Inter-Band Pairing Theory of Superconductivity

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ABSTRACT

A model for high temperature superconductors based on the idea of Cooper pairs comprised of electrons from different bands is studied. We propose that the two bands relevant for the cuprates are comprised of Cu \(d_{x^2-y^2}, d_{z^2}\), planar O \(p_\sigma\), and apical O \(p_z\) orbitals. Along the diagonal, \(k_x = k_y\) in the Brillouin zone, the two band Fermi surfaces may cross. We associate the optimal doping for the highest \(T_c\) with this point because only in the vicinity of this touching point are inter-band Cooper pairs energetically possible. Due to the lack of time reversal invariance of an inter-band Cooper pair with itself, the standard interpretation of Josephson tunneling is altered such that the detailed nature of the single particle tunneling matrix elements contributes to the supercurrent. The \(d_{x^2-y^2}\) gap observations from Josephson tunneling are shown to arise from our model with pairing due to phonons. A Hubbard model is written down for the two bands at the Fermi energy with realistic parameters for \(La_{1.85}Sr_{0.15}CuO_4\). The anomalous normal state features in the nmr are calculated and qualitatively explained as due to the character of the two bands in the vicinity of the crossing point. The Hall effect is calculated using standard Bloch-Boltzmann transport theory. The observed strong temperature dependence of the Hall coefficient is reproduced and is due to the strong reshaping of the current carrying band Fermi surface due to band repulsion with the other band for dopings very close to the Fermi surface touching point. Reasonable quantitative agreement is also obtained for the nmr and Hall effect. A linear resistivity at optimal doping is expected due to the proximity of the second band in \(k\) space which can strongly relax the current and the “smallness” of the current carrying Fermi surface.

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I. INTRODUCTION

In a previous publication the author proposed an Inter-Band Pairing (IBP) model for high temperature superconductors. We suggested that the fundamental idea of Cooper pairs composed of electrons in states $k \uparrow$ and $-k \downarrow$ be retained but rather than $k \uparrow$ and $-k \downarrow$ being from the same band, we consider pairs such that $k \uparrow$ and $-k \downarrow$ come from different bands at the Fermi surface. Such Cooper pairs, if they exist, are not time reversal invariant with themselves in contrast to all BCS-like (Intra-Band) Cooper pairs. The full Hamiltonian is time reversal invariant, though. We showed that with such Inter-Band pairs, the orbital character of the two bands plays a significant role in all Josephson tunneling experiments. The phase difference across a junction is no longer simply the phase difference of the two gap functions but also includes a contribution due to the phases of the hopping matrix elements across the junction. With BCS-like Cooper pairs, the product of the single particle tunneling matrix elements is mod-squared due to the time reversal invariance of the pair. This is not the case with IBP. We suggest that the observed $d_{x^2-y^2}$ character of the Josephson tunneling can be resolved by an “s-like gap” coupled with a “$d_{x^2-y^2}$” Cooper pair. These issues will be explained in detail below.

Clearly, in order to have any possibility of creating an Inter-Band Cooper pair, $(k \uparrow_U, -k \downarrow_L)$ where U, L are labels for the two distinct bands (eventually taken to represent the Upper and Lower bands), the single particle energies $\epsilon_k^{(U)} = \epsilon_{-k}^{(L)} = \epsilon_{-k}^{(L)}$ must be close to the Fermi energy. Such a circumstance is easily available when the U and L band Fermi surfaces intersect. Of course, bands repel each other in general unless there is a symmetry that forbids mixing. Thus, Cooper pairing will occur in the vicinity of special symmetry points in the Brillouin zone.

Our previous paper dealt with the unphysical situation of two distinct bands with exactly coincident Fermi surfaces at a given doping which was associated with the optimal doping for superconductivity. In this regard, the previous study of IBP must be regarded as an overly simplistic model that serves to illustrate some of the general principles of IBP but cannot account for quantitative features. This paper considers realistic bands for the cuprates and derives some quantitative consequences of the theory.

We propose the two relevant bands for high $T_c$ are comprised predominantly of Cu $d_{x^2-y^2}$, Cu $d_{z^2}$, planar O $p_{\sigma}$, and apical O $p_z$ orbitals. The two bands are strong mixtures of these orbitals except at special k points only. A simple Hubbard model is written down for the system. The parameters used in our Hubbard model are derived in the following paper by Perry and Tahir-Kheli using ab-initio calculations on finite clusters for La$_{1.85}$Sr$_{0.15}$CuO$_4$. Contrary to the results of local density approximation (LDA) band structure calculations on the cuprates, we find two bands at the Fermi energy comprised primarily of the above orbitals. The difference between our results and previous band structure calculations are attributed to correlation effects. The optimal doping is the doping where the two band Fermi surfaces touch. This can happen along the diagonal where $k_x = k_y$. La$_{1.85}$Sr$_{0.15}$CuO$_4$ is primarily considered here so the 3D dispersion is small.

