}] \quad (3.108)
\]
Since the intersite correlation is weak, we can include the $U_{dp}$ terms in our calculation by the HF approximation, which replaces $U_{dp} n_{d_i\sigma} n_{p_j\sigma'}$ by $\frac{1}{2} U_{dp} (n_{d_i\sigma} < n_{p_j\sigma'} > + < n_{d_i\sigma} > n_{p_j\sigma'} )$. Therefore the effect of the $U_{dp}$ is just a constant shift of the on-site energies given by

$$\epsilon_d \rightarrow \epsilon_d + 2U_{dp} < n_O >$$

(3.109)

$$\epsilon_p \rightarrow \epsilon_p + U_{dp} < n_{Cu} > .$$

(3.110)

In order to study the antiferromagnetic ordering, we consider two CuO$_2$ formula units per unit cell. Thus we now have six orbitals per unit cell. The half-filled upper band case, one hole per CuO$_2$ unit, corresponds to 10 electrons (or 2 holes) per unit cell. The ground state of the system at half-filling, $n=1$ per CuO$_2$, is found to be an antiferromagnetic insulator in our calculation. The band gap and the magnetic moment calculated by the POMF method is found to be $2.0eV$ and $0.65\mu_B$ assuming $g = 2.0$, and the corresponding results in experiment are given by $1.5eV \sim 2.0eV$ [89, 90] and $(0.55 \pm 0.05)\mu_B$ [91, 92]. They agree quite well. The hole occupation on the Cu site and the root mean square magnetic moment $\sqrt{< S_z^2 >}$ are given by $0.708e$ and $0.83\mu_B$. Thus most of the hole is located on the Cu site, and the spin fluctuation, which is given by $\sqrt{< S_z^2 >} - < S_z >^2$, is quite strong.

When the system is doped away from half-filling, for example $n=1.1$, the system is found to be a paramagnetic metal by experiment. Therefore we present both the paramagnetic (PM) and antiferromagnetic (AF) solution for the case with doping, $n=1.1$. The hole occupation on the Cu site and $\sqrt{< S_z^2 >}$ are found to be $0.698e$ and
0.78\mu_B for the PM solution and 0.741e and 0.834\mu_B for AF solution respectively. Thus, consistent with experiment when holes are doped to the system away from half-filling they go mainly to oxygen sites, 110\% for the PM solution and 67\% for the AF solution in our calculation [82]. Also when the antiferromagnetism is destroyed by hole doping the \sqrt{<S_z^2>} show little dependence on doping [91, 92]. Both these observations are consistent with our POMF results.

The electronic energy band structure in the electron picture along the (11) direction calculated using the POMF approximation for the AF solution at n=1.0, the AF solution at n=1.1, and the PM solution at n=1.1 are shown in Figure 3.7, and the corresponding density of states are shown in Figure 3.8. One general feature of our results is that we obtain twelve bands instead of six bands for the system with six orbitals per unit cell. This is a consequence of the POMF method which keeps track of single and double occupancy. The number of electrons for the filled nth band with spin index \sigma is determined by

\[ N_{\ell \sigma}^{(n)} = \frac{1}{N} \sum_{k\nu} < C_{k\nu\sigma}^+(n) C_{k\nu\sigma}(n) >, \]  

(3.111)

which is called the weight of that band. The weight for each band is usually less than one; however, the sum rule

\[ \sum_{n=1}^{12} N_{\ell \sigma}^{(n)} = 6 \]  

(3.112)

is satisfied. For the AF solution at half-filling, 10 electrons filled per unit cell, there is a gap opened by antiferromagnetic splitting between bands 11 and 12. If the weight
of the 12th band, $N_{t\sigma}^{12}$, is equal to one, then the gap is at the Fermi level, and forms an insulator. However, the weight of the 12th band calculated for this case is equal to 0.9817 instead of 1.0. Therefore the 11th band cuts the Fermi level and leaves a small part of the 11th band unoccupied. We believe that this is mainly caused by the inconsistency mentioned previously in our method, and the ground state for the half-filling should in fact be an antiferromagnetic insulator.

There are many features of the density of states in Figure 3.8 which agree with experimental measurement. There is a gap opening for the half-filled case. The structures around 5 eV below Fermi level with mainly O p character and around 13 eV with mainly Cu d character below Fermi level which are in reasonable agreement with experiment [93]. The structure around 13 eV below Fermi level, the satellite, is caused by the Coulomb repulsion $U$ between two holes on the same Cu site, which has drawn much attention during the past decade.

