GAS SENSOR ARRAY MODELING
AND
CUPRATE SUPERCONDUCTIVITY
FROM CORRELATED SPIN DISORDER

DISSERTATION

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By

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ABSTRACT

In part I, a kernel regression method is developed for modeling gas sensor response functions, for the purpose of identifying the composition of gas mixtures. A quantitative measure of orthogonality in sensor arrays is introduced. The method is applied to TiO$_2$ sensor arrays exposed to O$_2$ and CO. A sensing mechanism is analyzed by applying Wolkenstein’s theory of chemisorption to the single grain TiO$_2$ response to O$_2$ and CO. It is found that this mechanism, in combination with Wolkenstein’s theory, can adequately describe the response of granular TiO$_2$ sensors.

In part II, a spin-dependent tight-binding model for the hole-doped cuprates is developed. The model incorporates the effects of antiferromagnetism and spin disorder. In the coherent potential approximation, the effective medium Green’s function is derived and single-particle properties are obtained. When the spin disorder is correlated, an effective interaction between holes leads to $d_{x^2-y^2}$ superconductivity. The pseudogap region of the cuprate phase diagram is interpreted within this theory.
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PART I

GAS SENSOR ARRAY MODELING
Gas chemical sensors respond to the presence of gases. Ideally, one would prefer to use selective sensors, with each sensor responding to the presence of a unique gas. In reality, gas chemical sensors respond to multiple gases. For example, the resistance of metal oxide sensors can be altered due to changes in the concentrations of \( \text{O}_2 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{CH}_4 \), and other hydrocarbons. In this case, multiple sensors with orthogonal responses are necessary to identify the components of a gaseous mixture. When used simultaneously, such a collection of sensors is commonly called a sensor array.

### 1.1 Approaches to Gas Mixture Detection

Many studies have utilized a pattern recognition approach to gas mixture identification. These approaches have been most successful when applied to a classification problem. For example, Corcoran et al. have achieved a 90% success rate for correctly classifying three loose leaf teas [1], employing a neural network to learn to recognize the aroma signatures. A host of other studies have been done using principle components analysis, including an extension to vapor mixture recognition by Park et al. [2]. Jurs et al. have reviewed various computational methods used with sensor arrays [3]. The methods applicable to gas mixtures are all extensions of pattern recognition approaches.
Identifying the composition of a gas mixture poses an additional challenge. This is not fundamentally a classification problem, since the possible mixtures cannot be neatly categorized. Since each gas concentration in a mixture is a continuous variable, the number of categories necessary would be inversely proportional to the desired resolution. For this reason, an alternative to the pattern recognition approach is desirable.

The development of a more suitable method for identifying gas mixture compositions is the subject of chapter 2. The general approach is to model the multi-gas response functions of the sensors in the array. For this task, a method known as kernel regression is used. The kernel is a function that implicitly determines the family of nonlinear basis functions used in the regression. I have derived the reciprocal kernel, which works particularly well for fitting gas sensor responses.

Once the response functions have been modeled, the composition of an unknown gas mixture can be pinned down provided that the sensor responses are orthogonal. The method developed is applied to the case of a two-sensor TiO$_2$ array detecting mixtures of O$_2$ and CO. Applications of this test case include the areas of fire detection, environmental monitoring, and combustion engine emissions. The modeling method is very general and can be applied to arrays with any number of sensors for the detection of multiple gas mixtures.

The concept of orthogonality is developed for the general case of multiple gases and sensors. For any sensor array, an orthogonality index can be used to characterize the effectiveness of the array at identifying mixtures. The use of a quantitative measure of orthogonality appears to be a first in the literature. To demonstrate the application of the orthogonality index, two different sensor arrays based on TiO$_2$ are characterized.
1.2 A Sensing Mechanism for TiO$_2$

Chapter 3 develops a mechanism for n-type TiO$_2$ gas sensors. Wolkenstein’s theory of chemisorption is used to couple the adsorption chemistry of CO and O$_2$ at the surface of TiO$_2$ grains to a self-consistent solution of the grain carrier concentration profile. Qualitative agreement with experimental testing of TiO$_2$ sensors is achieved. The theory is based on the response of a single grain, so a quantitative comparison with granular TiO$_2$ is not feasible. However, the theory can also be applied to a thin film geometry, which would make an interesting quantitative test case.

In particular, insight is gained from the theory on how to design orthogonal sensors. It is found that if one of the sensors has a very small doping, its response will be nearly independent of the CO concentration. Thus two TiO$_2$ sensors are orthogonal in the gas concentration space of CO and O$_2$ if one of the sensors has a very small n-type doping.
CHAPTER 2

GAS SENSOR ARRAY MODELING

A gas sensor array consists of two or more sensors that respond to the presence of different gases. Most often, a given sensor will not be selective. It will respond to the presence of more than one type of gas. Thus an array of sensors is necessary to extract information about the types and quantities of gases present. To use a sensor array to detect gases, the response of each sensor to the various gases present must be known. Then the collective response of the array can be translated into quantitative information about the composition of a mixture of gases. A method of modeling gas sensor arrays from experimental data is presented here. With such a model, one can use a gas sensor array to identify the composition of a mixture of gases.

The chapter is organized as follows. Section 2.1 formulates the problem of identifying the concentrations of gases in a mixture. In section 2.2, a method of modeling sensor responses using kernel ridge regression is presented. In section 2.3, I propose a kernel that is particularly well suited for modeling gas sensors. This kernel is discussed in detail in section 2.4. Section 2.5 discusses how to use a modeled sensor array to find the composition of a gas mixture. The key concept of orthogonality is introduced in section 2.6. In section 2.7, a measure of orthogonality is defined for an array with multiple sensors exposed to a mixture of many gases. This measure of orthogonality quantifies the ability of
the array to identify the component gas concentrations in a mixture. Finally, the method is applied to a TiO$_2$ sensor array in section 2.8.

2.1 Quantifying a Multicomponent Mixture

A given sensor may respond differently to each gas as a function of concentration. Therefore the $j^{th}$ sensor response function can be written as $f_j(\bar{x})$, where the components of $\bar{x}$ denote the individual gas concentrations. Suppose we expose the sensor array to a mixture, obtaining the value $s_j$ for the measured response of the $j^{th}$ sensor. This measurement yields the following set of equations:

$$s_j = f_j(\bar{x}), \quad \forall j.$$  \hspace{1cm} (2.1)

We see that the number of gases must not exceed the number of sensors if we want to fully determine the composition of a mixture. Otherwise the number of unknowns in $\bar{x}$ is greater than the number of constraints, and the problem is under-determined.

From the above discussion, it is clear that the task at hand is to model the sensor response functions $f_j(\bar{x})$. This can be accomplished through multivariate nonlinear regression on a set of experimental data. Then the composition of an unknown mixture can be found by exposing the sensor array and solving equations (2.1).

2.2 Modeling the Sensor Array Using Kernel Regression

The following discussion applies to each sensor of the array, but for clarity, the subscript $j$ will be omitted. Suppose we have a set of data points $\{(\bar{x}_i, y_i)\}$, where the $\bar{x}_i$ cover the desired domain of concentrations and the corresponding values of $y_i$ give the measured value of the sensor response. Our task is to find a smooth fit to the data, $y = f(\bar{x})$.  

5
Assume the following form for $f(\vec{x})$:

$$f(\vec{x}) = \sum_n w_n \phi_n(\vec{x}). \tag{2.2}$$

The set $\{\phi_n(\vec{x})\}$ is a fixed family of nonlinear basis functions that will be used in the regression. The weights $\{w_n\}$ are found through the regression analysis. If the weights are found directly, the computational time increases with the number of basis functions, and only a limited number of functions can be used.

Fortunately, there is a way around this limitation by using a “kernel trick”. For a large (or even infinite) number of basis functions $\{\phi_n(\vec{x})\}$, the following method can be used. The optimal weights can be expressed as linear combinations of the basis functions:

$$w_n = \sum_i \alpha_i \phi_n(\vec{x}_i). \tag{2.3}$$

Upon substitution of equation (2.3) into equation (2.2), the dual representation of $f$ is obtained:

$$f(\vec{x}) = \sum_i \alpha_i K(\vec{x}_i, \vec{x}). \tag{2.4}$$

The kernel function $K$ is defined by

$$K(\vec{x}, \vec{x}') \equiv \sum_n \phi_n(\vec{x}) \phi_n(\vec{x}'). \tag{2.5}$$

Thus the representation of $f$ has been changed from the primal form in equation (2.2) to the dual form in equation (2.4). Instead of determining the primal weights $\{w_n\}$ directly, one now solves for the dual variables $\{\alpha_i\}$. Since there is one dual variable for each data point $(\vec{x}_i, y_i)$, the size of the problem thus scales with the number of data points instead of the number of basis functions.

One might argue that we have not really accomplished any simplification by introducing the dual representation. After all, the kernel function (2.5) still involves a sum over all
basis functions. For a large basis set, evaluating the kernel can be very expensive computationally. However, the method is most powerful when we know the kernel function without having to perform the summation in equation (2.5) numerically. Section 2.3 tackles the problem of choosing the kernel function. The choice of the kernel function is based on an uncountably infinite set of basis functions. Such a choice is possible because the kernel function can be obtained analytically.

To solve for the dual variables \( \{ \alpha_i \} \), kernel ridge regression is used. Cristianini and Shawe-Taylor [4] have provided the details of kernel ridge regression within the framework of dual Lagrangian theory. For convenience and notational consistency, I have included a simple derivation in appendix A.

2.3 Choosing the Kernel

The kernel function (2.5) implicitly defines the family of basis functions to use in the regression. Thus the kernel must be carefully chosen. Two approaches are possible. The first is to define a suitable family of basis functions, or feature space. Equation (2.5) then defines the kernel. The second approach involves choosing the kernel directly.

For sensors with monotonic responses that eventually saturate with gas concentrations, one approach is to use basis functions with similar features, such as exponentials. An appropriate family of functions is \( \{ \phi_b(\vec{x}) = e^{-\vec{b} \cdot (\vec{a} + \vec{x})} : \vec{b} \geq \vec{0} \} \), where \( \vec{b} \) controls the rate of decay and \( \vec{a} \) is a constant that introduces a cutoff for \( \vec{b} \) when \( \vec{x} \) is small. Using these functions, equation (2.5) is now evaluated in the continuum limit as an integral over all \( \vec{b} > \vec{0} \). This results in the reciprocal kernel,

\[
K(\vec{x}, \vec{x}') = \prod_v \left\{ \frac{1}{\left( 2a_v + x_v + x'_v \right)} + 1 \right\}. \tag{2.6}
\]
Figure 2.1: Kernel regression fit using the reciprocal kernel.

The product runs over all gas types, i.e. the components \( v \). The extra 1 is added to enable a constant shift in the fit for each gas. Figure 2.1 shows the result of such a fit to data taken on a granular anatase TiO\(_2\) sensor produced by Frank [7]. Note the sensible behavior of the fit beyond the data points, a consequence of using the reciprocal kernel.

A Gaussian kernel provides an example of using a kernel directly without explicit knowledge the underlying feature space. This kernel is given by

\[
K(\mathbf{x}, \mathbf{x}') = e^{-|\mathbf{x} - \mathbf{x}'|^2/\sigma^2}.
\]  

(2.7)

Kernel regression with the Gaussian kernel is equivalent to a radial basis function neural network. Figure 2.2 shows the result of such a fit to the same data that was used in
Figure 2.2: Kernel regression fit using the *gaussian* kernel.

This kernel tends to produce a more wavy fit than the reciprocal kernel. Furthermore, the fit does not generalize well beyond the data points. However, the Gaussian kernel is capable of fitting virtually any function due to its localized nature.

### 2.4 The Reciprocal Kernel

We now examine the class functions that the reciprocal kernel 2.6 is capable of reproducing. Without the addition of unity in equation 2.6, kernel regression with the reciprocal kernel would be equivalent to finding a function of the form

\[
    f(\vec{x}) = \int_{\vec{b} > 0} d\vec{b} w(\vec{b}) e^{-\vec{b} \cdot (\vec{a} + \vec{x})}.
\]  

\[
    (2.8)
\]
Written in this form, it is clear that \( f(\vec{x}) \) is a multidimensional Laplace transform of \( w(\vec{b})e^{-\vec{b} \cdot \vec{a}} \).

Note that in order for \( f(\vec{x}) \) to be independent of one of the components \( x_\nu \) of \( \vec{x} \), the weighting function \( w(\vec{b}) \) would have to be proportional to \( \delta(\vec{b}_\nu) \). However, note that the norm of \( w(\vec{b}) \) is minimized in kernel regression (see appendix A). A delta function has infinite norm and is excluded from the kernel regression solution for \( w(\vec{b}) \). The addition of unity in equation (2.6) solves this problem by allowing additive contributions to \( f(\vec{x}) \) that are independent of one or more of the components of \( \vec{x} \).

The reciprocal kernel is thus capable of reproducing any function that happens to be a Laplace transform. In fact, kernel regression with the reciprocal kernel finds an approximate inverse Laplace transform of a set of data. A sufficient condition for the existence of the inverse Laplace transform of a function \( f(s) \) is that it is analytic over a right half plane and satisfies [6]

\[
\lim_{|s| \to \infty} |sf(s)| < C. \tag{2.9}
\]

An example of a class of functions satisfying relation (2.9) is functions that can be written as the ratio

\[
f(s) = \frac{P(s)}{(s+a)^n}, \tag{2.10}
\]

where \( P(s) \) is a polynomial of degree \( n - 1 \) or less and \( a > 0 \). For a function of this form, there is clearly a tradeoff between increasing complexity and decaying amplitude as \( n \) increases. This example shows that the reciprocal kernel is most useful in cases where the range of the data to be fitted is limited or the function eventually exhibits a power law (or faster) decay in amplitude.
2.5 Extracting the Composition of an Unknown Mixture

Once the sensors have been modeled, the sensor array can be used to identify the composition of a multicomponent gas mixture. After sensor measurements on a mixture have been recorded, the set of equations (2.1) must be solved to find the composition of the mixture. The numerical solution of a set of nonlinear equations is a standard problem. Many numerical routines exist that can be applied to the solution of the set of equations (2.1). In Matlab, for example, the function `fsolve` can be used.

This section provides a conceptual description of the solution to equations (2.1). We begin with a criterion that will be used to identify a solution to the set of equations (2.1).

**Definition 1** Choose any \( \vec{x} \) in the domain of every \( f_j(\vec{x}) \). If \( |f_j(\vec{x}) - s_j| < \epsilon_j \forall j \), then \( \vec{x} \) is a solution of the set of equations (2.1) within the set of tolerances \( \{\epsilon_j\} \).