The NMR spin relaxation rates at the planar Cu and O nuclei are estimated with these
bands and so are the respective Knight shifts. Reasonable quantitative agreement with many of the anomalous NMR properties\textsuperscript{5-11} is obtained. The dramatically different temperature dependencies of the planar Cu and O spin relaxation rates is due to the conspiring of several important aspects of the orbital characters of the two bands U and L at the Fermi energy. The major reason is that there are two possible orbitals on the Cu, $d_{x^2-y^2}$ and $d_{z^2}$, whereas there is only one important orbital $p_\sigma$ on the planar O. The second most important reason is that the L band is almost full at optimal doping and the orbital character of the available L k states is dominated by the character at the top of the band at $k = (\pi, \pi)$.

The large spin relaxation anisotropy\textsuperscript{10} on the Cu site is discussed and we argue this is due to a small mixture of $d_{xy}$ character in the two bands. We show that mixing of $d_{xy}$ of a few percent is sufficient to produce the observed anisotropy ratio of $\approx 3.4$.

The Cu and O Knight shifts are shown to have similar T (temperature) dependence to the O relaxation rate although strictly speaking, we expect deviations to exist. Once again, the above mentioned reasons for the relaxation rates come into play. Finally, we show that the extra 3D dispersion one expects for these bands in optimally doped YBa$_2$Cu$_3$O$_7$ can resolve the lack of T dependence of the Knight shifts and O relaxation rate observed for this cuprate.

With the same parameters, the Hall effect is calculated using standard Bloch-Boltzman theory and is shown to have the observed monotonic decreasing T dependence varying by $\approx 50\%$ over the temperature range compared to the experimental\textsuperscript{12} value of $\approx 50\%$, with absolute values about 13 times larger than measured values.

The linear resistivity is also obtained due to phonon relaxation across the bands. The sensitivity of $R_h$ and $\rho$ to the doping follows naturally from the model. The qualitative features of the above experiments are straightforward from the considerations presented here. These features are very robust and do not depend sensitively at all on the choice of parameters used. This is particularly gratifying because these features are observed for a variety of different materials. Derivations of so many of the anomalous normal state properties of the cuprates lends confidence to the overall theory.

Section II motivates and defines the IBP model. A Hamiltonian is written down and solved within the BCS mean field approximation. The orbital character of our bands is chosen. The optimal doping for superconductivity as the Fermi surface touching point is discussed. The lack of a unique phase for the attractive coupling matrix element $V_{kk'}$ is discussed and the difference between Josephson tunneling in standard BCS-like intra-band pairing and IBP schemes is derived. IBP due to coupling through phonons is proposed. Up to this point the arguments and equations presented in Section II are quite general. There are several different channels through which IBP could occur. One particular channel is chosen and we restrict ourselves to singlet pairs only. There is nothing in the general theory that precludes IBP due to phonons with triplet pairs as far as we can see.

The 4 key Josephson tunneling experiments\textsuperscript{2,3,13,14} are discussed. We show that with our choice of pairing channel, the two “d-wave” results of Wollman\textsuperscript{2} et al and Tsuei\textsuperscript{3} et al can be understood. The observed c-axis tunneling of Dynes\textsuperscript{13} et al can also be understood as
due to BCS-like pairs formed away from the Fermi surface touching point. We are unable at present to decide whether the “s-wave” result of Chaudhari and Lim supports or contradicts our model due to the complexity of the single particle tunneling matrix elements in this case.

Section III presents quantitative calculations of the various normal state properties mentioned above and the final section is devoted to a summary of our results.

II. INTER-BAND PAIRING MODEL

A. The Model

The \( T_c \) of the cuprates is quite sensitive to the doping. Typically, there exists one optimal doping\(^{15}\) for the highest \( T_c \) and a rapid change in \( T_c \) above and below this doping. A notable exception is YBCO\(^{16}\) where one may argue that there are two optimal dopings, \( T_c = 62K, 92K \) with an intermediate crossover regime. Regardless, whether we argue for one or two optimal dopings for YBCO, it is natural to associate the change in \( T_c \) with doping to an attractive coupling that is strongly doping dependent. Experimentally,\(^{17}\) many normal state properties are simultaneously strongly dependent on the doping. Thus, one is led to propose a bosonic excitation that couples to the electronic charge where either (or both) the bosons or their electronic coupling is strongly renormalized by the doping level. Rather than such dynamic schemes for the change in the attractive coupling with doping, we ask if there exists a simple kinematic scheme for the doping dependence of \( T_c \). In such a scheme, we hope to find a pairing strength that weakly depends on doping with the suppression of \( T_c \) due primarily to a kinematic mechanism. IBP is such a mechanism.

Consider two bands labeled U and L with dispersions \( \epsilon_k^{(U)} \), \( \epsilon_k^{(L)} \) and further suppose there exists some attractive coupling leading to Cooper pairs of the form \((k_U \uparrow, -k_L \downarrow)\) or \((k_L \uparrow, -k_U \downarrow)\). In general, \( \epsilon_k^{(U)} \neq \epsilon_k^{(L)} \). It is only when \( \epsilon_k^{(U)} \) and \( \epsilon_k^{(L)} \) are both close to the Fermi energy that there is any possibility of a lowering of the overall energy by the formation of a Cooper pair. In BCS superconductors, pairs are formed for k states satisfying,

\[
|\epsilon_k - \epsilon_F| < \hbar \omega_D,
\]

where \( \hbar \omega_D \) is the Debye energy and \( \epsilon_F \) is the Fermi energy. For IBP, the analogous criteria are

\[
|\epsilon_k^{(U)} - \epsilon_F| < \hbar \omega_D, \quad (2)
\]

\[
|\epsilon_k^{(L)} - \epsilon_F| < \hbar \omega_D. \quad (3)
\]