We also calculated the magnetic moment as a function of doping. Antiferromagnetic, ferromagnetic (FM), and paramagnetic solutions were investigated. The magnetic moment on the Cu site for AF solution and the magnetic moment on the Cu site and the oxygen site for FM solution calculated using POMF approximation are shown in Figure 3.9a. Here the magnetic moment on the Cu site for the AF solution calculated using the HF approximation is also included in Figure 3.9a for comparison. Figure 3.9b shows the energy difference between the AF solution and the PM solution, $E(\text{AF})-E(\text{PM})$, and the energy difference between the FM solution and the PM solution, $E(\text{FM})-E(\text{PM})$, calculated using the POMF approximation. We can see that there is a small region around $n=1.1$ where the FM solution is the ground state. However, this does not agree with experiment. The $U_{dp}$ term strongly
favors the FM solution. No FM ground state was found if we reduced the value of $U_{dp}$ down to 0.8eV. The magnetic moment and the energy differences as a function of hole concentration for $U_{dp} = 0.8eV$ are shown in Figures 3.10a and 3.10b. Therefore the value of $U_{dp}$ determined by Hybertsen's group, $U_{dp} = 1.2eV$, may be too large. By replacing the value of $U_{dp}$ by 0.8eV, we found the AF magnetic moment and band gap are given by 1.8eV and 0.635$\mu_B$ for half-filling. The squared magnetic moment is given by 0.823$\mu_B$ which indicates that the spin fluctuation is quite strong. When the system is doped away from half-filling, we found that the holes introduced by doping go mainly to oxygen sites, 66% for AF solution and 106% for PM solution; and the squared magnetic moment are almost not changed, 0.826$\mu_B$ for AF solution and 0.778$\mu_B$ for PM solution. All these results are also in reasonable agreement with experiment.

The magnetic moment calculated using the POMF approximation is depressed by doping and disappears for doping of about 0.25 holes or 0.4 electron per CuO$_2$ unit. The disappearance of long range ordering is faster for hole doping than that for electron doping. The HF approximation gives a larger moment at half-filling, and the long range ordering is less rapidly destroyed than that in the POMF approximation. Experimentally, the magnetic order of $La_{2-x}(Sr/Ba)_xCuO_4$ disappears at the concentration of $x \approx 0.03$ [64, 94, 95], which is about a factor of 10 faster than what we have in the POMF approximation. Although we obtain an AF ground state at $n=1.1$, we believe the PM solution will give a better description of the real system for that hole concentration. Thus, we will focus on the AF solution for $n = 1$ and the PM solution for $n = 1.1$ in the rest of this chapter.

Before we study the ferromagnetic response with an applied field, let us examine
the PM solution for the half-filled case. We find there is a single band crossing
the Fermi level, which is the anti-bonding band of $Cu \, d_{x^2-y^2}$ - $O \, p_{x,y}$, and the
amount of oxygen $p_{x,y}$ admixed into the $Cu \, d_{x^2-y^2}$ conduction bands near the
Fermi level is less than 25%. This is considerably less than the 60% obtained in the
LSDA calculations for $La_2CuO_4$. Since the contribution of the $O \, p$ states is small,
the induced moment on the oxygen site by an applied magnetic field will be small,
which is contrary to what we obtained from LSDA but consistent with experimental
observation. To calculate the moment on each site induced by the applied field,
we need to reduce the charge transfer energy $\Delta$ from 3.6eV to 2.0eV in order to
prevent a spontaneous ferromagnetic solution. For $\Delta = 2.0eV$, the induced moment
on the $Cu$ site and the oxygen site are given by 0.0167$\mu_B$ and 0.0037$\mu_B$ when we
shift the spin up (down) bands by -0.005 (+0.005) eV corresponding to a magnetic
field of $8.64 \times 10^5 G$. If we reduce the value of $\Delta$ further, $\Delta = 1.5eV$, we find the
induced moment on the $Cu$ site and the oxygen site are now given by 0.0069$\mu_B$ and
0.00212$\mu_B$ when the same amount of energy shift is applied. The contribution of the
total induced moment per unit cell by the oxygen sites is given by 38% for $\Delta = 1.5eV$
and 30% for $\Delta = 2.0eV$. Therefore, we conclude that there is only small amount of
oxygen $2p$ admixture into the $Cu \, 3d$ conduction bands and the contribution of the
oxygen sites to the induced ferromagnetic form factor is small, all these are consistent
with the experimental observation [70, 71].
Figure 3.7: The electronic structure along the (11) direction calculated using the POMF approximation for (a) antiferromagnetic solution at n=1.0, (b) antiferromagnetic solution at n=1.1, and (c) paramagnetic solution at n=1.1. Parameters are the same as in Table 3.1.
Figure 3.8: The density of states calculated using the POMF approximation for (a) antiferromagnetic solution at n=1.0, (b) antiferromagnetic solution at n=1.1, and (c) paramagnetic solution at n=1.1. Parameters are the same as in Table 3.1.
Figure 3.9: (a) The magnetic moment on the Cu site for AF solution and the magnetic moment on the Cu site and the oxygen site for FM solution as a function of hole concentration calculated using the POMF approximation. The magnetic moment on the Cu site for AF solution calculated using the HF approximation is also included for comparison. (b) The magnetic energy, $E(\text{AF})-E(\text{PM})$ and $E(\text{FM})-E(\text{PM})$, as a function of hole concentration calculated using the POMF approximation. Parameters are the same as in Table 3.1.
Figure 3.10: (a) The magnetic moment on the Cu site for AF solution and the magnetic moment on the Cu site and the oxygen site for FM solution as a function of hole concentration calculated using the POMF approximation for $U_d^p = 0.8eV$. The magnetic moment on the Cu site for AF solution calculated using the HF approximation is also included for comparison. (b) The magnetic energy, $E(AF)-E(PM)$ and $E(FM)-E(PM)$, as a function of hole concentration calculated using the POMF approximation for $U_d^p = 0.8eV$. The other parameters are as given in Table 3.1.
We have shown that the POMF approximation does give reasonable results for the three-band Hubbard model by comparing our results to those of the QMC. We also have shown that the POMF approximation of the three-band Hubbard model with the parameters determined by constrained local density functional gives a reasonable description of the CuO$_2$ plane of some High $T_C$ superconductors. It is also of interest to study the effect on the solution of each parameter. In the following, we will use the parameters obtained from the constrained local density functional approximation as the basis, and change the value of one parameter at a time to see its effect on the solution.