Due to error in the measurement, one expects the actual gas composition and the solution of equations (2.1) to be approximately, but not precisely, equal. The concept of a tolerance is useful in identifying the range of concentrations that satisfy the set of equations (2.1) within the experimental error of the measurement. It is important to realize that the set of equations (2.1) may admit more than one distinct solution. Furthermore, the sensors must be orthogonal for a solution to be well defined.

2.6 Sensor Orthogonality

Orthogonality refers to the relative directions of the gradients of the sensor responses with respect to the gas concentrations. The term orthogonality is used loosely to mean
Figure 2.3: Illustration of contours of constant resistance for two sensors. Given measured resistances of the sensors, the intersection of the two corresponding contours indicates the composition of the mixture.

a substantial degree of linear independence. If the sensors’ gradients are parallel everywhere in the space of gas concentrations, then the sensors are completely redundant: Measurements on the sensors yield identical information. However, orthogonal sensors with linearly independent gradients do provide independent information.

The concept of orthogonality is easily demonstrated for the case of two sensors and two gases. Suppose the two sensor response functions, \( f_1(x_1, x_2) \) and \( f_2(x_1, x_2) \), are shown in overlapping contour plots, as in figure (2.3). Each of the contours represents a continuous
set of possible gas concentrations, given the measured resistance of the corresponding sensor. The point of intersection of the contours identifies the concentrations of the two gases that satisfy the set of equations (2.1). If the two sensors have parallel contours, then they are redundant and cannot pinpoint the composition of the gas mixture. In contrast, contours that intersect at right angles are maximally orthogonal and, when allowing for uncertainty in the measurements, do the best job at pinpointing the composition. Since the gradient of a function at a given point is always perpendicular to the contour running through that point, the gradient can be used as an equivalent description of orthogonality.

2.7 Orthogonality in a Multiple Sensor Array

Sensor orthogonality has a simple geometric interpretation. Two sensors are most orthogonal when the gradients of their responses as a function of gas concentrations are perpendicular:
\[ \vec{\nabla} f_1(\vec{x}) \perp \vec{\nabla} f_2(\vec{x}). \]  
(2.11)
Conversely, if the gradients are parallel or anti-parallel, then the sensors are not orthogonal at all. Thus a direct measure of orthogonality is the angle \( \theta \) between the gradients. The area \( A \) of the parallelogram spanned by the gradient vectors, as illustrated in figure (2.4), is also a direct measure of orthogonality. Since
\[ A = |\vec{\nabla} f_1(\vec{x})||\vec{\nabla} f_2(\vec{x})||\sin(\theta)|, \]  
(2.12)
\( A \) is a maximum when \( \theta = \pi/2 \).

The extension to more than two sensors is straightforward. For three sensors, the volume of the parallelepiped spanned by the three gradient vectors is a measure of the orthogonality of the set of three sensors. For an array \( m \) sensors, orthogonality is measured by
the volume $V_m$ of the $m$-dimensional parallelepiped spanned by the $m$ gradient vectors. It is now shown how to calculate $V_m(\vec{x})$, the volume at the point $\vec{x}$ in gas concentration space, for the three cases $m = n$, $m > n$, and $m < n$.

(i) $m = n$. If the $m$ local sensor gradients are linearly independent, then the sensor responses provide precisely the right amount of information to determine the composition of the mixture of $n$ gases. $V_m$ can be written as the determinant of an $n \times n$ matrix whose $n$ rows are the sensor response gradients in the space of gas concentrations:

$$V_m(\vec{x}) = \begin{vmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n} \end{vmatrix}.$$  \hspace{1cm} (2.13)

(ii) $m > n$. In this case, all $m$ sensor gradients cannot be linearly independent. The identification of the gas mixture composition is over-determined. One can simply choose the most orthogonal subset of sensors that gives the maximum value of $V_m$, according to equation (2.13).

(iii) $m < n$. The identification of the gas mixture composition is under-determined. An additional $n - m$ orthogonal sensors are needed to determine the composition of the gas
mixture. However, the orthogonality of the $m$ sensors can still be quantified using a modification of equation (2.13). Fill the first $m$ rows of the matrix with the $m$ sensor gradients. Then use Gram-Schmidt orthogonalization to find $n - m$ more orthonormal vectors that are orthogonal to the subspace of $\mathbb{R}^n$ spanned by the $m$ sensor gradients. Fill in the last $n - m$ rows of the matrix using these orthonormal unit vectors. Then $V_m$ is given by the determinant of the matrix:

$$V_m(\mathbf{x}) = \begin{vmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_m}{\partial x_1} & \frac{\partial f_m}{\partial x_2} & \cdots & \frac{\partial f_m}{\partial x_n} \\ u_1^{m+1} & u_2^{m+1} & \cdots & u_n^{m+1} \\ \vdots & \vdots & \ddots & \vdots \\ u_1^n & u_2^n & \cdots & u_n^n \end{vmatrix}. \quad (2.14)$$

$V_m(\mathbf{x})$ is a measure of orthogonality at a specific gas mixture composition $\mathbf{x}$. Therefore $V_m$ can be thought of as the orthogonality density of a sensor array. In practice, one is interested in the average orthogonality over a specific domain of gas concentrations. Thus the average orthogonality of a sensor array over a domain $D$ is defined as

$$\langle V_m \rangle_D = \frac{\int_D V_m(\mathbf{x}) \, dx_1 \, dx_2 \cdots dx_n}{\int_D dx_1 \, dx_2 \cdots dx_n}. \quad (2.15)$$

### 2.8 Application to TiO$_2$ Two-Sensor Arrays

The methods and concepts introduced in this chapter have been applied to two-sensor TiO$_2$ arrays. These sensors were fabricated, tested, and modeled by Frank et al. [7].

The resistances of the two sensors in each array are shown in figures 2.5 and 2.6. The fits are generated using kernel regression with the reciprocal kernel. A single anatase lanthanum sensor was used as the first sensor in both arrays. The difference in the response of this sensor in each array shows that sensor drift is a very big problem. The sensors are
operated at 600 °C, and the large drift could be a result of cracking and other structural changes during heating and cooling. The sensing interfaces in these sensors are at the grain boundaries. This likely enhances the effects of structural changes on resistance.

Overlapping contour plots like figure 2.3 show the orthogonality of the sensors in the array. This type of plot is shown for the two arrays in figures 2.7 and 2.8. Another type of plot that directly shows orthogonality of an array is a surface plot of equation (2.12). Plotting either the area $A$ or $\sin(\theta)$ can be quite informative. Figures 2.9 and 2.10 show these plots for the two sensor arrays. The area plot in figure 2.9 emphasizes the importance of large sensor gradients, while the $\sin(\theta)$ plot only incorporates the angle of intersection between contours. In figure 2.10, however, the area plot overemphasizes the region of low CO concentration. The overlapping contour plot of this array in figure 2.8 shows that the sensors are not orthogonal in the region of low CO concentration. The large rise in area is a result of the very large gradients of the two sensors at low CO concentrations. The data points are too sparsely spaced to accurately specify the response in a region of such large gradients. As a result, the precise contour directions are artifacts of the fit, not the data. Therefore for the second array, the area plot is not to be trusted. The plot of $\sin(\theta)$ does show a narrow swath of very high orthogonality.

The ability of the arrays to predict compositions of unknown mixtures of $O_2$ and CO were also tested directly. Due to the problem of drift mentioned earlier, predictions were successful only if the array was kept heated between the collection of calibration data and unknown data. Thus predictions were not successful for the first array.

For the second array, several unknowns were identified with varying degrees of accuracy. Figures 2.11, 2.12, and 2.13 show the distances in concentration space between the actual and predicted compositions for each unknown. The predictions were obtained using
Figure 2.5: The resistances of two sensors in the first tested array versus gas concentrations. The first sensor is anatase TiO$_2$ doped with lanthanum oxide. The second sensor is anatase TiO$_2$ doped with lanthanum oxide and 2% by weight copper oxide.
Figure 2.6: The resistances of two sensors in the second tested array versus gas concentrations. The first sensor is the same sensor as in the first array. The second sensor is anatase TiO$_2$ doped with lanthanum oxide and 8% by weight copper oxide, although a transition to the rutile phase may have occurred.
Figure 2.7: Contours of constant resistance are shown for the two sensors in the first array.
Figure 2.8: Contours of constant resistance are shown for the two sensors in the second array.
Figure 2.9: These plots show the orthogonality of the first array. The area plot emphasizes the importance of large sensor gradients in addition to orthogonal contours.
Figure 2.10: These plots show the orthogonality of the second array. The area plot clearly overemphasizes the region of low CO concentration. For this array, the sin(θ) plot is more informative.
Figure 2.11: Predicted and actual compositions of mixtures using the second array. The predicted compositions are plotted as open symbols, and the actual compositions are plotted as the corresponding filled symbols. The gray scale background of each plot is proportional to the orthogonality index \( \sin(\theta) \), with black corresponding to \( \sin(\theta) = 1 \). The data is split into three figures according to how closely the predicted and actual compositions agree. Good agreement is obtained for data located in regions of high orthogonality.

In figures 2.11 and 2.12, good agreement is obtained for data located in regions of high orthogonality. Conversely, in figure 2.13, large prediction errors arise in regions where the sensors in the array are not very orthogonal, even if the sensors give reproducible measurements individually.
Figure 2.12: See the caption for figure 2.11.
Figure 2.13: See the caption for figure 2.11. The predicted concentrations for the circle and square are too large to be pictured.
These experiments in sensor arrays show how the method outlined in this chapter can be put into practice. Furthermore, reasonably good predictions can be achieved using kernel regression to model sensor responses, even when the orthogonality of the sensors is not ideal. The method is in no way limited to a small number of sensors and gases. However, a larger set of sensors and gases implies a huge increase in experimental effort due to the ‘curse of dimensionality.’
CHAPTER 3

ORTHOGONALITY OF N-TYPE TiO\(_2\) GAS SENSORS

A gas sensor array consists of two or more sensors that respond to the presence of different gases. Most often, a given sensor will not be selective. It will respond to the presence of more than one type of gas. Thus an array of sensors is necessary to extract information about the types and quantities of gases present. To use a sensor array to detect gases, the response of each sensor to the various gases present must be known. Then the collective response of the array can be translated into quantitative information about the composition of a mixture of gases.

This chapter describes n-type granular TiO\(_2\) as a sensing material for oxygen and oxygen reducing gases. In granular anatase n-type TiO\(_2\), oxygen adsorbs onto the grain surfaces, forming O\(^-\). This surface charge produces potential barriers in the conduction band at the grain boundaries. Since the resistance of a grain boundary is exponentially dependent on the barrier height in units of \(kT\), where \(T\) is the temperature and \(k\) is Boltzmann’s constant, granular TiO\(_2\) is highly sensitive to the presence of O\(_2\). Oxygen reducing gases such as CO react with O\(^-\) on the grain surfaces and alter the potential barriers at the grain boundaries.

The chapter is organized as follows. In section 3.1, simple chemical reactions are proposed that account for the gas sensing properties of TiO\(_2\). Section 3.2 outlines the
self-consistent problem of oxygen adsorption and electronic equilibrium. In sections 3.3 and 3.4, Poisson’s equation is solved self-consistently when just oxygen is present and when both oxygen and carbon monoxide are present. The results are qualitatively compared with experiment. Finally, the chapter concludes with a discussion of orthogonality.

3.1 Gas Reactions at the Grain Surface

A universal mechanism is proposed for the high temperature conductive response of a TiO$_2$ sensor to changes in gas composition. This mechanism is simply the raising or lowering of the grain boundary barrier height through the addition or removal of O$^-$ from grain surfaces. However, the chemistry at the grain surface is different for each gas, which accounts for the varied response of the sensor to different gases.

In our experimental setup, flow meters are used to regulate the concentrations of gases moving over a sensor. Since gases are constantly flowing, equilibrium is never reached. Nevertheless, a steady state is obtained. The reactions are analyzed for a gas flow mixture of O$_2$ and CO in a background of N$_2$. The reactions considered are

\begin{align}
O_2(g) & \rightleftharpoons 2O^-(ads) \quad (3.1) \\
CO(g) + O^-(ads) & \rightleftharpoons CO_2^-(ads) \quad (3.2) \\
CO_2^-(ads) & \rightarrow CO_2(g). \quad (3.3)
\end{align}

The charge on the adsorbed species in reactions (3.1)-(3.3) serves as a reminder that the adsorbed gases tend to draw electrons out of the grain interior. However, the surface electron acceptor states are populated according to Fermi statistics and may not be occupied.
3.2 Oxygen Adsorption and Electronic Equilibrium

The theory of Wolkenstein [8, 9] is now applied to the steady state adsorption of oxygen. Wolkenstein’s theory of chemisorption accounts for both the chemical steady state and electronic equilibrium. In this theory, there are two kinds of chemisorption: ‘weak’ and ‘strong’. In weak chemisorption, the bond between the adsorbed molecule is weak and does not involve the transfer of a free lattice electron or hole, while strong chemisorption involves the transfer of free electrons or holes to the local surface state. In the case of oxygen adsorption via reaction (3.1), a neutral O atom is weakly chemisorbed, while an O atom with a net negative charge is strongly chemisorbed.

Geistlinger [10] points out that weak chemisorption corresponds to single electron occupation of the bond between an adsorbate and the semiconductor surface, and strong chemisorption corresponds to double occupation of this bond. Then Fermi-Dirac statistics in the grand canonical ensemble determines the occupation probability of these two states. The fractions of strongly and weakly adsorbed molecules, respectively, are [10]

\[
\eta_0 = \frac{1}{2 \exp[(E_O - \mu)/kT] + 1} \quad (3.4)
\]

\[
\eta_0^0 = 1 - \eta_0 = \frac{1}{\frac{1}{2} \exp[(\mu - E_O)/kT] + 1}. \quad (3.5)
\]

Here, \(E_O\) is the energy difference between the two-electron energy of the doubly occupied bond and the one-electron energy of the singly occupied bond, plus any shift in energy due to band bending relative to the Fermi level. The Fermi level \(\mu\) determines the concentration of conduction electrons in the bulk semiconductor. These bulk conduction electrons serve as a reservoir of particles with which the oxygen surface states equilibrate. When \(\eta^- > \frac{1}{3}\), \(E_O\) lies below the Fermi level.
First consider adsorption in the absence of CO. In this case, only reaction (3.1) is relevant. The rate of change of O atoms on the surface is governed by

\[
\frac{d\theta_O}{dt} = \alpha_O P_{O_2} (1 - \theta_O)^2 - \nu^0 (\theta_O^0)^2 \exp\left(-\frac{Q_0^0}{kT}\right) - \nu^- (\theta_O^-)^2 \exp\left(-\frac{Q^-}{kT}\right).
\]

\(P_{O_2}\) is the oxygen partial pressure and \(\theta_O\) is the fraction of oxygen adsorption sites that are occupied by O atoms, either weakly or strongly adsorbed. To distinguish the fraction of oxygen sites that are occupied by weakly and strongly adsorbed O atoms, one may define

\[
\theta_O^0 = \eta_O^0 \theta_O, \tag{3.7}
\]

\[
\theta_O^- = \eta_O^- \theta_O. \tag{3.8}
\]

\(Q_0^0\) is the heat of weak chemisorption of \(O_2\), including dissociation. \(Q^-\) is the heat of strong chemisorption, including dissociation, and is given by

\[
Q^- = Q_0^0 + 2(E_c - E_O), \tag{3.9}
\]

where \(E_c\) is the conduction band energy. The additional energy \(2(E_c - E_O)\) in the heat of strong chemisorption accounts for two conduction band electrons transitioning to two strong oxygen bonding states.