For BCS superconductors, there are always k states in the required energy range for pairing regardless of the doping. This is no longer the case for IBP because (2) and (3) must both be satisfied. It is only for special dopings that the U band and L band Fermi surfaces touch or are close to touching that any possibility exists for IBP. Hence, with IBP the doping sensitivity of \( T_c \) can be understood quite simply as due to the change in the minimal separation in k space of the U and L band Fermi surfaces. No change in the strength of the pair attraction is required. In effect, we have replaced the requirement of a doping dependent
pairing interaction by a geometric argument based upon the band energy differences in k space.

We will of course, take the mediator of the inter-band attraction to be phonons as in BCS. Because our pairs are comprised of electrons from two bands, the standard arguments for an upper bound of $T_c \approx 30$K do not apply. This is certainly gratifying as it does not exclude IBP with phonons as a theory for high temperature superconductors. At present we have no estimate for the expected range of values for $T_c$ with our mechanism.

There are some important differences between the pairing terms in the inter-band Hamiltonian and a BCS Hamiltonian. In order to highlight these differences we will briefly re-derive some of the well known aspects of the BCS Hamiltonian in order to both generalize to IBP and to establish our notation.

In general, spin is conserved. Thus, there are two kinds of scatterings of BCS-like $(k, -k)$ pairs: singlet to singlet, and triplet to triplet. Let the matrix elements for scattering a $(k, -k)$ singlet (triplet) to a $(k', -k')$ singlet (triplet),

$$\frac{1}{\sqrt{2}}(\phi_k \phi_{-k} \pm \phi_{-k} \phi_k) \frac{1}{\sqrt{2}}(\uparrow \downarrow \mp \downarrow \uparrow) \rightarrow \frac{1}{\sqrt{2}}(\phi_{k'} \phi_{-k'} \pm \phi_{-k'} \phi_{k'}) \frac{1}{\sqrt{2}}(\uparrow \downarrow \mp \downarrow \uparrow), \tag{4}$$

be $V_{k'k}^0 (V_{k'k}^1)$. $\phi_k$ is a single particle wavefunction of momentum k. The first important point is that although $\phi_k$ is uniquely defined only up to a phase $\phi_k \to e^{i\theta(k)} \phi_k$, with $\theta(-k) = -\theta(k)$, $V_{k'k}^{0,3}$ is uniquely defined due to the time reversal invariance of a pair with itself.

The Hamiltonian being Hermitian means $V_{k'k}^{0,1} = V_{kk'}^{0,1*}$ and time reversal invariance of $H$ implies $V_{k'k}^{0,1} = V_{kk'}^{0,1}$. Thus, $V_{k'k}^{0,1}$ is always real. In second quantized form,

$$\frac{1}{\sqrt{2}}(\phi_k \phi_{-k} \pm \phi_{-k} \phi_k) \frac{1}{\sqrt{2}}(\uparrow \downarrow \mp \downarrow \uparrow) = \frac{1}{\sqrt{2}}(a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger \mp a_{k\downarrow}^\dagger a_{-k\uparrow}^\dagger), \tag{5}$$

where $a_{k\sigma}^\dagger$ is the creation operator for an electron in state $\phi_k$ with spin $\sigma$. The general pair-pair interaction is,

$$\sum_{k'k} V_{k'k}^1 \left\{ \frac{1}{2}(a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger + a_{k\downarrow}^\dagger a_{-k\uparrow}^\dagger)(a_{-k\downarrow}a_{k\uparrow} + a_{-k\uparrow}a_{k\downarrow}) + 
\quad a_{k'\uparrow}^\dagger a_{-k'\downarrow}^\dagger a_{-k\uparrow}a_{k\downarrow} + a_{k'\downarrow}^\dagger a_{-k'\uparrow}^\dagger a_{-k\downarrow}a_{k\uparrow} \right\} + 
\sum_{k'k} V_{k'k}^0 \left( \frac{1}{2}(a_{k\uparrow}^\dagger a_{-k\downarrow}^\dagger - a_{k\downarrow}^\dagger a_{-k\uparrow}^\dagger)(a_{-k\downarrow}a_{k\uparrow} - a_{-k\uparrow}a_{k\downarrow}) \right), \tag{6}$$

which can be expressed as,

$$\sum_{k'k} V_{k'k} a_{k'\uparrow}^\dagger a_{-k'\downarrow}^\dagger a_{-k\downarrow}a_{k\uparrow} + \sum_{k'k} \frac{1}{4}(V_{k'k} - V_{k'\sigma}^1)a_{k'\uparrow}^\dagger a_{k'\downarrow}^\dagger a_{-k\downarrow}a_{k\uparrow} a_{k\sigma}, \tag{7}$$
where,

\[ V_{k'k} = \frac{1}{2} [(V_{k'k}^0 + V_{-k'k}^0 + V_{k'k}^0 + V_{-k'k}^0) + (V_{k'k}^1 + V_{-k'k}^1 - V_{k'k}^1 - V_{-k'k}^1)] \quad (8) \]

From the relations for \( V_{k'k}^{0,1} \), we have \( V_{k'k} = V_{kk'} \) in general, and \( V_{k'k} = V_{-k'k} \) for pure singlet pairing, and \( V_{k'k} = -V_{-k'k} \) for pure triplet pairing. Finally, \( V_{k'k} \) is always real and uniquely defined. For phonon coupling, \( V_{k'k} \) is constant leading to pure singlet pairs. The symmetry of \( V_{k'k} \) determines the total spin of the Cooper pairs in BCS. This is not true for IBP.