The first parameter we present here is $U_d$, which describes the Coulomb interaction of two holes on the same site. Figure 3.11 shows the density of states for the AF solution at $n = 1.0$ and the PM solution at $n = 1.1$ with $U_d$ given by 10.5eV, 8.5eV, and 6.5eV. Table 3.2 shows the corresponding hole occupation on the Cu site $<n_{Cu}>$, the magnetic moment $<S_z>$, $\sqrt{<S_z^2>}$, and the band gap $E_g$ for AF solution at $n=1.0$. Also given is the $<n_{Cu}>$, and $\sqrt{<S_z^2>}$ for the PM solution at $n = 1.1$. We can see that the value of $<n_{Cu}>$, $<S_z^2>$, $\sqrt{<S_z^2>}$, $E_g$, and from Figure 3.11 the binding energy of the satellite $E_B$ are increased by increasing the value of $U_d$. It should be noted that the increase of the value of $E_B$ is about the same as that of $U_d$, and that the value of $<n_{Cu}>$ is almost not affected by increasing the value of $U_d$. 
The comparison of the total density of states for $U_d = 10.5eV$, $8.5eV$, and $6.5eV$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1.
Table 3.2: Comparison of the POMF results for different values of $U_d$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$U_d$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$&lt; S_z &gt;$ ($\mu_B$)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
<th>$E_g$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>8.5</td>
<td>0.704</td>
<td>0.633</td>
<td>0.826</td>
<td>1.72</td>
<td>0.704</td>
<td>0.781</td>
</tr>
<tr>
<td>6.5</td>
<td>0.700</td>
<td>0.598</td>
<td>0.817</td>
<td>1.41</td>
<td>0.712</td>
<td>0.775</td>
</tr>
</tbody>
</table>

Since most of the holes are on the Cu site, there is very little chance to have two holes on the same oxygen site. Therefore, $U_p$ should not affect the solution much. Figure 3.12 and Table 3.3 show the results for $U_p = 6.0eV$, 4.0eV, and 2.0eV. We can see that the solutions are almost not affected by increasing the value of $U_p$ as expected. Nevertheless, the $U_p$ can enhance the tendency for antiferromagnetism.
Figure 3.12: The comparison of the total density of states for $U_p = 6.0 eV$, $4.0 eV$, and $2.0 eV$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1.
Table 3.3: Comparison of the POMF results for different values of $U_p$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$U_p$ (eV)</th>
<th>$&lt; n_{Cu}$ &gt; (e)</th>
<th>$S_z$ ((\mu_B))</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ((\mu_B))</th>
<th>$E_g$ (eV)</th>
<th>$&lt; n_{Cu}$ &gt; (e)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>0.716</td>
<td>0.661</td>
<td>0.836</td>
<td>2.02</td>
<td>0.708</td>
<td>0.790</td>
</tr>
<tr>
<td>4.0</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>2.0</td>
<td>0.700</td>
<td>0.644</td>
<td>0.827</td>
<td>1.90</td>
<td>0.684</td>
<td>0.777</td>
</tr>
</tbody>
</table>