From equations (3.4), (3.5), and (3.9), one finds that the second term on the right hand side of equation (3.6) is much larger than the third term. The ratio of the first and third terms is \(4 \exp\left[2(E_c - \mu)/kT\right]\). Thus for non-degenerate semiconductors one can ignore the contribution of the strongly chemisorbed species to desorption. Thus, as Wolkenstein first pointed out [9], it is the weakly chemisorbed species that desorb and equilibrate with the ambient gas phase.
In the steady state, the adsorption and dissociation of O\textsubscript{2} molecules is balanced by the desorption and reassociation of weakly chemisorbed O atoms. In equation (3.6), setting \(d\theta_O/dt = 0\) and solving for \(\theta_O\) yields

\[
\theta_O = \frac{\sqrt{\alpha_O P_{O_2}}}{\sqrt{\alpha_O P_{O_2} + \eta^0 \sqrt{\beta_O}}}, \quad \beta_O = \nu^0 \exp\left(-\frac{Q^0_O}{kT}\right).
\] (3.10)

Strong chemisorption leads to a net surface charge and band bending, which shifts all surface energy levels upward relative to the Fermi level, according to Poisson’s equation. Since \(\eta^0\) depends on \(E_O\), which in turn is shifted by band bending, equation (3.10) and Poisson’s equation must be solved together self-consistently.

### 3.3 Self-Consistent Solution of Poisson’s Equation

Geistlinger [10] has performed such a self consistent calculation for the adsorption of O\textsubscript{2} on thin film gas sensors. Here similar arguments are applied, with modifications appropriate for single grains of TiO\textsubscript{2}. Just as for thin films, small grains may be totally depleted when exposed to oxygen. Thus the finite size of the grain must be explicitly taken into account. For simplicity, consider a grain with spherical symmetry so that only the radial direction must be considered. Then Poisson’s equation is written

\[
\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dV}{dr}\right) = -\frac{\rho}{\epsilon},
\]

where the free charge density \(\rho\) is given by

\[
\rho(r) = \sigma \delta (r - R) + n_d - en(r).
\] (3.11)

\(\sigma\) is the surface charge density due to occupation of oxygen surface states. \(n_d\) is the density of electron donor ions, which are assumed to be fully ionized. The conduction band
electron density $n$ depends on $r$ because the potential $V(r)$ increases the thermally populated conduction band energies by $-eV(r)$. Following Geistlinger, reduced variables are introduced:

$$\phi = \left[ E_c - eV(r) - \mu \right]/kT, \quad t = r/L_D,$$

where $L_D = \varepsilon kT / e^2 n_d$. In terms of these reduced variables, Poisson’s equation becomes

$$\frac{1}{t^2} \frac{d}{dt} \left( t^2 \frac{d\phi}{dt} \right) = \frac{\rho}{en_d}.$$  \hspace{1cm} (3.13)

In terms of $\phi$, the free electron density for a non-degenerate semiconductor is simply

$$n(r) = n(\phi(r)) = N_c e^{-\phi},$$  \hspace{1cm} (3.14)

where $N_c$ is given by

$$N_c = \int_{E_c}^{\infty} dE g_c(E) \exp \left[ -(E - E_c)/kT \right].$$

Therefore the charge density $\rho$ inside the grain depends on $r$ only through the variable $\phi$.

The surface charge density, defined by

$$\sigma = -eN_{\text{chem}} \theta^-,$$

can be written as a function of $\phi(R/L_D)$ using the definition of $\phi$ (3.12) together with the fact that the energy $E_O$ is raised by band bending through the relation $E_O = E_O^0 - eV(R)$. Then Gauss’ Law applied just inside the grain surface, together with the assumption of charge neutrality, yields the boundary condition

$$\left. \frac{d\phi}{dt} \right|_{t=R^-/L_D} = \frac{\sigma}{en_d L_D}.$$  \hspace{1cm} (3.16)

By applying Gauss’ Law inside the grain and taking the limit $r \to 0$, one obtains the second boundary condition

$$\left. \frac{d\phi}{dr} \right|_{r=0} = 0.$$  \hspace{1cm} (3.17)
Poisson’s equation (3.13) and the boundary conditions (3.16) and (3.17) complete the specification of the function $\phi(t)$.

Poisson’s equation can be written as a system of two first order differential equations simply by introducing the definition

$$\frac{d\phi}{dt} = \phi'. \quad (3.18)$$

Then Poisson’s equation (3.13) can be written

$$\frac{d\phi'}{dt} = \rho(\phi) \frac{2}{en_d} - \frac{2}{\phi'} \phi'. \quad (3.19)$$

The relations (3.18) and (3.19) then constitute a system of first order differential equations and can be integrated numerically. The integration is started at the center of the grain using the boundary condition (3.17) as the initial condition for $\phi'$. Beginning with a guess at the initial value of $\phi(0)$, one may proceed with the integration until the boundary condition (3.16) is satisfied. At this point, the final value of $t$, denoted by $t_R$, is noted. The electronic problem of chemisorption for a grain size $R = t_R L_D$ has been solved. By choosing different values of $\phi(0)$, this procedure can easily be iterated until the desired grain size is reached.

The carrier concentration is a minimum near the grain surface, where band bending has moved $E_c$ upward to its maximum value. The surface carrier concentration thus limits conduction, since all current paths invariably pass through grain boundaries. The surface carrier concentration is defined by

$$n_s = n(R). \quad (3.20)$$

The parameter values used are listed in table 3.1. The solution for $n_s$ vs. $O_2$ partial pressure is shown in figure 3.1. $n_s$ falls very rapidly as $O_2$ is introduced. This behavior is verified by the experimental observation of sensor resistances higher than several megohms.
Figure 3.1: The surface carrier concentration $n_s$ falls very rapidly as $O_2$ is introduced. Eventually, as atmospheric levels of $O_2$ are approached, the decrease in $\log(n_s/n_d)$ moderates. The units of $[O_2]$ are particle fraction at atmospheric pressure.
Eventually, as atmospheric levels of O$_2$ are approached, the decrease in $\log(n_s/n_d)$ moderates. This is due to a saturation in the surface charge as band bending raises the oxygen surface states above the Fermi level. The oxygen surface coverage fractions $\theta_O$ and $\theta_{O^-}$ are shown in figure 3.2. Even though $\theta_O$ increases rapidly with [O$_2$], $\theta_{O^-}$ saturates due to a rapid decrease in $\eta_{O^-}$.
3.4 Solution with O$_2$ and CO Present

If both CO and O$_2$ are present, then one must also consider reactions (3.1) and (3.2). A mechanism is assumed in which adsorbed O$^-$ serves as adsorption centers for CO [9]. The resulting adsorbed CO$_2$ molecule then provides an electronic surface state, presumably with an energy $E_{CO_2} > E_O$. Then CO$_2$ can be either weakly or strongly adsorbed, according to Fermi statistics.

With the addition of CO, equation (3.6) is replaced by two rate equations for the fractions of adsorbed O and CO:

$$\frac{d\theta_O}{dt} = \alpha_OP_{O_2}(1 - \theta_O - \theta_{CO_2})^2 - \beta_O(\theta_O^0)^2 - \alpha_{CO}P_{CO}\theta_O + \beta_{CO}\theta_{CO_2}$$  \hspace{1cm} (3.21)

$$\frac{d\theta_{CO_2}}{dt} = \alpha_{CO}P_{CO}\theta_O - \beta_{CO_2}\theta_{CO_2}$$  \hspace{1cm} (3.22)

In the steady state, the time derivatives are zero and one obtains a quadratic equation in $\theta_O$.
Poisson’s equation (3.13) is solved in the same manner as for the case where only O$_2$ is present. The only modification that needs to be made is including strongly adsorbed CO$_2$ in the surface charge density,

$$\sigma = -eN_{chem}(\theta_O^- + \theta_{CO_2}^-).$$  \hspace{1cm} (3.23)

Figure 3.4 shows $1/n_s$ as a function of [O$_2$] and [CO]. The parameters of the model are set according to those listed in table 3.1. The change in $1/n_s$ moderates as the concentration of each gas is increased, but there is no saturation at these levels. The reciprocal of $n_s$ is plotted for purposes of comparison with experimental data. In a simple model of conduction, the resistance of a TiO$_2$ sensor is proportional to $1/n_s$. Figure 3.3 shows a plot of
The similar behavior of $1/n_s$ in figure 3.4 to the experimental resistance depicted in figure 3.3 testifies to the success of the Wolkenstein model is describing the sensitivity of TiO$_2$ to CO and O$_2$. In light of equation (3.14), where $n$ depends exponentially on the band bending inherent in $\phi$, the moderation of the change in resistance for higher concentrations of gases is not easily explained. In the Wolkenstein model, this subtle moderation results from the gradual saturation of the surface charge.

### Table 3.1: Default values used in the numerical calculations. The units of the kinetic coefficients are arbitrary. The units of partial pressures are particle fraction at atmospheric pressure.

<table>
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<th>coefficient</th>
<th>(arb. units)</th>
<th>quantity</th>
<th>value</th>
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</thead>
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<tr>
<td>$\alpha_O$</td>
<td>1.0</td>
<td>$N_c$</td>
<td>$1 \times 10^{20}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\beta_O$</td>
<td>0.005</td>
<td>$n_d$</td>
<td>$1 \times 10^{18}$ cm$^{-3}$</td>
</tr>
<tr>
<td>$\alpha_{CO}$</td>
<td>500</td>
<td>$kT$</td>
<td>0.09 eV</td>
</tr>
<tr>
<td>$\beta_{CO}$</td>
<td>0.01</td>
<td>$N_{chem}$</td>
<td>1.0 sites/nm$^2$</td>
</tr>
<tr>
<td>$\beta_{CO_2}$</td>
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<td>$E_c$</td>
<td>0 eV</td>
</tr>
<tr>
<td></td>
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<td>$-1.00$ eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E^0_{CO_2}$</td>
<td>$-0.95$ eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$L_D$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$R$</td>
<td>60 nm</td>
</tr>
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</table>
Figure 3.3: Experimental resistance of a TiO$_2$ sensor vs. [O$_2$] and [CO]. The surface was modeled using kernel regression with the reciprocal kernel.

Figure 3.4: The reciprocal of $n_s$, as calculated in the Wolkenstein theory in a mixture of CO and O$_2$. 
3.5 Orthogonality within the Wolkenstein Theory

The resistance measurement of a granular TiO$_2$ sensor involves conduction through many grains. Thus a sensor’s properties are an average of the sensing properties of individual grains. The electronic theory of chemisorption predicts that grains can provide orthogonal sensing information upon exposure to a gas mixture of CO and O$_2$. The concept of orthogonality was discussed in chapter 2.

In the Wolkenstein model, changes in the parameters listed in table 3.1 can lead to orthogonality. For example, changing the relative strengths of the gas adsorption coefficients leads to orthogonality. However, the gas adsorption coefficients cannot easily be altered in practice. One such quantity that is experimentally alterable is the donor concentration $n_d$. The directions of the contours of constant $n_s$ shift most dramatically when $n_d$ is decreased to the point at which $L_D$, introduced in equation (3.12), approaches the grain radius $R$. At this point, the grain becomes completely depleted. Note that there is a geometrical cross-over as $n_d$ decreases. For $L_D \ll R$, the spherical grain has a thin depleted shell, and behaves similarly to a planar thin film. But as $L_D$ increases, the spherical geometry of the grain manifests itself. This geometrical cross-over, while not entirely responsible for orthogonality, does seem to enhance it.

Figure 3.5 shows overlapping contour plots of $n_s$ using the values listed in table 3.1. For one set of contours, $n_d$ is decreased by a factor of 25. The contours intersect at relatively large angles. Two sensors characterized by these differing values of $n_d$ are orthogonal. Thus orthogonality can be obtained by reducing the carrier concentration of one sensor.

The grain with a reduced $n_d$ is not affected by the presence of CO as much. As $n_d$ is reduced even further, the surface concentration $n_s$ becomes nearly independent of $[\text{CO}]$. This happens once the grain has been thoroughly depleted to the point where $\theta_O^-$ saturates
Figure 3.5: Overlapping contours of constant $n_s$ in the Wolkenstein model. For the dashed set of contours, $n_d$ is decreased by a factor of 25. Such a decrease in $n_d$ reduces the response of the grain to CO. The units of gas concentration are particle fraction at atmospheric pressure.
as $[O_2]$ increases. After $\theta_O$ saturates, the overall surface coverage of oxygen continues to increase, as shown in figure 3.2. The over-abundant neutral adsorbed oxygen then serves as a buffer capable of replacing any charged surface oxygen lost in the reaction with CO.

Wolkenstein’s theory of chemisorption has been applied to adsorption of oxygen on single grains of n-type TiO$_2$. Coupled with a solution of Poisson’s equation, the theory is capable of explaining resistance measurements on granular TiO$_2$ sensors exposed to mixtures of O$_2$ and CO. The Wolkenstein theory also predicts orthogonality of sensors that are characterized by different doping levels. The theory presented here thus provides a framework for designing orthogonal sensors.
PART II

CUPRATE SUPERCONDUCTIVITY FROM CORRELATED SPIN DISORDER
CHAPTER 4

INTRODUCTION

The high temperature cuprate superconductors all have copper oxide planes as a common structural feature. These planes play a dominant role in determining the properties of the copper oxide materials. Examples of the cuprate superconductors include several families of compounds, including YBa$_2$Cu$_3$O$_{7-\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$. The structure of YBa$_2$Cu$_3$O$_7$ is shown in figure 4.1.