For IBP, let the matrix elements for the scatterings,

\[ \frac{1}{\sqrt{2}} (\phi_{Uk} \phi_{L-k} \pm \phi_{L-k} \phi_{Uk}) \frac{1}{\sqrt{2}} (\downarrow \uparrow \downarrow \uparrow) \rightarrow \frac{1}{\sqrt{2}} (\phi_{Uk'} \phi_{L-k'} \pm \phi_{L-k'} \phi_{Uk'}) \frac{1}{\sqrt{2}} (\uparrow \downarrow \downarrow \uparrow), \quad (9) \]

be \( V_{k'k}^0 \), \( V_{k'k}^1 \). Here, \( \phi_{U,Lk} \) are the single electron wavefunctions for each band with momentum \( k \). In this case \( V_{k'k}^{0,1} \) is no longer uniquely defined for a change in the definitions of \( \phi_{Uk} \) and \( \phi_{Lk} \),

\[ \phi_{Uk} \rightarrow e^{i\theta_{U}(k)} \phi_{Uk}, \quad (10) \]
\[ \phi_{Lk} \rightarrow e^{i\theta_{L}(k)} \phi_{Lk}, \quad (11) \]

where \( \theta_{U,L}(-k) = -\theta_{U,L}(k) \) implies,

\[ V_{k'k}^{0,1} \rightarrow e^{-i[\theta_{U}(k') - \theta_{L}(k')]} e^{i[\theta_{U}(k) - \theta_{L}(k)]} V_{k'k}^{0,1}. \quad (12) \]

Hermiticity implies, \( V_{k'k}^{0,1} = V_{k'k}^{1,0*} \) and time reversal symmetry leads to \( V_{k'k}^{0,1} = V_{-k'k}^{1,0} \) rather than \( V_{k'k}^{0,1} = V_{kk'}^{0,1} \) for BCS. This is due to inter-band Cooper pairs not being time reversal invariant with themselves.

The general pair-pair inter-band pairing interaction is,

\[ \sum_{k'k} V_{k'k}^{1} \left\{ \frac{1}{2} (a_{Uk'\uparrow}^{\dagger} a_{L-k'\downarrow}^{\dagger} a_{L-k\uparrow}^{\dagger} a_{L-k\downarrow}) (a_{L-k\downarrow} a_{Uk\uparrow} + a_{L-k\uparrow} a_{Uk\downarrow}) + a_{Uk'\uparrow}^{\dagger} a_{L-k\downarrow}^{\dagger} a_{L-k\uparrow} a_{Uk\downarrow} + a_{Uk'\uparrow}^{\dagger} a_{L-k\downarrow}^{\dagger} a_{Uk\downarrow} + a_{Uk'\uparrow}^{\dagger} a_{L-k\downarrow}^{\dagger} a_{L-k\uparrow} a_{Uk\downarrow}) \right\} + \sum_{k'k} V_{k'k}^{0} \left( \frac{1}{2} (a_{Uk'\uparrow}^{\dagger} a_{L-k'\downarrow}^{\dagger} a_{L-k\uparrow}^{\dagger} a_{L-k\downarrow} - a_{Uk'\uparrow}^{\dagger} a_{L-k\downarrow}^{\dagger} a_{L-k\uparrow} a_{Uk\downarrow}) (a_{L-k\downarrow} a_{Uk\uparrow} - a_{L-k\uparrow} a_{Uk\downarrow}) \right), \quad (13) \]

These equations make it clear that one cannot even speak of the symmetry of the pairing \( V_{k'k} \) without first specifying the phase convention on the single particle orbitals. Secondly, say we found a phase convention such that \( V_{k'k}^{0,1} \) is pure s-wave. Unlike BCS phonon pairing,
IBP does not preclude triplet pairing due to phonons. Experimentally, pure triplet pairs are not consistent with the observed Josephson tunneling between a BCS superconductor and the cuprates. There must be some singlet pairs for tunneling to occur. This does not exclude the possibility of some pairs being triplet paired, though. For the rest of this paper however, we will only consider the case of pure singlet pairs, i.e. $V_{k,k'}^1 = 0$.

The IBP Hamiltonian becomes,

$$H = \sum_{k\sigma} \left[ \epsilon_k^{(U)} a_{Uk\sigma}^\dagger a_{Uk\sigma} + \epsilon_k^{(L)} a_{Lk\sigma}^\dagger a_{Lk\sigma} \right] +$$

$$\sum_{k'k} \frac{1}{2} V_{k'k} (a_{Uk'\uparrow}^\dagger a_{L-k'\downarrow}^\dagger - a_{Uk'\downarrow}^\dagger a_{L-k'\uparrow}^\dagger)(a_{L-k\downarrow} a_{Uk\uparrow} - a_{L-k\uparrow} a_{Uk\downarrow}),$$

(14)

where we write $V_{k'k} = V_{k'k}^0$ for simplicity.