The value of the nearest neighbor repulsion $U_{dp}$ is small, and we have considered values from $0.0eV$ to $1.2eV$. Since the hole occupation on oxygen is small, we would expect $U_{dp}$, like $U_p$, does not affect the solution much. Figure 3.13 and Table 3.4 demonstrate the effect of $U_{dp}$ on the solution. We can see that increasing $U_{dp}$ enhances the tendency toward antiferromagnetism. By increasing the value of $U_{dp}$ from $0.0eV$ to $1.2eV$ the magnetic moment increases from $0.602\mu_B$ to $0.654\mu_B$ and the band gap increases from $1.6eV$ to $1.97eV$, that is about the same effect as increasing the value of $U_d$ from $6.5eV$ to $10.5eV$, except that the binding energy of the satellite is almost unaffected by increasing the value of $U_{dp}$.
Figure 3.13: The comparison of the total density of states for $U_{dp} = 1.2eV$, $0.6eV$, and $0.0eV$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1.
Table 3.4: Comparison of the POMF results for different values of $U_{dp}$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$U_{dp}$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$&lt; S_z &gt;$ ($\mu_B$)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
<th>$E_g$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>0.6</td>
<td>0.688</td>
<td>0.626</td>
<td>0.819</td>
<td>1.76</td>
<td>0.680</td>
<td>0.775</td>
</tr>
<tr>
<td>0.0</td>
<td>0.668</td>
<td>0.602</td>
<td>0.807</td>
<td>1.60</td>
<td>0.668</td>
<td>0.769</td>
</tr>
</tbody>
</table>

We now study the effect of the hopping terms. Figure 3.14 and Table 3.5 show the results for $t_{dp} = 0.8eV, 1.3eV, and 1.8eV$. The value of $< n_{Cu} >$, $< S_z >$, $\sqrt{< S_z^2 >}$, $E_g$ are depressed and the value of $E_B$ is enhanced significantly by increasing the value of $t_{dp}$. It should be noted that the binding energy of the satellite is very strongly dependent on $t_{dp}$. In order to understand why $t_{dp}$ can enhance the binding energy of the satellite, let us study the E-matrix, equations (3-78) to (3-80), in detail. We can see that the $k$-independent self-energy for the single occupied state and the double occupied state are different. They are given by $W_{Cu\sigma}/(1 - n_{Cu\bar{\sigma}})$ for the single occupied state and $W_{Cu\sigma}/n_{Cu\bar{\sigma}}$ for the double occupied state, where
\[
W_{Cu\sigma} = \frac{1}{N} \sum_{kO_1} t_k C^{uO_1} = \left< F^+_k C_{CuO_1} C^+_{kO_1} \right> - \left< C^+_{-kO_1} f_{-kCuO_1} \right>.
\]
Here we have used the relations \( Q_{Cu\sigma} =< n_{Cu\sigma} > \), and \( q_{Cu\sigma} = 1 - Q_{Cu\sigma} \). The \( W_{Cu\sigma} \) term may be interpreted as the expectation value of the energy to create the electron-hole pairs following the quasiparticle we are studying. When the quasiparticle is hopping around, it is dressed by the many body system. The difference

\[
\epsilon_{\text{dressed}-\text{particle}} - \epsilon_{\text{bare}-\text{particle}} = \epsilon_{\text{self}}
\]