In the cuprate superconductors, the planar copper atoms contain a hole in the 3$d_{x^2-y^2}$ orbital [11]. Thus each copper atom is electronically spin-$\frac{1}{2}$. In La$_2$CuO$_4$, as well as in the parent compounds of other cuprate families, the copper spins order antiferromagnetically. There is one hole per copper atom on average. The mechanism for the antiferromagnetic order may be superexchange [12] between the copper 3$d_{x^2-y^2}$ holes, mediated by the empty (unoccupied by holes) oxygen 2$p_\sigma$ orbitals. As the strontium content $x$ is increased in La$_{2-x}$Sr$_x$CuO$_4$, additional holes occupy the 2$p_x$ and 2$p_y$ oxygen orbitals. Superexchange thus becomes less effective and the long range antiferromagnetic order is destroyed, although short range antiferromagnetic correlations between the copper spins remain. Figure 4.2 shows a representative temperature versus doping phase diagram for the high temperature cuprate superconductors. Superconductivity sets in after the antiferromagnetic insulating phase disappears (i.e. the Neél temperature vanishes).
Figure 4.1: The unit cell for YBa$_2$Cu$_3$O$_{7-\delta}$.
Figure 4.2: The classic phase diagram of the hole-doped cuprates.
In the cuprate phase diagram, it is possible to view the proximity of antiferromagnetism to superconductivity in two opposing ways. The first view is that antiferromagnetism inhibits superconductivity. Only when the antiferromagnetism is destroyed can the superconducting phase occur. The second view is that antiferromagnetism, or at least antiferromagnetic correlations, coexist with superconductivity. This work fits into the second viewpoint. In fact, in the model presented here, correlated defects in the spin order lead to pairing.

4.1 Superconductivity from Correlated Antiferromagnetic Disorder

Ordinarily, disorder does not play a helpful role in establishing superconductivity. At best, disorder does not inhibit superconductivity when Anderson’s Theorem applies [13]. However, a special type of correlated disorder is treated in this work. As the CuO$_2$ is doped with holes, occupied oxygen sites inhibit superexchange between neighboring copper sites. The incentive for holes to localize on the affected copper sites is removed. The disorder envisioned is thus the absence of localized holes on neighboring copper sites.

In chapter 5, a simple tight-binding model is developed that includes antiferromagnetism while avoiding the complexity of a full many-body Hamiltonian with interactions. Defects in the spin order are treated in the coherent potential approximation. An effective medium single-particle Green’s function is obtained from the solution for the self energy. Correlated spin disorder leads to an effective interaction between holes. When solving for the particle-particle Green’s function, the interaction leads to a divergence which signals the onset of superconductive pairing. This model will hereafter be referred to as the correlated spin disorder (CSD) model.

In chapter 6, the results for various electronic properties of the copper oxide plane are predicted from the theory of chapter 5. Various single-particle properties such as the
density of states, heat capacity, and paramagnetic susceptibility are predicted for various doping levels. Also the spectral function is plotted at the Fermi level for several doping levels. The superconducting transition temperature is derived as a function of doping, and the symmetry of the transition is found to be d-wave, which is the experimentally observed symmetry in the hole doped cuprates. Finally, the results for superconductivity are interpreted in light of the existence of the pseudogap phase.

4.2 Comparison to Alternative Theories

The literature on high-$T_c$ theory is vast, and no attempt to be comprehensive will be made here. Instead, several approaches involving antiferromagnetic spin fluctuations are mentioned.

In 1989, Bickers, Scalapino, and White proposed the fluctuation exchange approximation (FLEX) for treating the two-dimensional Hubbard model [14]. This work was especially significant in that the theory predicted existence of both the antiferromagnetic and $d_{x^2-y^2}$ superconducting states. At a doping of around 0.06, the antiferromagnetic transition gives way to the superconducting transition. This work has been extended by Schäfer, Schmalian, and Bennemann [15] to the three-band Hubbard model (including the oxygen sites explicitly). They achieve similar results when using parameters that correspond to the effective one-band Hubbard model, and also extend the calculation to the both the normal and superconducting states. In the FLEX theories, the calculated self-consistent spin susceptibility $\chi$ near $\vec{q} = (\pi, \pi)$ is the cause of both the magnetic and superconducting transitions.

In 1991, Monthoux, Balatsky, and Pines showed that a phenomenological form for $\chi$ based on NMR experiments leads to $3d_{x^2-y^2}$ superconductivity [16]. Stojković and Pines
have derived normal state properties of the cuprates based on their theory of a nearly anti-ferromagnetic Fermi liquid (NAFL) [17], again using the phenomenological form for $\chi$.

The CSD model introduced in the next chapter differs from the spin susceptibility approaches in two major ways. First, the Hubbard Hamiltonian, includes a two-body on-site Coulomb repulsion term. In the CSD model, the on-site Coulomb repulsion is included as a mean field potential in the antiferromagnetic state. Second, in the spin susceptibility approaches, pairing is mediated by spin fluctuations about the antiferromagnetic wavevector $\vec{Q} = (\pi, \pi)$. In contrast, pairing in the CSD model occurs due to an effective interaction arising from absence of localized holes on neighboring copper sites.
Chapter 5

A Coherent Potential Description of the Hole-Doped Copper Oxide Plane

This chapter is concerned with the development of a spin-dependent tight-binding model of the CuO\(_2\) plane that includes antiferromagnetism. Antiferromagnetism is achieved through the introduction of an extra positive mean field Coulomb potential \(U\) for holes of spin \(-\sigma_{AF}\) on Cu sites, where \(\sigma_{AF}\) denotes the spin of a hole on a given Cu site consistent with antiferromagnetic order. This model is formulated in section 5.1.

As the CuO\(_2\) plane is doped with holes, antiferromagnetic order breaks down. This effect is included by randomly removing the potential \(U\) from a fraction of the Cu sites, and performing an impurity average of the single-particle Green’s function over all defect configurations. Accordingly, the spin-dependent coherent potential approximation [18, 19] for the self-consistent single-particle Green’s function is developed in section 5.2.

The coherent potential approximation (CPA) can also be applied to the two-particle Green’s function. Velicky [21] has developed the formalism for finding the two-particle
Green’s function in the particle-hole channel. Section 5.3 develops the formalism for finding the two-particle Green’s function in the singlet particle-particle channel, in which superconducting pairing correlations occur. Although there are not any formal two-body interactions in the model, we shall see that the two-particle CPA does introduce an effective interaction which can lead to pairing.

5.1 Holes in an Antiferromagnetic Background

The insulating cuprates exhibit long range antiferromagnetic order. At small doping fractions, the antiferromagnetic phase is still present with a reduced Neél temperature $T_N$. Accordingly, a hole tight-binding model is developed to be consistent with antiferromagnetic order. The model applies to holes in the CuO$_2$ plane of the underdoped cuprates below $T_N$. The Hamiltonian is

$$H = \sum_{\langle i,j \rangle,\sigma} t_{ij} (d_{i\sigma}^\dagger p_{j\sigma} + \text{h.c.}) + \sum_{j,\sigma} \epsilon_p p_{j\sigma}^\dagger p_{j\sigma} + \sum_{i,\sigma} \epsilon_d d_{i\sigma}^\dagger d_{i\sigma} + \sum_i U d_{i-\sigma AF}^\dagger d_{i-\sigma AF}. \quad (5.1)$$

The operator $d_{i\sigma}^\dagger$ creates a hole with spin $\sigma$ on the $i$th copper site. This hole resides in the $d_{x^2-y^2}$ orbital of the copper atom. The operator $p_{j\sigma}^\dagger$ creates a hole with spin $\sigma$ on the $j$th oxygen site. This hole resides in the $p_\sigma$ orbital of the oxygen atom.

The first term in equation (5.1) describes hole hopping between nearest-neighbor copper and oxygen sites. The hopping coefficients $t_{ij}$ have magnitude $t$. Their signs are determined by the overlap of the $d_{x^2-y^2}$ and $p_\sigma$ orbitals, as shown in figure 5.1. The second and third terms describe the energy of holes on oxygen and copper sites. Antiferromagnetic order is assumed, and the last term describes the additional energy cost of holes on copper
Figure 5.1: The relative phases of the copper $d_{x^2-y^2}$ and the oxygen $p_\sigma$ orbitals. The overlap of these orbitals determines the sign of the hopping coefficients.

sites with spins opposite the antiferromagnetic order. Holes with spins arranged antiferromagnetically occupy the copper sites first with energy $\varepsilon_d$. A hole with spin opposite the antiferromagnetic order may then doubly occupy a copper site, but its energy is increased by the Coulomb repulsion energy $U$.

In order for this model to be consistent with antiferromagnetic order, careful attention must be paid to the values of the energies $\varepsilon_d$, $\varepsilon_p$, and $\varepsilon_d + U$. The order $\varepsilon_d \leq \varepsilon_p \ll \varepsilon_d + U$ guarantees that, in the case of the antiferromagnetic insulator, holes of a given spin are localized on a central copper site and its oxygen nearest neighbors. With increasing doping, holes then further occupy the oxygen sites.
Figure 5.2: The magnetic unit cell contains two copper $d_{x^2-y^2}$ and four oxygen $p_\sigma$ orbitals. The energy of a hole on a copper site is increased by the Coulomb repulsion $U$ if its spin is opposite the antiferromagnetic order shown.

Note that the Hamiltonian given in equation (5.1) describes the independent motion of holes through the copper oxide plane. Due to the use of the spin-dependent Hartree potential to establish antiferromagnetic order, there are no explicitly many body interactions. Therefore the Hamiltonian can simply be diagonalized.

To solve for the band structure, we diagonalize the Hamiltonian given in equation (5.1). Since the Hamiltonian is block diagonal in the spin index $\sigma$, spin up and spin down may be treated independently. Figure 5.2 shows the magnetic unit cell, which contains two copper $d_{x^2-y^2}$ and four oxygen $p_\sigma$ orbitals for each spin. Let $|r\vec{R}\sigma\rangle$ be the state of one hole with spin $\sigma$ occupying orbital $r$ within the unit cell $\vec{R}$. If we introduce the discrete Fourier transform

$$|r\vec{k}\sigma\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} |r\vec{R}\sigma\rangle,$$  \hspace{1cm} (5.2)

then we find

$$\langle r\vec{k}\sigma |H| r'\vec{k}'\sigma' \rangle \propto \delta_{k,k'} \delta_{\sigma,\sigma'}.$$  \hspace{1cm} (5.3)
Figure 5.3: The lowest two bands for holes, shown along two directions from the zone center to the (magnetic) zone boundary. This calculation used the values \( t = 1, \varepsilon_{p} = 0, \varepsilon_{d} = 0, U = 5 \).

Since there are 6 orbitals \( r \) within the unit cell, the problem has been reduced to diagonalizing a 6x6 matrix for each \( \vec{k}, \sigma \). We obtain 6 hole energy bands, whose eigenstates can be written

\[
|n \vec{k} \sigma\rangle = \sum_{r} \langle r \vec{k} \sigma | n \vec{k} \sigma \rangle |r \vec{k} \sigma\rangle, \quad (5.4)
\]

where \( n \) is the band index. Only the lowest two bands are relevant for the cuprates.

Figure 5.3 shows the lowest two bands from the zone center to the zone boundary. The two bands are separated by an antiferromagnetic energy gap whose magnitude is always less than \( 2t \). The energy gap is precisely \( 2t \) in the large \( U \) limit. For finite \( U \), the gap is lowered by the dispersion of the upper band.

In the case of the antiferromagnetic insulator, the lowest band is filled with holes. Hole doping then places holes in the upper band near the zone boundary, while electron doping
removes holes near the zone boundary from the lowest band. Figure 5.4 shows the resulting Fermi surface for both hole and electron doping.

As shown in figure 5.3, both bands are fairly flat near the zone boundary, especially near \((\pi, 0)\). In addition, the band widths are less than the hopping \(t\). As \(U\) increases, the band widths scale as \(t^2/U\). The reason for the small band widths is that for very large \(U\) and in the absence of oxygen-oxygen hopping, a hole cannot move between neighboring copper sites since the spins on neighboring sites are oppositely oriented.

### 5.2 The Single-Particle Green’s Function in the CPA

To describe the effects of spin disorder, we turn to the Green’s function method. The reader is referred to Rickayzen’s book [22] and Zagoskin’s book [23] for in-depth introductions to the subject.

The Green’s function describes the propagation of a particle through the lattice. There are actually several different Green’s functions, but here we will focus on the temperature Green’s function and its analytical continuation to the complex frequency plane. The analytically continued Green’s function will simply be referred to as the Green’s function.

When there is no disorder, the Green’s function of a hole with wavevector \(\vec{k}\) propagating according to the Hamiltonian (5.1) is simply

\[
G_0(n, \vec{k}, n', \vec{k}'; \omega) = \frac{1}{\omega - \epsilon_{nk}} \delta_{k,k'} \delta_{n,n'}.
\]  
(5.5)

The electronic density of states of the system is defined by

\[
N(\omega) = \sum_{n,k} A_n(\vec{k}, \omega),
\]
(5.6)

where the spectral function is determined from the Green’s function according to

\[
A_n(\vec{k}, \omega) = -\frac{1}{\pi} \text{Im} G(n, \vec{k}, n, \vec{k}; \omega + i\delta).
\]
(5.7)
Figure 5.4: The electron-doped (n=1 band) and hole-doped (n=2 band) Fermi surfaces corresponding to the band structure shown in figure 5.3 are shown within the magnetic Brillouin zone (BZ). Note that the coordinate system pictured here corresponds to the non-magnetic unit cell. For reference, the coordinate system corresponding to the magnetic unit cell is shown on the left. The magnetic coordinate system is used in figure 5.3 and throughout chapter 6.
Equations (5.6) and (5.7) are general relations.

If $G_0$ in equation (5.5) is substituted for $G$ in equation (5.7), then the spectral function takes the form

$$A_n(\vec{k}, \omega) = \delta(\omega - \varepsilon_{nk}). \quad (5.8)$$

This means that when there is no disorder, a particle of wavevector $\vec{k}$ and band index $n$ definitely carries an energy $\varepsilon_{nk}$. The particle simply occupies an eigenstate of the non-interacting system. When disorder is present, the width of the spectral function broadens so that the energy and momentum of the particle are no longer definite. Such a particle may generally be referred to as a *quasiparticle* of energy $\varepsilon$, if the spectral function maintains a well defined peak at a frequency $\omega = \varepsilon$. However, in contrast to the interacting electron gas in Fermi liquid theory, the quasiparticle’s lifetime does not become infinite at the Fermi surface at zero temperature.

Our task then is to find the single-particle Green’s function in the presence of disorder. For this purpose, we turn to scattering theory and the coherent potential approximation (CPA).

### 5.2.1 Scattering Theory and the Coherent Potential

Scattering theory in the context of the CPA is discussed by several authors [20, 21, 22, 24]. The main points relevant to the CPA are summarized here.