In the pairing approximation, we consider excitations of the form,

$$\psi_0(k) = \left( u_k + v_k a_{Uk\uparrow}^\dagger a_{L-k\downarrow}^\dagger \right) |0\rangle, \quad p_0(k) = (1 - f_k^{(U)})(1 - f_k^{(L)}),$$

(15)

$$\psi_1(k) = a_{Uk\uparrow}^\dagger |0\rangle, \quad p_1(k) = f_k^{(U)} (1 - f_k^{(L)}),$$

(16)

$$\psi_2(k) = a_{L-k\downarrow}^\dagger |0\rangle, \quad p_2(k) = (1 - f_k^{(U)}) f_k^{(L)},$$

(17)

$$\psi_3(k) = \left( -v_k + u_k a_{Uk\uparrow}^\dagger a_{L-k\downarrow}^\dagger \right) |0\rangle, \quad p_3(k) = f_k^{(U)} f_k^{(L)},$$

(18)

$$|u_k|^2 + |v_k|^2 = 1,$$

(19)

with probabilities $p_i(k)$ where $f_k^{(U)}$ and $f_k^{(L)}$ are the occupation numbers of U and L band particles of momenta $k$ and $-k$ respectively. There are four other excitations $\psi_4, \ldots, \psi_7$ obtained from the above by replacing $a_{Uk\uparrow}^\dagger a_{L-k\downarrow}^\dagger$ with $a_{L-k\uparrow}^\dagger a_{Uk\downarrow}^\dagger$ in $\psi_0$ and $\psi_3$, $a_{Uk\uparrow}$ with $a_{L-k\uparrow}$ in $\psi_1$ and $a_{Uk\downarrow}$ with $a_{L-k\downarrow}$ in $\psi_2$. The ordering of the creation operators is chosen such that Cooper pairs consist only of singlet pairs.

The coefficients $u_k$ and $v_k$ are chosen to minimize the free energy $F = H - \mu N - TS$. The solution is,

$$|u_k|^2 = 1 - |v_k|^2 = \frac{1}{2} \left( 1 + \frac{\xi_k}{E_k} \right), \quad u_k v_k = \frac{\Delta_k}{2E_k},$$

(20)

$$\xi_k = \omega_k - \mu, \quad \omega_k = \frac{1}{2} \left( \epsilon_k^{(U)} + \epsilon_k^{(L)} \right),$$

(21)

$$E_k = \sqrt{\xi_k^2 + |\Delta_k|^2},$$

(22)

$$E_k^{(U)} = \frac{1}{2} [\epsilon_k^{(U)} - \epsilon_k^{(L)}] + E_k,$$

(23)
\[ E_k^{(L)} = -\frac{1}{2}[\epsilon_k^{(U)} - \epsilon_k^{(L)}] + E_k, \]  
with gap equation,

\[ \Delta_k = \sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} (1 - f_{k'}^{(U)} - f_{k'}^{(L)}). \]

Conservation of the total number of particles \( N \) leads to an equation for the chemical potential \( \mu \),

\[ N = \sum_k 2|\psi_k|^2(1 - f_k^{(U)} - f_k^{(L)}) + (f_k^{(U)} + f_k^{(L)}), \]  

Unlike BCS, the quasiparticle excitation energies are different for the U and L particles and are given by \( E_k^{(U)} \) and \( E_k^{(L)} \). These energies are the sum of half the difference in the U and L band energies and the term \( E_k \) which is analogous to the BCS quasiparticle energy. The most important point of all is that, although the sum \( E_k^{(U)} + E_k^{(L)} = 2E_k \) is always positive, the U or L excitation energy can be negative or have lower energy than the gap energy \( \Delta \). This new piece of physics will be considered in more detail below.

Also, the BCS quasiparticle energy \( E_k \) is formed from a band \( \omega_k \) that is the mean of the U and L bands. One can see why this is the case by noting that in the BCS ground state, pairs are either fully occupied or completely unoccupied. The individual band energies always appear summed together, \( \epsilon_k^{(U)} + \epsilon_k^{(L)} = 2\omega_k \). For these states, the system “doesn’t know” that the U and L pairing electrons have different energies. The three equations for the pair occupation amplitudes \( u_k \) and \( v_k \), incorporate the difference between the two band dispersions only through the gap \( \Delta_k \). This is to be expected by the same argument as above because \( u_k \) and \( v_k \) represent pair occupations. Similarly, the gap equation incorporates the U and L band differences through the quasiparticle occupation numbers, \( f_k^{(U)} \) and \( f_k^{(L)} \).

Looking at the expressions for the quasiparticle excitation energies \( E_k^{(U)} \) and \( E_k^{(L)} \), one sees that the size of the difference in energies of the two bands \( \epsilon_k^{(U)} - \epsilon_k^{(L)} \) is what determines the size of the excitation. A negative energy implies that no Cooper pair is formed at \( T = 0 \). Instead, there is a single free electron in one band and no electron in the other. When \( \epsilon_k^{(U)} - \epsilon_k^{(L)} \) is large, it is energetically unfavorable to occupy both k states or empty both k states. Thus no pair is formed. Near a Fermi surface touching point, \( \epsilon_k^{(U)} \approx \epsilon_k^{(L)} \). Therefore, inter-band pairs are always energetically favored.