is called the self-energy. Due to the interaction between the bare particle and the many body system, the bare particle creates a cloud of polarized neighbors, and the cloud reacts back on the particle, disturbing its motion, and changing its own energy. The bare on-site energy is equal to \( \epsilon_d \) for the single occupied state on the \( Cu \) site, and equal to \( \epsilon_d + U_d \) for the double occupied state on the \( Cu \) site. When we turn off the \( Cu - O \) hopping, the quasiparticle on the \( Cu \) site does not interact with the many body system, and we find the splitting between the single occupied band and the double occupied band are exactly equal to the value of \( U_d \) as expected. When we turn on the \( Cu - O \) hopping, the self energy comes into play. Due to the difference between the self energy of the single occupied state and that of the double occupied state, the splitting between the single occupied band and double occupied band increases as the value of \( t_{dp} \) is increased. The first term in \( W_{Cu\sigma} \) is the kinetic energy contributed by \( Cu - O \) hopping when the hole on the \( Cu \) site is in double occupied state, while the second term is the corresponding kinetic energy when the hole on the \( Cu \) site is single occupied. The hopping of the electrons will lower the kinetic energy of the system, hence both terms in \( W_{\nu\sigma} \) are negative. When the hole concentration are not too far from half-filled, that is the case we want to study, the holes on the \( Cu \) sites are mainly single occupied. Then the second term is more negative than the
first term and gives a positive value of $W_{\nu\sigma}$. Therefore the self energy for both the single occupied states and the double occupied states on the Cu sites are positive, and they are given by $W_{Cu\sigma}/(1 - <n_{Cu\bar{\sigma}}>)$ for the single occupied state and $W_{Cu\sigma}/ <n_{Cu\bar{\sigma}}>$ for the double occupied state. For simplicity, we only consider the paramagnetic case. When the system is not too far from half-filling, $<n_{Cu\bar{\sigma}}>$ is always smaller than 0.5. Note that $<n_{Cu\bar{\sigma}}>$ is equal to $\frac{1}{2} <n_{Cu}>$ for the paramagnetic case. Thus the self energy for the double occupied state is stronger than that of the single occupied state. That is why the value of $E_B$ is larger than that of $U_d$ when we turn on the $Cu-O$ hopping. Note that either an increase in the value of $W_{Cu\sigma}$ or a decrease in the value of $<n_{Cu\bar{\sigma}}>$ will give a higher binding energy for the satellite. On the other hand, decreasing the hole occupation on Cu sites gives less chance of the excited hole to be double occupied, and decreases the intensity of the satellite.

We now examine the effect on the $E_B$ of the $Cu-O$ hopping $t_{dp}$. Increasing $t_{dp}$ gives stronger $Cu-O$ hopping with lower hole density at Cu sites, and leads to a larger value of $W_{Cu\sigma}$. The values of $W_{Cu\sigma}$ and $<n_{Cu\bar{\sigma}}>$ for $t_{dp} = 1.8eV$, 1.3eV, and 0.8eV are given by $(0.795eV, 0.32e)$, $(0.583eV, 0.35e)$, and $(0.319eV, 0.43e)$ respectively. These give the corresponding self energies for the single and double occupied states equal to $(1.17eV, 2.48eV)$, $(0.89eV, 1.65eV)$, and $(0.56eV, 0.74eV)$. Since the satellite arises from doubly occupied states, the biggest splitting will occur for the biggest self-energy differences. We conclude that by increasing the value of $t_{dp}$ the binding energy of the satellite is enhanced due to the self energy contributions and the intensity of the satellite depressed due to the decrease of the hole density on the Cu sites.
Figure 3.14: The comparison of the total density of states for $t_{dp} = 1.8eV$, $1.3eV$, and $0.8eV$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1.
Table 3.5: Comparison of the POMF results for different values of $t_{dp}$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$t_{dp}$ (eV)</th>
<th>$&lt;n_{Cu}&gt;$ (e)</th>
<th>$&lt;S_z&gt;$ ($\mu_B$)</th>
<th>$\sqrt{&lt;S_z^2&gt;}$ ($\mu_B$)</th>
<th>$E_g$ (eV)</th>
<th>$&lt;n_{Cu}&gt;$ (e)</th>
<th>$\sqrt{&lt;S_z^2&gt;}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.632</td>
<td>0.529</td>
<td>0.778</td>
<td>1.57</td>
<td>0.636</td>
<td>0.740</td>
</tr>
<tr>
<td>1.3</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>0.8</td>
<td>0.828</td>
<td>0.818</td>
<td>0.909</td>
<td>2.50</td>
<td>0.856</td>
<td>0.888</td>
</tr>
</tbody>
</table>

Figure 3.15 and Table 3.6 show the results for $t_p = 1.0eV$, $0.65eV$, and $0.0eV$. We can see that the values of $<S_z>$, $\sqrt{<S_z^2>}$, the band gap, and $E_B$ are depressed and the values of $<n_{Cu}>$ and the intensity of the satellite increase as the value of $t_p$ increases. Note that $t_p$ significantly destabilizes the antiferromagnetism and depresses the band gap. For the paramagnetic case the values of $W_{Cu\sigma}$ and $<n_{Cu\sigma}>$ for $t_p = 1.0eV$, $0.65eV$, and $0.0eV$ are given by $(0.606eV, 0.309e)$, $(0.583eV, 0.35e)$, and $(0.523eV, 0.409e)$. These give the self energy for single occupied and double occupied states equal to $(0.876eV, 1.96eV)$, $(0.89eV, 1.66eV)$, and $(0.88eV, 1.27eV)$. The number of holes on the Cu site decreases by increasing the
value $t_p$, and that will depress the values of $\langle F^{+}_{Cu\bar{\sigma}}C_{O\bar{\sigma}} \rangle$ and $\langle C^{+}_{O\bar{\sigma}}f_{Cu\bar{\sigma}} \rangle$. Nevertheless, the depression for $\langle F^{+}_{Cu\bar{\sigma}}C_{O\bar{\sigma}} \rangle$ is stronger than that of $\langle C^{+}_{O\bar{\sigma}}f_{Cu\bar{\sigma}} \rangle$, and it will give a larger value of $W_{Cu\sigma}$ when the value of $t_p$ is increased. This clarifies why $t_p$ enhances the binding energy of the satellite and depresses its intensity.