When written in the atomic site representation, the Green’s function $G(r, r'; \omega)$ can be regarded as a matrix with elements $(G(w))_{rr'}$. Then in the presence of an external potential, with the Hamiltonian given by $H = H_0 + V$, $G$ satisfies the equation of motion

$$G = G_0 + G_0 V G. \quad (5.9)$$
\( G_0 \) is the Green’s function of the metallic system:

\[
G_0 = (\omega - H_0)^{-1}.
\]  (5.10)

The elements of the diagonal matrix \( V \) take on the value of the potential at each site. Thus \( V \) can be decomposed into individual site contributions as

\[
V = \sum_r V_r.
\]  (5.11)

Each site matrix \( V_r \) has all zero entries except for the one entry \((V_r)_{rr}\) on the diagonal. In a disordered binary alloy, the potential at each site can randomly take on the values \( V_A \) or \( V_B \). One is generally interested in finding the average Green’s function \( \langle G \rangle \) of the medium rather than \( G \) for one particular configuration of the alloy.

The equation of motion (5.9) can be rewritten as

\[
G_0^{-1}G = 1 + VG.
\]  (5.12)

Subtracting a quantity \( \Sigma G \) from both sides, we obtain

\[
(G_0^{-1} - \Sigma)G = 1 + (V - \Sigma)G.
\]  (5.13)

The self-energy \( \Sigma \) is chosen to satisfy Dyson’s equation:

\[
G_0^{-1} - \Sigma = \langle G \rangle^{-1}.
\]  (5.14)

With this definition, equation (5.13) reads

\[
G = \langle G \rangle + \langle G \rangle(V - \Sigma)G.
\]  (5.15)

Let us now pause and compare the equation of motion (5.15) with the original form for the equation of motion (5.9). In equation (5.15), the unperturbed Green’s function is now
taken to be \( \langle G \rangle \) rather than \( G_0 \). Furthermore the perturbing potential in equation (5.15) is the actual potential minus the coherent potential \( \Sigma \).

The t-matrix can now be introduced. If we write

\[
G = \langle G \rangle + \langle G \rangle T \langle G \rangle,
\]

then it is clear that \( T \) contains all the effects of scattering from the effective potential \( V - \Sigma \). Comparison with equation (5.13) shows that the t-matrix is defined by

\[
T = (V - \Sigma) G \langle G \rangle^{-1}.
\]

(5.17)

Substituting for \( G \) using equation (5.16) yields an equation of motion for the t-matrix:

\[
T = (V - \Sigma)(1 + \langle G \rangle T).
\]

(5.18)

Finally, we can solve this equation for \( T \) to obtain

\[
T = [1 - (V - \Sigma) \langle G \rangle]^{-1} (V - \Sigma).
\]

(5.19)

If equation (5.16) is averaged, then it is clear that self-consistency requires

\[
\langle T \rangle = 0,
\]

(5.20)

with \( T \) given by equation (5.19). If this equation could be solved exactly for \( \Sigma \), we would then immediately know \( \langle G \rangle \) from relation (5.14). In practice, an approximation must be made.

### 5.2.2 The Single Site Approximation for the Self-Energy

Without loss of generality, the self-energy can be written

\[
\Sigma = \sum_r \Sigma_r.
\]

(5.21)
Likewise, the t-matrix can be written in the form

\[ T = \sum_r Q_r. \]  \hfill (5.22)

If \( Q_r \) satisfies

\[ Q_r = V_r - \Sigma_r + (V - \Sigma) \langle G \rangle Q_r, \]  \hfill (5.23)

then equation (5.22) is consistent with the equation of motion (5.18) for the t-matrix.

The single atom t-matrix satisfies

\[ T_r = (V_r - \Sigma_r)(1 + \langle G \rangle T_r). \]  \hfill (5.24)

Solving for \( T_r \), we obtain

\[ T_r = [1 - (V_r - \Sigma_r) \langle G \rangle]^{-1} (V_r - \Sigma_r) \]  \hfill (5.25)

With a bit of algebra, it can be shown that \cite{25}

\[ Q_r = T_r \left( 1 + \langle G \rangle \sum_{r' \neq r} Q_{r'} \right). \]  \hfill (5.26)

In the single site approximation, \( T_r \) and \( Q_{r'} \) are averaged independently. Thus averaging equation (5.26) yields

\[ \langle Q_r \rangle = \langle T_r \rangle \left( 1 + \langle G \rangle \sum_{r' \neq r} \langle Q_{r'} \rangle \right). \]  \hfill (5.27)

For identical scatterers, the self-consistency condition (5.20) requires \( \langle Q_r \rangle = 0 \). Equation (5.27) then yields

\[ \langle T_r \rangle = 0. \]  \hfill (5.28)

This condition determines the self-energy in the single site coherent potential approximation.
5.2.3 Application of the CPA to the Cuprates

The CPA is now applied to the hole Hamiltonian (5.1). It is convenient to divide the Hamiltonian into two contributions:

\[ H = H_0 + V \]  (5.29)

\[ H_0 = \sum_{i,j,\sigma} t_{ij} (d_i^{\dagger} \sigma p_j + \text{h.c.}) + \sum_{j,\sigma} \varepsilon_p p_j^{\dagger} \sigma p_j^{\sigma} + \sum_{i,\sigma} \varepsilon_d d_i^{\dagger} \sigma d_i^{\sigma} \]  (5.30)

\[ V = \sum_i U_i d_i^{\dagger} \sigma_{AF} d_i^{\sigma_{AF}} \]  (5.31)

\( H_0 \) is the Hamiltonian for a metallic tight-binding model. \( V \) introduces the repulsive potential due to antiferromagnetically occupied copper sites. However, in contrast to equation (5.1), each \( U_i \) is randomly allowed to take on the values \( U \) or 0:

\[ U_i = \begin{cases} \begin{array}{l} U^A \equiv U \quad \text{with probability } 1 - c \\ U^B \equiv 0 \quad \text{with probability } c \end{array} \end{cases} \]  (5.32)

In order to avoid ambiguity, matrix potentials are denoted by \( V \)'s and scalars are denoted by \( U \)'s. Note that there is no sum over \( \sigma \) in the potential (5.31). Rather, the potential is only applied to holes with spin opposite the antiferromagnetic order. Equivalently, we can write

\[ V = \sum_{i,\sigma} V_{i\sigma} \]  (5.33)

as long as \( V_{i\sigma} \) is defined as

\[ V_{i\sigma} \equiv V_i \delta_{\sigma,-\sigma_{AF}} \]  (5.34)

The entries of \( V_i \) are zero except for the \( i \)th diagonal entry. Thus \( V_{i\sigma} \) takes the form

\[ V_{i\sigma} = |i\rangle U_i \delta_{\sigma,-\sigma_{AF}} \langle i |. \]  (5.35)

Physically, setting the potential \( U_i \) to zero corresponds to the possibility that the \( i \)th copper site is not occupied by a hole. The fraction of unoccupied copper sites is \( c \). In the
cuprates, $c$ should increase with the doping fraction $x$. Furthermore, one might expect the effective Coulomb repulsion $U$ to be screened with increased doping. In absence of a more detailed theory, a physically reasonable parametrization of $c$ and $U$ vs. doping is

$$c = 1 - (1 - x)^\gamma \quad (5.36)$$
$$U = U_0 (1 - x)^\gamma. \quad (5.37)$$

The parameter $\gamma$ controls the rate of increase of $c$ and the rate of decrease of $U$.

Equation (5.32) means that the configurational average of a function $f(U_i)$ is given by

$$\langle f(U_i) \rangle = (1 - c)f(U_i^A) + cf(U_i^B). \quad (5.38)$$

This expression is valid if

$$\langle f(U_i) \rangle = \int dU_i P(U_i) f(U_i), \quad (5.39)$$

and the probability distribution is given by

$$P(U_i) = (1 - c)\delta(U_i - U_A) + c\delta(U_i - U_B). \quad (5.40)$$

Thus equation (5.28) reads

$$(1 - c)T^A_{i\sigma} + cT^B_{i\sigma} = 0, \quad (5.41)$$

where the superscript $A$ or $B$ means replace all occurrences of $U_i$ by $U_A$ or $U_B$, respectively. The form of $T_{i\sigma}$ is given in equation (5.25). Some algebraic manipulation then yields the CPA equation for the self-energy [18]:

$$\Sigma_{i\sigma} = (1 - c)V^A_{i\sigma} + cV^B_{i\sigma} - (V^A_{i\sigma} - \Sigma_{i\sigma})\langle G \rangle (V^B_{i\sigma} - \Sigma_{i\sigma}). \quad (5.42)$$

Finally, we see from equation (5.42) that $\Sigma_{i\sigma}$ can be written

$$\Sigma_{i\sigma} = |i\rangle \Sigma_0 \delta_{\sigma, -\sigma_{AF}} \langle i|, \quad (5.43)$$
where $\Sigma_0$ is a scalar that does not depend on the copper site $i$. This leads us to the scalar equation for the self-energy:

$$
\Sigma_0 = (1-c)U_A + cU_B - (U_A - \Sigma_0)\langle G \rangle_{00}(U_B - \Sigma_0).
$$

This last equation can be solved self-consistently for $\Sigma_0$. The full self-energy operator is then given by

$$
\Sigma = \sum_{i,\sigma} |i\rangle \Sigma_0 \delta_{\sigma,-\sigma_{AF}} \langle i|.
$$

The reader is reminded that the sum runs over all copper sites $i$ in the lattice.

According to equations (5.10) and (5.14), the Green’s function of the medium is determined once $\Sigma$ is known through the relation

$$
\langle G \rangle = (\omega - H_0 - \Sigma)^{-1}.
$$

Many single-particle properties can be determined from the Green’s function. These are discussed in the next chapter.

### 5.3 The Particle-Particle Green’s Function in the CPA

Pairing correlations appear in the particle-particle Green’s function, denoted by $K$, as the temperature approaches $T_c$. Since there are no two-body interactions in the Hamiltonian (5.29), $K$ factors into the product of two single-particle Green’s functions. However, the configurational average in the CPA introduces an effective interaction between the particles. For a certain range of doping, the interaction leads to the superconducting transition.

The temperature Green’s functions are appropriate for the study of systems at finite temperature. The definition of the single-particle temperature Green’s function is

$$
G_{\sigma\sigma'}(\vec{r},\tau,\vec{r}',\tau') \equiv -\langle T_\tau \psi_M^{\sigma}(\vec{r},\tau)\bar{\psi}_M^{\sigma'}(\vec{r}',\tau') \rangle
$$

$$
= -\text{tr}\{ \rho_T \bar{\psi}_M^{\sigma}(\vec{r},\tau)\psi_M^{\sigma'}(\vec{r}',\tau') \}.
$$
The average appearing in equation (5.47) is the thermodynamic average in the grand canonical ensemble. The density matrix is \( \rho = e^{-\beta (H - \mu N)} \), where \( \beta = 1/k_B T \) and \( \mu \) is the chemical potential. The Fermi Matsubara field operators are given by

\[
\begin{align*}
\psi^M (\vec{r}, \tau) &= e^{H \tau} \psi(\vec{r}) e^{-H \tau} \\
\bar{\psi}^M (\vec{r}, \tau) &= e^{H \tau} \psi^\dagger(\vec{r}) e^{-H \tau}.
\end{align*}
\]

Finally, \( \tau = it \) is the imaginary time and \( T_\tau \) is the imaginary time ordering operator. Operators that depend on imaginary time are ordered from the largest time on the left to the smallest time right. Use of imaginary time allows \( \tau \) to be treated on the same footing as \( \beta \).

The temperature Green’s function depends only on the time difference \( \tau - \tau' \). For fermions, \( G \) is anti-periodic in time with a period of \( \beta \). Thus, \( G \) can be expanded as the Fourier series

\[
G(\tau - \tau') = \frac{1}{\beta} \sum_{l=-\infty}^{\infty} \tilde{G}(\zeta_l) e^{-i\zeta_l(\tau - \tau')},
\]

where \( \zeta_l = (2l + 1)\pi T \) is an odd Matsubara frequency for the fermion case. The Fourier transform \( \tilde{G}(\zeta_l) \) is simply related to the Green’s function introduced in section 5.2:

\[
\tilde{G}(\zeta_l) = G(\mu + i\zeta_l).
\]

Pairing correlations occur in the particle-particle Green’s function. Specifically, consider the quantity

\[
K(1,1',2,2') = -\left\langle T_\tau \psi^M_\uparrow(1) \psi^M_\uparrow(1') \bar{\psi}^M_\downarrow(2') \bar{\psi}^M_\downarrow(2) \right\rangle,
\]

where \( 1 \equiv (\vec{r}_1, \tau_1) \) and the remaining arguments are similarly defined. \( K \) describes the propagation of a pair of particles from the coordinates \( (1,1') \) to the coordinates \( (2,2') \). Since the Hamiltonian (5.29) contains no two-body interactions, \( K \) factors into the product.
of two single-particle Green’s functions:

\[ K(1, 1', 2, 2') = G\uparrow(1, 2)G\downarrow(1', 2') \tag{5.53} \]

As in reference [26], set \( \tau_1 = \tau'_1 \) and \( \tau_2 = \tau'_2 \). Then \( K(\tau_1, \tau_2) = K(\tau_1 - \tau_2) \) can be expanded in a Fourier series analogous to equation (5.50):

\[ K(\tau_1 - \tau_2) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} \tilde{K}(\omega_n) e^{-i\omega_n\tau}. \tag{5.54} \]

Since \( K \) involves an even number of Fermi operators, the Matsubara frequencies are even, \( \omega_n = 2n\pi T \). Due to the factorization (5.53), \( \tilde{K} \) can be expressed as the convolution of \( \tilde{G}\uparrow \) and \( \tilde{G}\downarrow \):

\[ \tilde{K}(\omega_n) = \frac{1}{\beta} \sum_{l=-\infty}^{\infty} \tilde{G}\uparrow(\zeta_l) \tilde{G}\downarrow(\omega_n - \zeta_l). \tag{5.55} \]

Since \( K \) factors into a product \( G\uparrow G\downarrow \), it would seem that \( K \) would not contain any new information about pair correlations. However, the configurational average \( \langle K \rangle \) is non-trivial. That is, \( \langle K \rangle \neq \langle G\uparrow \rangle \langle G\downarrow \rangle \). In the CPA, an effective interaction arises between particles that leads to pairing. The configurational average of equation (5.55) is

\[ \langle \tilde{K}(\omega_n) \rangle = \frac{1}{\beta} \sum_{l=-\infty}^{\infty} \langle \tilde{G}\uparrow(\zeta_l) \tilde{G}\downarrow(\omega_n - \zeta_l) \rangle. \tag{5.56} \]

Since the superconducting transition occurs at zero total frequency, the external frequency \( \omega_n \) is set to zero. The average \( \langle \tilde{G}\uparrow(\zeta_l) \tilde{G}\downarrow(-\zeta_l) \rangle \) must be carried out in a manner consistent with the CPA for \( \langle G \rangle \).