These equations are very similar to the equations for gapless superconductivity. In gapless superconductivity, an \( \uparrow \) spin electron has a slightly different dispersion than the \( \downarrow \) spin electrons due to the presence of magnetic impurities. These \( \uparrow \) and \( \downarrow \) spin bands are the analogues of the U and L bands in IBP.
B. The Two Relevant Bands

Perry and Tahir-Kheli\(^4\) have calculated ab-initio the existence of two bands near the Fermi energy for La\(_{1.85}\)Sr\(_{0.15}\)CuO\(_4\). The results of that work are briefly summarized in this sub-section.

La\(_2\)CuO\(_4\) has two structural phases. A high temperature body-centered tetragonal crystal with D\(_{4h}\) point group and a low temperature orthorhombic lattice with C\(_{2h}\) point group. In the low temperature phase, the CuO\(_6\) octahedra are tipped by 4.3\(^\circ\) from their high temperature positions thereby reducing the symmetry of the crystal. The low temperature phase is the structure for superconductivity. In the tetragonal crystal, there are two reflection planes defined by the z-axis and the lines \(x = y\) and \(x = -y\) respectively. For the orthorhombic crystal, there is only one reflection plane defined by the z-axis and \(x = y\).

In either case, there will be a rigorous band crossing along \(k_x = k_y\) for our two bands. The tetragonal phase will also have a crossing along \(k_x = -k_y\). The orthorhombic phase will come close to crossing along \(k_x = -k_y\), but cannot cross. For IBP to occur, it is imperative that a crossing exist, for otherwise it is hard to see how IBP can overcome the band repulsion. For the remainder of this paper and in the following paper, we will take the LASCO crystal structure to be the high temperature tetragonal phase for simplicity. The small difference in structures can have a big effect on \(T_c\), but for most normal state properties, the difference will be small.

In undoped La\(_2\)CuO\(_4\), the O sites have a formal charge of \(-2\), the Cu charge is \(+2\) and is in a \(d^9\) state. The point charge field on the Cu site due to the surrounding atoms makes the \(d_{x^2-y^2}\) orbital the most unstable leading to holes in this orbital in the undoped system. The next highest (unstable) orbital on the Cu is \(d_{z^2}\) due to the field of the apical oxygens. Undoped, each Cu \(d_{x^2-y^2}\) has a single electron and \(d_{z^2}\) has 2 electrons. We propose that as the system is doped to its metallic/superconducting phase, holes start to appear in the Cu \(d_{z^2}\) orbital. At an arbitrary k point in the Brillouin zone, \(d_{z^2}\) can mix with \(d_{x^2-y^2}\), O \(p_\sigma\), and apical O \(p_z\) orbitals. Thus, the two relevant bands at the Fermi energy are comprised primarily of these four orbitals.

This assumption of the existence of \(d_{z^2}\) holes near the Fermi energy along with the assumption of inter-band pairing must be regarded as the two most important postulates of the IBP model for the cuprates. The former postulate is discussed in detail using ab-initio calculations on small clusters in the following paper\(^4\) where we conclude that there are two bands near the Fermi energy with the character described above.

We will call the two bands the Upper (U) and Lower (L) bands where \(\epsilon_k^{(U)} \geq \epsilon_k^{(L)}\). The lower band should be full or almost full in the undoped case and the upper band is half full with all of its holes predominantly of \(d_{x^2-y^2}\) character. For LaSrCuO, the U and L bands will be almost completely 2D, while for optimally doped YBa\(_2\)Cu\(_3\)O\(_7\), the bands will have a measurable amount of 3D character. Underdoped YBa\(_2\)Cu\(_3\)O\(_6\),\(_{63}\) will have less 3D dispersion than optimally doped YBa\(_2\)Cu\(_3\)O\(_7\). Additionally, for YBCO there are potentially 4 relevant bands due to the 2 CuO planes per unit cell. Here, we restrict our attention to LaSrCuO and briefly discuss the differences to expect for YBCO where appropriate.
The unit cell of two formula units of La$_2$CuO$_4$ is tetragonal with lattice spacing $a = 4.0$ Å in the $x$, $y$ direction and $c = 12.0$ Å in the $z$-direction. The Brillouin zone of the primitive unit cell is given by $-\pi/a \leq k_x \leq \pi/a$, $-\pi/a \leq k_y \leq \pi/a$, $-2\pi/c \leq k_z \leq 2\pi/c$.

To a first approximation, we may take the U and L bands for LaSrCuO to be purely 2D and add in the weak $z$-axis dispersion as a first order perturbation. This is done primarily for further computational simplicity and to convey the key aspects of the model. A more correct description will not qualitatively alter the behaviors we obtain for the NMR and Hall effect and more importantly, will not affect the general arguments for the various normal state properties.