The results for $\Delta = 4.6eV$, $3.6eV$, and $2.6eV$ are shown in Figure 3.16, and Table 3.7. The holes will be more localized on the $Cu$ sites as the value of $\Delta$ increases. This will depress the hopping and narrow the band width as shown in Figure 3.16. The values of $\langle S_z \rangle$, $\sqrt{\langle S_z \rangle^2}$, the band gap, and $E_B$ are enhanced and the value of $\langle n_{Cu} \rangle$ and the intensity of the satellite decrease as the value of $\Delta$ increases. The values of $W_{Cu\sigma}$ and $\langle n_{Cu\bar{\sigma}} \rangle$ for $\Delta = 4.6eV$, $3.6eV$, and $2.6eV$ are given by $(0.535eV, 0.395e)$, $(0.583eV, 0.35e)$, and $(0.619eV, 0.298e)$ respectively. The corresponding self energies for the single and double occupied states are given by $(0.884eV, 1.35eV)$, $(0.895eV, 1.665eV)$, and $(0.881eV, 2.083eV)$. The hole occupation on $Cu$ sites increases with increasing values of $\Delta$, and this leads to a larger value of $\langle F^{+}_{Cu\bar{\sigma}}C_{O\bar{\sigma}} \rangle$ and depresses the value of $W_{Cu\sigma}$. Therefore, the binding energy of the satellite is depressed and its intensity is enhanced by increased values of $\Delta$. 
Figure 3.15: The comparison of the total density of states for $t_p = 1.0\,\text{eV}$, $0.65\,\text{eV}$, and $0.0\,\text{eV}$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1.
Table 3.6: Comparison of the POMF results for different values of $t_p$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$t_p$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$&lt; S_z &gt;$ ($\mu_B$)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
<th>$E_g$ (eV)</th>
<th>$&lt; n_{Cu} &gt;$ (e)</th>
<th>$\sqrt{&lt; S_z^2 &gt;}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.616</td>
<td>0.518</td>
<td>0.770</td>
<td>1.04</td>
<td>0.616</td>
<td>0.740</td>
</tr>
<tr>
<td>0.65</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>0.00</td>
<td>0.812</td>
<td>0.794</td>
<td>0.899</td>
<td>3.47</td>
<td>0.820</td>
<td>0.849</td>
</tr>
</tbody>
</table>