5.3.1 Averaging with Nearest-Neighbor Correlations

Let us revisit the form chosen for the random potential probability distribution. Equation (5.40) is appropriate for independent averaging of the potential on a given copper site.
Suppose one wants to find the average \( \langle f(U_i)g(U_j) \rangle \). If the potentials \( U_i \) and \( U_j \) were independent of one another, then the average would factor into the product of the individual averages,

\[
\langle f(U_i)g(U_j) \rangle = \langle f(U_i) \rangle \langle g(U_j) \rangle ,
\]

with the individual averages defined as in equation (5.38). However, if \( i \) and \( j \) are nearest neighbors, the averages should not be performed independently. The antiferromagnetic order arises from nearest-neighbor coupling. Therefore, the values of the potentials \( U_i \) and \( U_j \) on nearest-neighbor sites should be correlated.

For copper sites that are not nearest neighbors, independence is assumed. The joint probability is

\[
P(U_i,U_j) = P(U_i)P(U_j)
\]

\[
= (1-c)^2 \delta(U_i-U_A)\delta(U_j-U_A) \\
+ c^2 \delta(U_i-U_B)\delta(U_j-U_B) \\
+ c(1-c) \delta(U_i-U_A)\delta(U_j-U_B) \\
+ c(1-c) \delta(U_i-U_B)\delta(U_j-U_A).
\]

For nearest neighbors \( i \) and \( j \), the potentials \( U_i \) and \( U_j \) are likely to be the same beyond mere coincidence. The following form for the nearest-neighbor joint probability is proposed:

\[
P_{(i,j)}(U_i,U_j) = (1-c)(1-\alpha c) \delta(U_i-U_A)\delta(U_j-U_A) \\
+ \alpha c(1-c) \delta(U_i-U_B)\delta(U_j-U_B)
\]

\[
+ \alpha c(1-c) \delta(U_i-U_A)\delta(U_j-U_B) \\
+ \alpha c(1-c) \delta(U_i-U_B)\delta(U_j-U_A).
\]

65
The difference between equation (5.58) and equation (5.59) can be understood by considering the last two terms. In equation (5.58), the likelihood of two site potentials being different is simply the product of their individual occurrence probabilities, \( c(1-c) \). In equation (5.59), this likelihood is reduced by the factor \( \alpha \), with \( 0 < \alpha \leq 1 \). The coefficients of the first two terms in equation (5.59) are then chosen to be consistent with equation (5.40) if either \( U_i \) or \( U_j \) is integrated out.

The parameter \( \alpha \) is a measure of clustering of like potentials. When \( \alpha = 1 \), the values of the potentials \( U_i \) and \( U_j \) are completely uncorrelated. In this case, the effective interaction between particles vanishes, and \( \langle K \rangle = \langle G_↑ \rangle \langle G_↓ \rangle \). In the limit \( \alpha \to 0 \), phase separation occurs between the antiferromagnetic and metallic states. The interaction strength increases as \( \alpha \) decreases from 1, reaching a maximum at \( \alpha = 0 \). Above a doping-dependent critical value of \( \alpha \), the superconducting transition never occurs.

The joint probability defined in equation (5.59) satisfies

\[
P_{(i,j)}^{\alpha}(U_i, U_j) = \alpha P_{(i,j)}^{\alpha=1}(U_i, U_j) + (1 - \alpha) P_{(i,j)}^{\alpha=0}(U_i, U_j)
\] (5.60)

Thus the correlation parameter \( \alpha \) linearly interpolates between the phase-separated and uncorrelated nearest-neighbor joint probabilities.

### 5.3.2 The Equation for \( \langle K \rangle \)

The derivation of the equation for \( \langle K \rangle \) closely follows Velicky’s derivation. However, Velicky was concerned with the particle-hole channel. Some modifications must be made when considering the singlet pairing (particle-particle) channel. Differences also arise due to the nature of the Hamiltonian (5.29) and the use of the joint probability distribution in equation (5.59).
In dealing with the particle-particle channel, it is useful to introduce the direct product between matrices. The direct product between two matrices, $A$ and $B$, is denoted $A \otimes B$. The direct product creates a new matrix whose entries are all possible products between the matrix elements of $A$ and $B$:

$$
(A \otimes B) = \begin{pmatrix}
A_{11}(B) & A_{12}(B) & \ldots & A_{1n}(B) \\
A_{21}(B) & A_{22}(B) & \ldots & A_{2n}(B) \\
\vdots & \vdots & \ddots & \vdots \\
A_{m1}(B) & A_{m2}(B) & \ldots & A_{mn}(B)
\end{pmatrix}.
$$

(5.61)

In the matrix above, an entry $A_{ij}(B)$ denotes the sub-matrix

$$
\begin{pmatrix}
A_{ij}B_{11} & A_{ij}B_{12} & \ldots & A_{ij}B_{1n'} \\
A_{ij}B_{21} & A_{ij}B_{22} & \ldots & A_{ij}B_{2n'} \\
\vdots & \vdots & \ddots & \vdots \\
A_{ij}B_{m'1} & A_{ij}B_{m'2} & \ldots & A_{ij}B_{m'n'}
\end{pmatrix}.
$$

One important property of the direct product that will be utilized extensively is the distributive property of the direct product over ordinary matrix multiplication:

$$(AB) \otimes (CD) = (A \otimes C)(B \otimes D).$$

(5.62)

On the left-hand side of equation (5.62), ordinary matrix multiplication is performed first. Then the direct product is taken. On the right-hand side, the direct products are taken first. Then ordinary matrix multiplication is performed.

Using the direct product, equation (5.53) can be written

$$K = G_{\uparrow} \otimes G_{\downarrow}.$$ 

(5.63)
The task at hand is to find an equation for $\langle K \rangle$ that is consistent with the single-site CPA. Substituting equation (5.16) into equation (5.63) and averaging yields

$$\langle K \rangle = \left[ \langle G^\uparrow \rangle + \langle G^\downarrow \rangle T^\uparrow \langle G^\uparrow \rangle \right] \otimes \left[ \langle G^\downarrow \rangle + \langle G^\uparrow \rangle T^\downarrow \langle G^\downarrow \rangle \right].$$  \hspace{1cm} (5.64)

Using property (5.62), this equation can be written

$$\langle K \rangle = \langle G^\uparrow \rangle \otimes \langle G^\downarrow \rangle + \left[ \langle G^\uparrow \rangle \otimes \langle G^\downarrow \rangle \right] \left[ T^\uparrow \otimes T^\downarrow \right] \left[ \langle G^\downarrow \rangle \otimes \langle G^\uparrow \rangle \right].$$  \hspace{1cm} (5.65)

Our goal is to write equation (5.65) as a self-consistent equation involving $\langle K \rangle$ only. We proceed by defining

$$\Gamma \equiv \left[ T^\uparrow \otimes T^\downarrow \right] \left[ \langle G^\downarrow \rangle \otimes \langle G^\uparrow \rangle \right].$$  \hspace{1cm} (5.66)

In terms of $\Gamma$, equation (5.65) reads

$$\langle K \rangle = \left[ \langle G^\uparrow \rangle \otimes \langle G^\downarrow \rangle \right] \left( 1 + \Gamma \right).$$  \hspace{1cm} (5.67)

The $t$-matrices can be decomposed according to equation (5.22) with the scattering matrices $Q^\uparrow$ and $Q^\downarrow$ each satisfying equation (5.26). Since the potential only exists on copper sites, $Q^\sigma_r = 0$ if the index $r$ refers to an oxygen site. Thus the sum in equation (5.26) only runs over copper sites. The single-site approximation, in which $T^\sigma_i$ and $Q^\sigma_j$ are averaged separately, then yields

$$\left\langle T^\uparrow \otimes T^\downarrow \right\rangle = \sum_{\langle i, j \rangle} \left\langle Q^\uparrow_i \otimes Q^\downarrow_j \right\rangle,$$  \hspace{1cm} (5.68)

$$\left\langle Q^\uparrow_i \otimes Q^\downarrow_j \right\rangle = \left\langle T^\uparrow_i \otimes T^\downarrow_j \right\rangle \times \left( 1 + \left[ \langle G^\uparrow \rangle \otimes \langle G^\downarrow \rangle \right] \sum_{\langle i', j' \rangle \neq \langle i, j \rangle} \left\langle Q^\uparrow_{i'} \otimes Q^\downarrow_{j'} \right\rangle \right).$$  \hspace{1cm} (5.69)

The sum over copper sites in equation (5.68) is restricted to nearest neighbors because $\left\langle T^\uparrow_i \otimes T^\downarrow_j \right\rangle = 0$ when $i$ and $j$ are not nearest neighbors, according to equations (5.57) and (5.28).
From equation (5.68), note that

\[
\langle T_i \otimes T_j \rangle - \langle Q_{i\uparrow} \otimes Q_{j\downarrow} \rangle = \sum_{(i', j') \neq (i, j)} \langle Q_{i'\uparrow} \otimes Q_{j'\downarrow} \rangle.
\]

Thus equation (5.69) can also be written

\[
\langle Q_{i\uparrow} \otimes Q_{j\downarrow} \rangle = \langle T_i \otimes T_j \rangle \times \left\{ 1 + \left[ \langle G_{i\uparrow} \rangle \otimes \langle G_{i\downarrow} \rangle \right] \left[ \langle T_i \otimes T_j \rangle - \langle Q_{i\uparrow} \otimes Q_{j\downarrow} \rangle \right] \right\}.
\]
(5.70)

Given equations (5.66) and (5.68), we can decompose \( \Gamma \) according to

\[
\Gamma = \sum_{(i, j)} \Gamma_{ij},
\]
(5.71)

\[
\Gamma_{ij} \equiv \langle Q_{i\uparrow} \otimes Q_{j\downarrow} \rangle \left[ \langle G_{i\uparrow} \rangle \otimes \langle G_{i\downarrow} \rangle \right].
\]
(5.72)

Then equation (5.69) can be converted into an equation for \( \Gamma \) by right multiplying through by \( \langle G_{i\uparrow} \rangle \otimes \langle G_{i\downarrow} \rangle \):

\[
\Gamma_{ij} = \langle T_i \otimes T_j \rangle \left[ \langle G_{i\uparrow} \rangle \otimes \langle G_{i\downarrow} \rangle \right] \left( 1 + \Gamma - \Gamma_{ij} \right)
\]
(5.73)

Furthermore, if we use equation (5.67), equation (5.73) becomes an equation for \( \Gamma_{ij} \) in terms of \( \langle K \rangle \):

\[
\Gamma_{ij} = \langle T_i \otimes T_j \rangle \left\{ \langle K \rangle - \left[ \langle G_{i\uparrow} \rangle \otimes \langle G_{i\downarrow} \rangle \right] \Gamma_{ij} \right\}.
\]
(5.74)

Equation (5.74) can be simplified if the form of the single-site t-matrices are taken into account. With the forms of \( \Sigma_{i\sigma} \) and \( V_{i\sigma} \) given in equations (5.35) and (5.43), \( T_{i\sigma} \) also takes the same form:

\[
T_{i\sigma} = |i\rangle t_i \delta_{\sigma_{\uparrow} - \sigma_{\downarrow}} \langle i|.
\]
(5.75)

By substituting equations (5.35), (5.43), and (5.75) into equation (5.24), the scalar \( t_i \) can be found:

\[
t_i = \frac{(U_i - \Sigma_0)}{1 - (U_i - \Sigma_0) \langle G \rangle_{00}}
\]
(5.76)
Using this simple form (5.75) for $T_{i\sigma}$, equation (5.74) becomes

$$\Gamma_{ij} = \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left\{ \langle K \rangle - \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \Gamma_{ij} \right\} .$$

Upon moving $\Gamma_{ij}$ to the left-hand side, we obtain

$$\left\{ 1 + \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \right\} \Gamma_{ij}$$

$$= \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \langle K \rangle .$$

(5.77)

Now introduce $\gamma_{ij}$ through the relation

$$\Gamma_{ij} = \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \gamma_{ij} .$$

(5.78)

The introduction of $\gamma_{ij}$ allows us to solve for $\Gamma$ after a series of operations on the left-hand side of equation (5.77):

$$\left\{ 1 + \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \right\} \Gamma_{ij}$$

$$\left\{ 1 + \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \right\} \gamma_{ij}$$

$$\left\{ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) + \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \right\} \gamma_{ij}$$

$$\left\{ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) + \langle t_{ij} \rangle \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \left[ \langle G_{i} \rangle \otimes \langle G_{i} \rangle \right] \right\} \gamma_{ij}$$

$$\left[ 1 + \langle t_{ij} \rangle \langle G_{i} \rangle \langle G_{i} \rangle \right] \Gamma_{ij}$$

Thus equation (5.77) reduces to

$$\Gamma_{ij} = \mathcal{L} \left[ (|i\rangle \langle i|) \otimes (|j\rangle \langle j|) \right] \langle K \rangle ,$$

(5.79)

where $\mathcal{L}$ is the effective interaction strength and is given by

$$\mathcal{L} = \langle t_{ij} \rangle / \left[ 1 + \langle t_{ij} \rangle \langle G_{i} \rangle \langle G_{i} \rangle \right] .$$

(5.80)
Upon substituting for $\Gamma$ in equation (5.67), we obtain the equation for $\langle K \rangle$:

$$\langle K \rangle = \left[ \langle G_\uparrow \rangle \otimes \langle G_\downarrow \rangle \right] \left\{ 1 + 2 \sum_{i,j} \left[ \left( \langle i \rangle \otimes \langle j \rangle \right) \right] \langle K \rangle \right\}. \quad (5.81)$$

Equation (5.67) is the particle-particle analogue of the equation for $\langle K \rangle$ in the particle-hole channel obtained by Velicky [21].