The relevant orbitals are $d_{z^2}$, $d_{x^2-y^2}$ on the Cu, $p_\sigma$ orbitals on the two planar O sites ($\sigma$ along the CuO bond direction) and $p_z$ orbitals for the two apical O sites above and below the Cu atom. Additional orbitals that appear are the Cu 4$s$, $d_{xy}$, and O $p_\pi$ in the plane and the $p_x$, $p_y$ orbitals on the apical O’s. None of these additional orbitals will lead to a big change in the band structure but can affect the nmr. In particular, a small amount of Cu 4$s$ is required for an understanding of the sign of the Knight shift on Cu and some (a few percent) $d_{xy}$ is necessary for explaining the large anisotropy in the Cu spin relaxation rates for planar and $z$-axis magnetic fields.

The tight-binding Hubbard model is (we use the electron picture),

$$H = H_{\text{orb}} + H_{\text{hop}},$$

$$H_{\text{orb}} = \sum_{n\sigma} \epsilon_{d_{z^2}} d_{z^2}^\dagger d_{z^2} + \sum_{n\sigma} \epsilon_{p_\sigma} (p_{x\sigma}^\dagger p_{x\sigma} + p_{y\sigma}^\dagger p_{y\sigma}) + \epsilon_{d_{xy}} d_{xy}^\dagger d_{xy} + \sum_{n\sigma} \epsilon_{p_z} (p_{Uz\sigma}^\dagger p_{Uz\sigma} + p_{Lz\sigma}^\dagger p_{Lz\sigma}),$$

$$H_{\text{hop}} = \pm t_{x^2-y^2,\sigma} \sum_{<nm>\sigma} p_{xn\sigma}^\dagger p_{yn\sigma} \pm t_{z^2,\sigma} \sum_{<mn>\sigma} d_{z^2n\sigma}^\dagger (p_{xn\sigma} + p_{yn\sigma}) + \pm t_{\sigma\sigma} \sum_{<nm>\sigma} p_{xn\sigma}^\dagger p_{yn\sigma} \pm t_{p_x,d_{z^2}} \sum_{n\sigma} d_{z^2n\sigma}^\dagger (p_{zU\sigma} - p_{zL\sigma}) + t_{p_z,d_{z^2}} \sum_{n\sigma} p_{zU\sigma}^\dagger p_{zL\sigma} + \pm t_{\sigma\sigma} \sum_{<nm>\sigma} (p_{xn\sigma}^\dagger p_{xn\sigma} + p_{yn\sigma}^\dagger p_{yn\sigma}) \pm t_{p_x,d_{z^2}} \sum_{<nm>\sigma} (p_{zU\sigma}^\dagger - p_{zL\sigma}^\dagger) (p_{xn\sigma} - p_{yn\sigma}) + \text{c.c.},$$

where $d_{z^2n\sigma}$ creates a $d_{z^2}$ orbital with spin $\sigma$ at site $n$. $p_{xn\sigma}^\dagger$ ($p_{yn\sigma}^\dagger$) creates a $p_\sigma$ electron on a planar O site along the $x$ ($y$) axis and $p_{zU\sigma}^\dagger$ ($p_{zL\sigma}^\dagger$) creates a $p_z$ electron on the apical O site above (below) the CuO plane. $\epsilon_{d_{z^2}}$ is the self (orbital) energy of the $d_{z^2}$, etc. The t’s are
the various hopping matrix elements. The ± sign in front of the hopping matrix elements represents the fact that the sign of the matrix element depends on the relative position of the two relevant orbitals. \((nm)\) represents neighboring sites. The values of the parameters are shown in Table 1. The values in Table 1 for the hopping \(t's\) is for the antibonding combination of the two relevant orbitals.

Except for the value of the difference \(\epsilon_{d_{x2}} - \epsilon_{d_{x2-y^2}}\), there is nothing particularly surprising or out of the ordinary with these parameters. \(\epsilon_{d_{x2}} - \epsilon_{d_{x2-y^2}}\) being positive is what brings the \(d_{x2}\) orbital up to the Fermi energy. This is the essential parameter for a two band description like ours of superconductivity. These points are discussed in detail in the following paper\(^4\) where our parameters are derived from ab-initio calculations on small clusters. As we stated in the introduction, the theory presented here is very robust and at a qualitative level does not depend sensitively on the values for these parameters at all.

The point group of LaSrCuO is \(D_{4h}\) and \(d_{x^2-y^2}, d_{z^2}\) transform as \(B_{1g}\) and \(A_{1g}\) respectively. Under a \(\sigma_d\) reflection about the diagonals \(x = \pm y\), \(\sigma_d d_{x^2-y^2} = -d_{x^2-y^2}\) and \(\sigma_d d_{z^2} = d_{z^2}\). Thus, for diagonal \(k\) vectors \((k_x = \pm k_y)\) a single electron wavefunction must have \(d_{x^2-y^2}\) character or \(d_{z^2}\) character. Along \(k_x = \pm k_y\), two bands may cross if one band has \(d_{x^2-y^2}\) character and the other has \(d_{z^2}\) character. A plot of the top two bands (most unstable) is shown in figure 1 along the closed path \((0,0) - (\pi,\pi) - (\pi,0) - (0,0)\) in \(k\) space. For all \(k\) points not on the diagonal, there is no symmetry to keep \(d_{x^2-y^2}\) and \(d_{z^2}\) from mixing. Thus, the two bands will repel leading to \(\epsilon^{(U)}_k > \epsilon^{(L)}_k\).