At last, we examine the effect on the satellite by the hole concentration $n$ which is shown in Figure 3.17, and Table 3.8. Only paramagnetic solutions are considered. By increasing the value of $n$, the value of $< n_{Cu} >$ increases and the value of $W_{Cu\sigma}$ decreases, and leads to a lower binding energy and higher intensity of the satellite as shown in Figure 3.17. This agrees with experimental observation. Figure 3.18 shows the extended valence band spectra for $YBa_2Cu_3O_6.9$ and $YBa_2Cu_3O_6.25$ Crystal measured by Arko et al. [93]. The binding energy of the satellite of $YBa_2Cu_3O_6.9$, which has more holes in the $CuO_2$ plane, is lower than that of $YBa_2Cu_3O_6.25$. We note that much of the experimental spectra which is evident between $6eV$ and $E_F$ comes from the $Cu$ and oxygen bands which were not considered in our model.
Figure 3.16: The comparison of the total density of states for $\Delta = 4.6\text{eV}, 3.6\text{eV}, \text{and } 2.6\text{eV}$ (a) antiferromagnetic solution at $n = 1.0$, (b) paramagnetic solution at $n = 1.1$. The other parameters are as given in Table 3.1
Table 3.7: Comparison of the POMF results for different values of $\Delta$. The other parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$\Delta$ (eV)</th>
<th>$&lt;\frac{n_{Cu}}{e}&gt;$</th>
<th>$&lt;\frac{S_z}{\mu_B}&gt;$</th>
<th>$\sqrt{&lt;\frac{S_z^2}{\mu_B^2}&gt;}$</th>
<th>$E_g$ (eV)</th>
<th>$&lt;\frac{n_{Cu}}{e}&gt;$</th>
<th>$\sqrt{&lt;\frac{S_z^2}{\mu_B^2}&gt;}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>0.784</td>
<td>0.749</td>
<td>0.879</td>
<td>2.86</td>
<td>0.788</td>
<td>0.834</td>
</tr>
<tr>
<td>3.6</td>
<td>0.708</td>
<td>0.654</td>
<td>0.832</td>
<td>1.97</td>
<td>0.700</td>
<td>0.784</td>
</tr>
<tr>
<td>2.6</td>
<td>0.604</td>
<td>0.509</td>
<td>0.763</td>
<td>1.07</td>
<td>0.596</td>
<td>0.727</td>
</tr>
</tbody>
</table>
Figure 3.17: The comparison of the total density of states of paramagnetic solution for $n = 0.8, 0.9, 1.0, 1.1$, and 1.2. Parameters are the same as in Table 3.1.
Figure 3.18: The extended valence band spectra for $YBa_2Cu_3O_x$ and $YBa_2Cu_3O_{6.25}$ Crystal measured by Arko et al. (Ref. 93)
Table 3.8: The $W_{Cu\sigma}$, $\langle n_{Cu\sigma} \rangle$, self-energy for a single occupied state on the Cu site, and the self energy for a double occupied state on the Cu site for the paramagnetic solution calculated using the POMF approximation for different hole concentrations. The parameters are the same as in Table 3.1

<table>
<thead>
<tr>
<th>$n$</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\langle n_{Cu\sigma} \rangle$</td>
<td>0.245</td>
<td>0.280</td>
<td>0.314</td>
<td>0.350</td>
<td>0.385</td>
</tr>
<tr>
<td>$W_{Cu\sigma}$</td>
<td>0.500</td>
<td>0.533</td>
<td>0.560</td>
<td>0.583</td>
<td>0.599</td>
</tr>
<tr>
<td>$E_{self}(Single)$</td>
<td>0.662</td>
<td>0.740</td>
<td>0.816</td>
<td>0.897</td>
<td>0.974</td>
</tr>
<tr>
<td>$E_{self}(Double)$</td>
<td>2.041</td>
<td>1.904</td>
<td>1.783</td>
<td>1.666</td>
<td>1.556</td>
</tr>
</tbody>
</table>
Discussion

We have used a projection operator method to study the one-band Hubbard model and the three-band Hubbard model, and compared the results to those calculated using the HF approximation, the Hubbard I approximation, and Quantum Monte Carlo simulation. We find our method gives better results than those of the HF approximation and the Hubbard I approximation. The excellent agreement with QMC results encouraged us to further examine the parameters for the CuO$_2$ plane. Therefore, we used the parameters determined by the constrained local density functional method [83] to study the CuO$_2$ plane with the POMF method. We obtained an antiferromagnetic insulator ground state with magnetic moment and band gap given by 0.65$\mu_B$ and 2.0eV which is in good agreement with experiment [89, 90, 91, 92].

The value of $\sqrt{<S_z^2>}$ is given by 0.83$\mu_B$. Thus spin fluctuations are quite strong, $\sqrt{<S_z^2> - <S_z>^2} \sim 0.51\mu_B$. We also showed the suppression of the antiferromagnetism by hole doping is faster than that by electron doping. The long range magnetic ordering disappears at $\delta$ equal to 0.3 for hole doping and 0.4 for electron doping. This is too large compared with experimental measurements, which suggest $\delta = 0.03$ for $La_{2-x}Ba_xCuO_4-y$ [64, 94, 95].

By study of the paramagnetic solution of the CuO$_2$ plane at $n = 1.1$, we obtain a reasonable description of the normal state properties of the High $T_C$ superconducting materials. There are two key features in the total density of states, around 5eV and 13eV below the Fermi level, which correspond with experiment [93]. The 13eV feature is the satellite of the Cu band, which is a consequence of strong electron correlations. The $\sqrt{<S_z^2>}$ with small doping, $n = 1.1$, in the paramagnetic solution is given by 0.78$\mu_B$, which indicates that the local moments are preserved when the...
long range magnetic ordering is destroyed by a small amount of doping. This is again in agreement with experimental observation [92]. When holes are doped to the system away from half-filling they go mainly to oxygen sites, 110% for the PM solution and 67% for the AF solution in our calculation [82]. This also agrees with experimental observation [91]. We also show that the $U_{dp}$ strongly favors the FM solution, and the value of $U_{dp}$ should be small in order to prevent the FM ground state. The amount of oxygen 2p admixture into the Cu 3d conduction bands is reduced by strong correlation effect as caused by larger $U$. The contribution of the oxygen sites to the induced ferromagnetic form factor is smaller than 30% which is consistent with experiment [70, 71].