### 5.3.3 Solution of the Equation for $\langle K \rangle$

We now seek the formal solution for $\langle K \rangle$ of equation (5.67). Applying property (5.62) twice, equation (5.67) takes the form

$$\langle K \rangle = \left( \langle G_\uparrow \rangle \otimes \langle G_\downarrow \rangle \right) \left\{ 1 + 2 \sum_{i,j} \left( \langle i \rangle \otimes \langle j \rangle \right) \langle K \rangle \right\}. \quad (5.82)$$

Equation (5.82) suggests that we left multiply by $\left( \langle i \rangle \otimes \langle j \rangle \right)$ to obtain an equation for the left nearest-neighbor matrix elements of $\langle K \rangle$:

$$\left( \langle i \rangle \otimes \langle j \rangle \right) \langle K \rangle = \left( \langle i \rangle \otimes \langle j \rangle \right) \left( \langle G_\uparrow \rangle \otimes \langle G_\downarrow \rangle \right) + 2 \sum_{i,j} \langle G_\uparrow \rangle \langle G_\downarrow \rangle \langle i \rangle \langle j \rangle \langle K \rangle. \quad (5.83)$$

Since $i$ and $j$ are nearest neighbors, only one site index varies independently. We make this explicit by writing $j = i + \delta$ and $j' = i' + \delta'$, where $\delta$ and $\delta'$ can be any of the four copper sites that are nearest neighbors to site $i$. Then equation (5.83) reads

$$\left( \langle i \rangle \otimes \langle i + \delta \rangle \right) \langle K \rangle = \left( \langle i \rangle \otimes \langle i + \delta \rangle \right) \left( \langle G_\uparrow \rangle \otimes \langle G_\downarrow \rangle \right) + 2 \sum_{i', \delta'} \langle G_\uparrow \rangle \langle G_\downarrow \rangle \langle i' \rangle \langle i' + \delta' \rangle \langle K \rangle. \quad (5.84)$$

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Equation (5.84) can now be solved by Fourier transformation. If the transforms are defined by

\[
B_{k\delta} = \sum_i e^{-i\vec{k} \cdot \vec{R}_i} \left( \langle i | \otimes | i + \delta \rangle \right) \langle K \rangle 
\]

(5.85)

\[
a_{k\delta} = \sum_i e^{-i\vec{k} \cdot \vec{R}_i} \left( \langle i | \otimes | i + \delta \rangle \right) \left( \langle G_{\uparrow} \rangle \otimes \langle G_{\downarrow} \rangle \right) 
\]

(5.86)

\[
A_{k\delta\delta'} = \sum_i e^{-i\vec{k} \cdot \vec{R}_i} \langle G_{\uparrow} \rangle \langle G_{\downarrow} \rangle_{i+\delta0+\delta'} 
\]

(5.87)

then equation (5.84) transforms to give

\[
B_{k\delta} = a_{k\delta} + \Sigma \sum_{\delta'} A_{k\delta\delta'} B_{k\delta'} . 
\]

(5.88)

Finally, if \( A_k \) is the \( 4 \times 4 \) matrix with elements \( A_{k\delta\delta'} \), then the solution for \( B_{k\delta} \) is

\[
B_{k\delta} = \sum_{\delta'} \left( 1 - \Sigma A_k \right)^{-1}_{\delta\delta'} a_{k\delta'} . 
\]

(5.89)

We are now in a position to see how the superconducting transition develops as the temperature is lowered. The matrices \( G_{\uparrow} \) and \( G_{\downarrow} \) carry a frequency dependence that has been suppressed. This means that any quantity depending on \( \langle G_{\sigma} \rangle \) also depends on frequency. To find the superconducting transition, one looks for a pole in \( K \) at zero total frequency. According to equation (5.56) and equation (5.51), we have

\[
\langle \tilde{K}(\omega_n = 0) \rangle = \frac{1}{\beta} \sum_{l=-\infty}^{\infty} \langle G_{\uparrow} (\mu + i\xi_l) G_{\downarrow} (\mu - i\xi_l) \rangle 
\]

(5.90)

Thus the Green’s functions should be evaluated at conjugate frequencies.

In light of equation (5.89), it would appear that a pole in \( \langle K \rangle \) arises when the matrix \( 1 - \Sigma A_k \) becomes singular. In the next chapter, we shall see that this can occur when the total pair frequency and momentum are zero. Furthermore, the divergence can be associated with the \( l = 0 \) term (or equivalently \( l = -1 \)) of the sum in equation (5.90) when the temperature is lowered to a critical value.
CHAPTER 6

ELECTRONIC PROPERTIES OF THE COPPER OXIDE PLANE IN THE CPA

This chapter applies the formalism of chapter 5 for the purpose of obtaining electronic properties of the CuO$_2$ plane. Section 6.1 discusses the details of calculating the self energy in the CPA. The single-particle density of states is obtained from the self energy. One instance of the self energy and density of states is plotted. In section 6.2, predictions of single-particle properties are given as functions of temperature and doping. Section 6.3 discusses the temperature and symmetry of the superconducting transition. The symmetry is found to be d-wave and the transition temperature is calculated as a function of doping. In the context of these results, section 6.3.3 concludes with a discussion of the pseudogap observed in the cuprates.

6.1 The CPA in Practice

We have seen in the previous chapter that the configurational average of the Green’s function can be determined in the CPA through a self-consistent solution for the self-energy. The problem boils down to solving equation (5.44) for the scalar self-energy. The self-energy and the Green’s function both depend on frequency. Writing the frequency
dependence explicitly, equation (5.44) becomes

\[ \Sigma_0(\omega) = (1 - c)U^A + cU^B - (U^A - \Sigma_0(\omega))\langle G(\omega) \rangle_{\omega 0}(U^B - \Sigma_0(\omega)). \quad (6.1) \]

\( \Sigma_0(\omega) \) is independent of spin and momentum.

At each step of the self-consistent calculation, \( \langle G(\omega) \rangle_{\omega 0} \) is found according to

\[ \langle G(\omega) \rangle_{\omega 0} = \sum_{\vec{k}}\langle r\vec{k} - \sigma_{AF} |\langle G(w)\rangle| r\vec{k} - \sigma_{AF} \rangle. \quad (6.2) \]

Here, \( r \) denotes the copper site in the unit cell upon which the coherent potential is applied. For example, if \( \sigma_{AF} = \uparrow \), then \( r \) denotes the copper site with the spin-up hole as shown in figure 5.2. The state \( | r\vec{k} - \sigma_{AF} \rangle \) is the discrete Fourier transform of \( | r\vec{R} - \sigma_{AF} \rangle \). This was first introduced in equation (5.2). The matrix \( \langle G(w) \rangle \) itself is determined from equation (5.46). Since \( H_0 \) is block diagonal in \( \vec{k} \) according to relation (5.3) for \( H_0 \), the inverse operation in equation (5.46) must be done for each allowed \( \vec{k} \) on the 6 × 6 complex matrix \( \omega - H_0 - \Sigma \). Then the sum over \( \vec{k} \) in equation (6.2) can be performed.

Equation (6.1) for the scalar self energy can easily be rewritten as \( f(\Sigma_0(\omega)) = 0 \). The function \( f \) is a complex analytic function of the complex variable \( \Sigma_0(\omega) \). Finding the solution is then as simple as doing a root search. Typically, the calculation begins at some starting frequency. Once \( \Sigma_0(\omega) \) is found, the frequency is incremented and the value of the self energy at the previous frequency is used as a starting point in the root search at the current frequency. In practice, I have found that this method works well, but often fails when moving from a frequency in a gap to a frequency where the density of states is finite. Repeating the calculation by incrementing the frequency in the opposite direction enables \( \Sigma_0(\omega) \) to be found at all frequencies of interest.

One can find \( \Sigma_0(\omega) \) for either real or complex frequencies. \( \Sigma_0(\omega) \) at real frequencies determines the density of states, according to equations (5.6) and (5.7). In practice, one
<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>description</th>
<th>appears in</th>
</tr>
</thead>
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<tr>
<td>$t_{pd}$</td>
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<td>oxygen-copper hopping amplitude</td>
<td>Hamiltonian</td>
</tr>
<tr>
<td>$t_{pp}$</td>
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<td>oxygen-oxygen hopping amplitude</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
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<td>energy of oxygen orbital</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_d$</td>
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<td>energy of copper orbital</td>
<td></td>
</tr>
<tr>
<td>$U$</td>
<td>varies</td>
<td>copper hole double occupation energy</td>
<td></td>
</tr>
<tr>
<td>$U_0$</td>
<td>5.</td>
<td>double occupation energy at half filling</td>
<td>$U = U_0(1-x)\gamma$</td>
</tr>
<tr>
<td>$c$</td>
<td>varies</td>
<td>fraction of spin defects</td>
<td>$c = 1 - (1-x)\gamma$</td>
</tr>
<tr>
<td>$x$</td>
<td>varies</td>
<td>doping of CuO$_2$ plane</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>4.</td>
<td>disorder exponent</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0. to 1.</td>
<td>correlation coefficient</td>
<td>nearest neighbor joint probability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = 1 \rightarrow$ uncorrelated</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha = 0 \rightarrow$ maximum correlation</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Default values of parameters and variables. All energies are scaled relative to $t_{pd} = 1$.

does not need to include the small imaginary frequency $i\delta$ if one is careful about obtaining the correct sign of the imaginary part of the self-energy. In fact, when $\omega$ is real, equation (6.1) admits both $\Sigma_0(\omega)$ and $\Sigma_0(\omega)^*$ as solutions. The correct sign of $\text{Im}(\Sigma_0(\omega))$ is the one for which the spectral function, given by equation (5.7), is positive. The correct solution is also obtained if one approaches the real frequency axis from above.
Table 6.1 contains the default parameters used in these calculations. All energies are scaled relative to $t_{pd} = 1$. This default energy scale is used throughout this chapter, unless indicated otherwise. The value of $t_{pd}$ used in other theoretical studies [15, 27] is about 1 eV.

As an example, figure (6.1) shows the self-energy and density of states for a doping of $x = 0.09$. A gap occurs in the density of states whenever $\text{Im}(\Sigma_0(w)) = 0$. Note that the ‘noninteracting’ Hamiltonian, equation (5.30), does not contain the antiferromagnetic potential. Thus $\Sigma$ includes all the differences between the effective medium Green’s function $\langle G \rangle$ and the metallic Green’s function $G_0$.

### 6.2 Single-Particle Properties

The single-particle spectral function determines the single-particle electronic properties of the system. These properties include the heat capacity and the Pauli paramagnetic susceptibility, which can be obtained from the density of states. Also, angle resolved photoemission spectroscopy (ARPES) is capable of probing the spectral function directly. The spectral function determines the shape of the Fermi surface, to the extent that the Fermi surface is still well defined.

The parameterizations of $c$ and $U$ (see table 6.1) phenomenologically tie the destruction of antiferromagnetism to the doping $x$. Figure 6.2 shows these parameterizations. For simplicity, the value $\gamma = 4$ has been chosen for both $c$ and $U$. At $x \sim 0.16$, $U = c = 0.5$ and antiferromagnetism is substantially reduced. Physically, the increase of $c$ and decrease of $U$ with doping reflects the competition between minimizing the system’s kinetic energy and lowering the overall energy through antiferromagnetic exchange. Minimizing the kinetic energy becomes increasingly dominant as the doping increases. At $x = 1$, all remaining
Figure 6.1: The density of states per unit cell for a doping of $x = 0.09$. The chemical potential for this doping at zero temperature is $-1.73$. The real and imaginary parts of the self-energy are also shown. The units of $\omega$ and $\Sigma$ are relative to $t_{pd} = 1$. This energy scale is used throughout this chapter, unless indicated otherwise.
Figure 6.2: The parameterization of $U$ and $c$ versus doping, as given by equations (5.37) and (5.36).
traces of antiferromagnetism vanish. This is reasonable because at this doping the CuO$_2$ plane contains an average of two holes per copper site, and the localization of two holes on the same site is energetically very costly.

The self-energy has been calculated for the doping range $0 < x \leq 0.30$ using the parameterizations (5.37) and (5.36). For this doping range, the density of states is found, and the specific heat and Pauli susceptibility are calculated as functions of temperature. Finally, the evolution of the Fermi surface is given using the spectral function.

### 6.2.1 Density of States

The density of states determines single-particle properties such as the electronic specific heat and the paramagnetic susceptibility. Figure 6.3 shows the evolution of the density of states versus doping. For $x = 0$, the density of states is completely gapped between the lowest two bands. For a small finite doping, however, an impurity band forms inside the gap. An impurity band also breaks off of the lowest band, but is quickly re-adsorbed.

A doping dependent density of states can have some unexpected consequences. For example, the chemical potential lies within the impurity band for all values of $x$, as indicated by the dashed lines in figure 6.3. This leads to semi-metallic single-particle properties. Furthermore, the position of the chemical potential within the impurity band is necessary for the occurrence of the superconducting transition.

### 6.2.2 Electronic Specific Heat

In calculating the electronic specific heat, we work at constant doping. This means that chemical potential varies with temperature. The temperature dependence of the chemical potential is shown in figure 6.4.
Figure 6.3: The density of states per unit cell for nine different doping levels $x$. The dashed line indicates the value of the chemical potential for the doping $x$ at zero temperature.
Figure 6.4: The variation of the chemical potential with temperature when the doping is held constant.
The specific heat can be obtained by simply taking the derivative of the total electronic energy with respect to temperature. The total electronic energy is

\[ U = \int_{\epsilon_A}^{\epsilon_B} d\omega N(\omega) \omega f \left( \frac{\omega - \mu}{T} \right), \]  

(6.3)

where \( \epsilon_B \) and \( \epsilon_A \) are the upper and lower limits of the energy spectrum, \( \mu \) is the chemical potential, \( T \) is the temperature, and \( f \) is the Fermi occupation function given by

\[ f(x) = \frac{1}{e^x + 1}. \]  

(6.4)

Thus the temperature dependence of \( U \) is solely contained in the Fermi function. Differentiating with respect to \( T \), we obtain

\[ \left. \frac{\partial U}{\partial T} \right|_n = \int_{\epsilon_A}^{\epsilon_B} d\omega N(\omega) \omega \frac{1}{T} f \left( \frac{\omega - \mu}{T} \right) f \left( -\frac{\omega - \mu}{T} \right) \left[ \frac{1}{T} (\omega - \mu) + \frac{\partial \mu}{\partial T} \right]. \]  

(6.5)

Figure 6.5 shows the specific heat for the same range of doping levels over which the density of states was calculated. For low temperatures, the specific heat is linear with temperature, and the slope is proportional to the density of states at the chemical potential. At higher temperatures, the heat capacity deviates from this metallic behavior. The Fermi function differs from the step function over an energy range of several \( k_B T \) about the chemical potential, and the density of states is no longer roughly a constant over this energy interval at higher temperatures.

The effect of the pseudogap on the specific heat is notably missing. Since the pseudogap is presumably pinned to the chemical potential, its effect would be to suppress the specific heat for low temperatures, when \( k_B T \) is less than the energy width of the pseudogap. When \( k_B T \) approaches the width of the pseudogap, the specific heat should rise rapidly as states above the pseudogap are thermally populated.
Figure 6.5: The specific heat for nine different doping levels $x$. 
6.2.3 Pauli Paramagnetic Susceptibility

The Pauli paramagnetic susceptibility is the response of electrons or holes to a magnetic field due to coupling with their intrinsic spin. A calculation of the full momentum and frequency dependent susceptibility is not attempted here. Rather, a static uniform magnetic field is assumed.

We follow the simple treatment of Pauli paramagnetism given by Ashcroft and Mermin [28]. The magnetization of the holes in the CuO$_2$ plane is given by

$$ M = -\frac{g}{2} \mu_B (n_\uparrow - n_\downarrow), \quad (6.6) $$

where $g = 2.0023$ is the electronic g-factor, $\mu_B = e\hbar/2mc$ is the Bohr magneton, and $n_\uparrow(\downarrow)$ is the number of spins parallel (anti-parallel) to the magnetic field.

The total density of states can be split into contributions from each spin:

$$ N(\omega) = N_\uparrow(\omega) + N_\downarrow(\omega). \quad (6.7) $$

The energy of a hole with spin parallel (anti-parallel) to the applied magnetic field $\mathcal{H}$ is shifted up (down) by $\mu_B \mathcal{H}$. Thus $N_\uparrow$ and $N_\downarrow$ are given by

$$ N_\uparrow(\omega) = \frac{1}{2} N(\omega - \mu_B \mathcal{H}), \quad (6.8) $$

$$ N_\downarrow(\omega) = \frac{1}{2} N(\omega + \mu_B \mathcal{H}). \quad (6.9) $$

The magnetization can then be evaluated using

$$ n_{\uparrow(\downarrow)} = \int_{E_A}^{\varepsilon_B} d\omega N_{\uparrow(\downarrow)}(\omega) f\left(\frac{\omega - \mu}{T}\right) \quad (6.10) $$

in equation (6.6). Finally, the paramagnetic susceptibility is defined by

$$ \chi = \frac{\partial M}{\partial \mathcal{H}} \bigg|_{\mathcal{H} \to 0}. \quad (6.11) $$
Using equations (6.6), (6.8), (6.9), and (6.10), one obtains

\[
\chi = \mu_B^2 \int_{\epsilon_A}^{\epsilon_B} d\omega N'(\omega) f\left(\frac{\omega - \mu}{T}\right).
\]  

(6.12)

Integrating by parts and using the fact that the density of states vanishes at the band edges, the expression for \(\chi\) becomes

\[
\chi = -\frac{g}{2} \mu_B^2 \int_{\epsilon_A}^{\epsilon_B} d\omega N'(\omega) \frac{\partial}{\partial \omega} \left[ f\left(\frac{\omega - \mu}{T}\right) \right],
\]

\[
\chi = \frac{g}{2} \mu_B^2 \int_{\epsilon_A}^{\epsilon_B} d\omega N(\omega) \frac{1}{T} f\left(\frac{\omega - \mu}{T}\right) f\left(\frac{-\omega - \mu}{T}\right).
\]  

(6.13)

Note that

\[
\int_{-\infty}^{\infty} \frac{d\omega}{T} f\left(\frac{\omega - \mu}{T}\right) f\left(-\frac{\omega - \mu}{T}\right) = 1 \quad \forall T.
\]

Furthermore, \(f\left(\frac{\omega - \mu}{T}\right) f\left(-\frac{\omega - \mu}{T}\right)\) becomes sharply peaked as \(T\) approaches zero, and we have

\[
\lim_{T \to 0} \frac{1}{T} f\left(\frac{\omega - \mu}{T}\right) f\left(-\frac{\omega - \mu}{T}\right) = \delta(\omega - \mu).
\]  

(6.14)

Thus the low temperature susceptibility is proportional to the density of states at the Fermi level:

\[
\lim_{T \to 0} \chi = \frac{g}{2} \mu_B^2 N(\mu).
\]  

(6.15)

Figure 6.6 shows the paramagnetic susceptibility for the same range of doping levels over which the density of states was calculated.

### 6.2.4 Formation of the Fermi Surface

For a system of noninteracting fermions with infinite lifetimes, the spectral function is \(\delta(\epsilon_k - \mu)\), and finding the Fermi surface is simply a matter of locating the \(\vec{k}\)-points in the first Brillouin zone that satisfy \(\epsilon_{\vec{k}} = \mu\). For particles with finite lifetimes, however, another
Figure 6.6: The paramagnetic susceptibility for nine different doping levels $x$. 
criterion must be used since the energies are not definite. If $\phi$ is the angle of $\vec{k}$ relative to the $k_x$ axis in the Brillouin zone, then the 2D Fermi surface can be defined by the equation

$$|\vec{k}| = k_F(\phi).$$

(6.16)

For any fixed $\phi$, $k_F$ is defined as the value of $k$ for which $A(\vec{k}, \omega = \mu)$ is a maximum.

Figure 6.7 shows plots of the spectral function $A(\vec{k}, \omega = \mu)$ as a function of $\vec{k}$ throughout the entire Brillouin zone. The gray scale is directly proportional to the spectral weight, with white corresponding to zero spectral weight. At low doping levels, the spectral function is not sharply peaked and the Fermi surface as defined by equation (6.16) does not represent a sharp boundary between occupied and unoccupied states. As the doping increases, however, the peak in the spectral function sharpens and the Fermi surface does represent a well defined boundary between occupied and unoccupied states. The location of the Fermi surface does not change much with doping. Thus, Luttinger’s theorem is violated.

The width of the spectral weight as a function of frequency is equal to the inverse lifetime of the quasiparticle state. Figure 6.8 shows the spectral weight at the Fermi surface as a function of frequency. For low doping, the spectral weight is very broad, extending over the entire width of the CPA impurity band. The spectral weight begins to coalesce into a peak with a shoulder as the doping increases. Upon comparison to the plots of the density of states shown in figure 6.3, it becomes clear that the spectral weight becomes peaked only after the CPA impurity band has merged into the upper band. However, the width is still very large, and there are no well defined quasiparticles.

The spectral weight has only a slight angular dependence. The amplitude is slightly depressed at $\phi = \frac{\pi}{4}$. Note that the coordinate system used in figure 6.8 is the magnetic one rotated by 45 degrees, so the angle $\phi = \frac{\pi}{4}$ corresponds to the copper-oxygen bond direction.
Figure 6.7: The spectral weight evaluated at the chemical potential is plotted throughout the Brillouin zone. As the doping increases, the spectral weight sharpens and a Fermi surface can be identified. The gray scale is directly proportional to the spectral weight, with white corresponding to zero spectral weight. The Fermi surface is identified by the maximum in the spectral function for a given angle, as indicated by the dashed red line.
Figure 6.8: The spectral weight evaluated at the Fermi surface is plotted as a function of frequency. The angle $\phi$ is measured from the magnetic $k_x$ axis in radians. The spectral function is shown for $0 \leq \phi \leq \frac{\pi}{2}$. 
6.3 The Superconducting Transition

In section 5.3.3, the equation for $K$ in the singlet particle-particle channel was formally solved. The form of the solution, equation (5.89), shows that a mode of $B_k$ diverges if the matrix $1 - \mathcal{L} A_k$ becomes singular. This can happen if the Green’s functions of opposite spin entering into $\mathcal{L}$ and $A_k$ are always evaluated at conjugate frequencies:

$$G_\uparrow \rightarrow G_\uparrow (\mu + i\zeta_l)$$  \hspace{1cm} (6.17)

$$G_\downarrow \rightarrow G_\downarrow (\mu - i\zeta_l).$$  \hspace{1cm} (6.18)

The restriction to conjugate frequencies is consistent with equation (5.90) for $\tilde{K}$. Furthermore, for this case the interaction strength $\mathcal{L}$ is real and $A_k$ is Hermitian. Thus the diverging mode of $B_k$ is obtained by diagonalizing $1 - \mathcal{L} A_k$ and searching for an eigenvalue equal to zero.

6.3.1 Transition Temperature vs. Doping

Although $\zeta_l = (2l + 1)\pi T$ is a discrete frequency with respect to the index $l$, it can be regarded as a continuous variable if the temperature is allowed to vary. The divergence in $B_k$ occurs at a conjugate frequency pair $(z_0, z_0^*)$. At high temperatures, $\zeta_l$ is larger than $\text{Im}(z_0)$ for all $l$. As $T$ is lowered, the smallest positive Matsubara frequency, $\zeta_l$ with $l = 0$, approaches $\text{Im}(z_0)$. At the critical temperature, $\zeta_l$ with $l = 0$ is equal to $\text{Im}(z_0)$ yielding

$$T_c = \frac{\text{Im}(z_0)}{\pi}. \hspace{1cm} (6.19)$$

The transition temperature is plotted versus doping in figure 6.9 for two values of the correlation parameter $\alpha$. For small doping levels, the superconducting transition occurs as long as the number of spin defects $c$ is greater than zero. $T_c$ rises rapidly to a peak at small
doping levels, and then falls off to zero roughly linearly with doping. High correlation in the spin disorder (small $\alpha$) leads to very high transition temperatures. If $t_{pd}$ is about 1 eV, then $T_c$ can be higher than 1000K for $\alpha = 0.2$.

For $\alpha > 0.5$, $T_c$ continues to decrease for all doping levels $x$. When $\alpha$ reaches $\sim 0.7$, $T_c$ is very small for small $x$ and vanishes for $x > 0.05$. $T_c$ vanishes for all doping levels upon any further increase in $\alpha$.

6.3.2 Symmetry of the Transition

The diverging mode of $B_{\vec{k}}$ is the linear combination

$$B_{\vec{k}u} = \sum_{\delta} u_\delta a_{\vec{k}\delta}.$$  

(6.20)

The definition of $a_{\vec{k}\delta}$ is given in equation (5.86). The index $\delta$ refers to each of the spin-down sites neighboring a central spin-up site. The diverging eigenmode $\vec{u}$ is found to be a d-wave linear combination of the spin-down sites surrounding a central spin-up copper site. Pairing occurs between holes of opposite spins on neighboring copper sites. If one considers each of the four possible pairings for a hole on a given copper site, the phase of the pairing amplitude exhibits $d_{x^2−y^2}$ symmetry, as shown in figure 6.10. The d-wave symmetry appears to be a result of antiferromagnetism and the phase of the hopping amplitude.

6.3.3 Relationship to the Pseudogap in the Cuprates

The gaps in the density of states have no relation to the pseudogap in the cuprates. Besides being gaps and not pseudogaps, the gaps are also not pinned to the chemical potential. In fact, a gap occurs at the chemical potential only in the limit of zero doping. That gap is then the antiferromagnetic gap. At any finite doping, the chemical potential lies within the impurity band, and the Fermi surface is not gapped.

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Figure 6.9: The superconducting transition temperature vs. doping is plotted for two values of the correlation parameter, $\alpha = 0.5$ and $\alpha = 0.2$. The units of $k_B T_c$ are relative to $t_{pd} = 1$. 
Figure 6.10: The symmetry of the diverging mode is $d_{x^2-y^2}$: The nearest neighbor pair amplitude changes sign under rotation by $\pi/2$.

There is a crucial difference between this model and the real copper oxide plane in the cuprates. This model assumes the existence of antiferromagnetic order. In the cuprates, antiferromagnetic order vanishes with the addition of a small fraction of holes. However, a consensus seems to have been reached that a temperature scale $T^*$ exists below which the pseudogapped state emerges. The pseudogapped state exhibits antiferromagnetic correlations, but not long range order.

One may make an alternative interpretation of the superconducting transition temperatures calculated in the previous section. In figure 6.9, suppose that $T_c$ is identified with $T^*$ in the real cuprate systems. Then $T^*$ may be interpreted as a pseudo transition temperature below which superconductivity would emerge if antiferromagnetic order were present. The actual superconducting transition would occur once antiferromagnetism is established.
Above the superconducting transition, the pseudogap emerges as a precursor to pairing. This interpretation of $T^*$ is consistent with the idea that the pseudogap become the full-fledged superconducting gap at $T_c$ in the cuprates. Also, Mook et al. have observed antiferromagnetism within the superconducting state using neutron scattering [29]. They see the moments first appear below $T^*$ and further increase in strength below $T_c$.

In this model of the cuprates, superconductivity and antiferromagnetism are not mutually exclusive. Correlated defects in the spin order lead to an effective interaction that causes pairing. Thus it is no coincidence that the antiferromagnetic state occurs in close proximity to the superconducting state.
APPENDIX A

KERNEL RIDGE REGRESSION

Given a set of data points \( \{(\vec{x}_i, y_i)\} \) and a set of basis functions \( \{\phi_n(\vec{x}_i)\} \), our task is to find a smooth fit to the data, \( y = f(\vec{x}) \). The function \( f \) is assumed to be a linear combination of the basis functions, as in equation (2.2). The primal ridge regression [5] problem can be stated as follows:

\[
\begin{align*}
\text{minimize} \quad & \lambda \sum_n w_n^2 + \sum_i \xi_i^2 \\
\text{subject to} \quad & y_i - \sum_n w_n \phi_n(\vec{x}_i) = \xi_i, \quad \forall i.
\end{align*}
\]

\( \lambda \sim 10^{-3} \) is a small positive number that serves to smooth the solution. Introduce a Lagrange multiplier \( \alpha_i \) for each data point. Then the problem can be written as

\[
\begin{align*}
\text{minimize} \quad L(\{w_n\}, \{\xi_i\}, \{\alpha_i\}) = \lambda \sum_n w_n^2 + \sum_i \xi_i^2 \\
+ \sum_i 2\lambda \alpha_i \left( y_i - \sum_n w_n \phi_n(\vec{x}_i) - \xi_i \right).
\end{align*}
\]

Writing the problem as the minimization of a Lagrangian enables the problem to be reformulated solely in terms of the Lagrange multipliers, which frees us from being restricted by the size of the set \( \{\phi_n(\vec{x})\} \). If one sets \( \partial L / \partial w_n = 0 \) and \( \partial L / \partial \xi_i = 0 \), which must hold at the minimum, one obtains

\[
\begin{align*}
w_n = \sum_i \alpha_i \phi_n(\vec{x}_i), \quad \xi_i = \lambda \alpha_i.
\end{align*}
\]
Equation (A.3) gives the values of the primal variables \( \{w_n, \xi_i\} \) that minimize the Lagrangian \( L(w_n, \xi_i, \alpha_i) \) for any fixed values of the dual variables \( \{\alpha_i\} \). Setting \( \partial L / \partial \alpha_i = 0 \) returns the constraint of problem (A.1). One need only substitute equation (A.3) into the constraint of problem (A.1) and solve for the dual variables \( \{\alpha_i\} \). The result is

\[
\alpha_i = \sum_j (K + \lambda \mathbf{1})^{-1}_{ij} y_j,
\]

(A.4)

where the kernel matrix \( K \) is defined by

\[
(K)_{ij} \equiv K(\vec{x}_j, \vec{x}_j) = \sum_n \phi_n(\vec{x}_i) \phi_n(\vec{x}_j)
\]

(A.5)

Upon evaluation of equation (2.4), the fit \( y = f(\vec{x}) \) has been determined using kernel ridge regression.
APPENDIX B

UNITS OF TEMPERATURE AND FREQUENCY

Throughout part II of this work, temperatures and frequencies are often given units of energy. To work in units of K and s\(^{-1}\), the following replacements need to be made:

\[ T \to k_B T, \quad \omega \to \hbar \omega. \]

Thus in ordinary units, the definition of the Matsubara frequencies given after equation (5.50) reads

\[ \hbar \zeta_j = (2l + 1)\pi k_B T, \]

and equation (6.19) for the transition temperature is written

\[ k_B T_c = h \Im(z_0) / \pi. \]