Finally, we studied the effect on the solution of each parameter. Our results show that increasing $U_d$, $U_p$, $U_{dp}$, and $\Delta$ enhances the antiferromagnetism, and increasing $t_{dp}$ and $t_p$ depresses the antiferromagnetism. Nevertheless, due to the small hole occupation of oxygen orbitals, the effect on the solution of $U_p$ is very small. We show that the binding energy of the satellite is enhanced by increasing the values of $t_{dp}$ and $t_p$, and depressed by increasing the value of $\Delta$. We also studied the effect on the satellite of hole concentration. We found the binding energy of the satellite decreases and its intensity increases as the hole concentration increases, which is again in agreement with experimental observation [93].
CHAPTER 4. CONCLUDING REMARKS

We have used the LSDA to study the electronic and magnetic properties of $La_2CuO_4$ and the related materials. The results of our studies demonstrated that the LSDA does not give a satisfactory solution for these systems. The failure is mainly caused by strong correlation effects. The LSDA can not handle the correlation accurately.

The extended Hubbard model plays a central role in the theoretical study of strongly correlated systems. Although the model is simple, its exact solutions are available only for very low $d = 1$ or very high $d = \infty$ dimensions. Quantum Monte Carlo (QMC) simulations are believed to be the most powerful and accurate method to study the extended Hubbard model. However, it is presently restricted to finite lattices, finite temperatures, and very large computers. On the other hand, the POMF method, presented in Chapter 3, has the desirable features that it can be generalized all the way to many atoms per unit cell with $s$, $p$, and $d$ orbitals included, and requires very small computer effort. We have shown that the POMF results are in excellent agreement with recent QMC results. Therefore, we conclude that the POMF method can give a resonable solution for extended Hubbard models.

Although the LSDA fails to give a correct ground state for strongly correlated
systems, it is believed that LSDA can provide realistic values for the parameters of the extended Hubbard Hamiltonians [98, 99, 100]. A. K. McMahan *et al.* [85] have developed a constrained local density functional technique to calculate individual parameters for states of arbitrary localization. Their results for $La_2CuO_4$ are consistent with those obtained from Mark S. Hybertsen *et al.* [83] except they included more orbitals in their Hubbard Hamiltonian. The results of our studies show that these parameters give a reasonable description for $La_2CuO_4$. Although the three-band Hubbard model is a very rough approximation for $La_2CuO_4$, it does gives some important features which are in agreement with experiment and can not be obtained by LSDA. With the use of the POMF approximation, we obtained an antiferromagnetic insulating ground state with reasonable band gap and magnetic moment, the satellite peak around 13 eV below Fermi level, holes introduced by the doping go mainly to oxygen sites, and the local moments, $\sqrt{<S_z>}$, are preserved when the long range magnetic ordering is destroyed by a small amount of doping. All these results are in agreement with the experiment and are not adequately described by the LSDA. Therefore, the POMF approximation together with the constrained local density functional technique may provide a reasonable first principle self-consistent method to study strongly correlated systems.

There are, however, several negative aspects in our method. Firstly, Luttinger’s theorem [101] is not fulfilled in our method. Secondly, there is an inconsistency in our solution, i.e. the calculated value of $<F_{\nu\sigma}^+ f_{\nu\sigma}>$ is nonzero, but it should be equal to zero exactly. Since these expectation values are not explicitly used in the calculation, maybe we need not worry about them too much. From the good agreement between our results and QMC results, we are encouraged to believe our results are reasonable.
Finally, the lifetime effects are not taken into account in our method, and inclusion of the dynamic properties in the calculation may be required for further progress.
BIBLIOGRAPHY


[33] Both the resistivity and the magnetic susceptibility show very little change at the orthorhombic to tetragonal transition (see Ref. 15) so we have restricted our ferromagnetic calculations to the tetragonal phase.

[34] C. Stassis and S. K. Sinha (private communication).


[42] see Ref. 39, p. 450.


[46] In calculations we have performed using a 3-band Hubbard model, the $< n_d >$ changed from 1.6 e to 1.2 e as $U_d$ was raised from 0 to 10 eV.


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This thesis is dedicated to his parents for their encouragement and support during his many years of studying.