The optimal doping for the highest \(T_c\) is the doping that leads to a Fermi energy equal to the energy at the band crossing or touching point. It is at this doping and this doping only that there is favorable energetics for inter-band pair formation. Figure 2 shows the Fermi surface at various doping from underdoped to overdoped.

We have adjusted the charge transfer of planar O \(p_\pi\) onto the La described in detail in the following paper\(^4\) such that this doping matches the experimentally observed optimal doping for La\(_{2-x}\)Sr\(_x\)CuO\(_4\) at \(x = 0.15\). Undoped, there are a total of 3 electrons in the U and L bands while for \(x = 0.15\) there are \(3 - 0.15 = 2.85\) electrons in the two bands.

The \(z\)-axis (normal to the CuO planes) dispersion is approximately calculated by observing the dominant coupling in the \(z\)-direction is the \(p_z\) orbital on the apical O above a CuO plane coupling to the \(p_z\) orbital on the apical O below the next higher CuO plane. We take this value to be \(T_{(0,0)} = 0.3\) eV. The coupling is added in via first order perturbation theory. Our choice for this matrix element is described below.

The additional energy of a \(k\) state due to \(p_z\) to \(p_z\) coupling from layer to layer is,

\[
\epsilon(k_x, k_y, k_z) = -2T_{(0,0)} P \cos \frac{1}{2}(k_x a) \cos \frac{1}{2}(k_y a) \cos k_z c, \tag{31}
\]

where \(P\) is the amount of apical O \(p_z\) character in the \(k\) state \((k_x, k_y)\) derived from the 2D Hamiltonian (28).

To incorporate the very small couplings through the \(p_x\) and \(p_y\) orbitals on the apical O above a CuO plane with the \(p_z\) on the apical O below the next higher plane, an additional
energy,

\[ \epsilon(k_x, k_y, k_z) = -2T_{(\pi,0)} P[\cos \frac{1}{2}(k_x a) \sin \frac{1}{2}(k_y a) + \sin \frac{1}{2}(k_x a) \cos \frac{1}{2}(k_y a)] \cos k_z c, \]  

(32)

is added. Finally, we add,

\[ \epsilon(k_x, k_y, k_z) = -2T_{(\pi,\pi)} \sin \frac{1}{2}(k_x a) \sin \frac{1}{2}(k_y a) \cos k_z c, \]  

(33)

to include the weak coupling of Cu \(d_{xy}\) with apical O \(p_z\). We take \(T_{(\pi,0)} = 0.05\) eV, \(T_{(\pi,\pi)} = 0.02\) eV.

The reason for naming the hopping matrix elements with the k space labels \((0,0)\), \((\pi,0)\), \((\pi,\pi)\) is that each one is multiplied by a combination of \(\cos \frac{1}{2}k_x a\), \(\cos \frac{1}{2}k_y a\), \(\sin \frac{1}{2}k_x a\), \(\sin \frac{1}{2}k_y a\) which is equal to 1 on the particular k space label and zero at the other two. We expect \(T_{(0,0)} > T_{(\pi,0)} > T_{(\pi,\pi)}\).

The primary effect of adding in the above z-axis couplings is to eliminate the logarithmic 2D van-Hove saddle point singularity in the density of states of the U band by a broadened 3D peak. The width of this peak is responsible for the T dependence (or lack thereof in \(\text{YBa}_2\text{Cu}_3\text{O}_7\)) of the Knight shifts in the normal state. This is shown further along in the calculation of the nmr.

Figure 3 shows the density of states of the two bands with the Fermi energy at the optimal doping indicated. The large peak in the U band density of states just above the optimal doping Fermi energy \(\epsilon_F = 0.0\) eV is due to the saddle point singularity at \((\pi,0)\) and \((0,\pi)\). The closeness of this peak to \(\epsilon_F\) is a robust feature of this model and is not sensitive to the choice of parameters.

Three other features of interest are shown in figures 4(a – c). They show the average amount of \(d_{x^2-y^2}\), \(d_{z^2}\), and \(p_\sigma\) character of the two bands at different energies. Near \(\epsilon_F\), the two bands are predominantly \(d_{z^2}\). Both of these features are once again robust.

**C. The Pairing Term**

There are several different choices for the detailed orbital coupling that can lead to IBP. Lacking a rigorous microscopic proof that IBP exists, we make a particular choice for the pairing term and compare it to experiment. We take the pairing term in equation (14) to be mediated by an attractive coupling of the form shown in figure 5. In this figure, \(d_{x^2-y^2}\) and \(d_{z^2}\) are defined as,

\[ d_{x^2-y^2}(r) = \frac{1}{\sqrt{N}} \sum e^{ik \cdot R} d_{x^2-y^2}(r-R), \]  

(34)

\[ d_{z^2}(r) = \frac{1}{\sqrt{N}} \sum e^{ik \cdot R} d_{z^2}(r-R), \]  

(35)

where \(R\) is the position of the Cu atom. Eventually, we will take the origin to be a center of inversion. Figure 5 depicts a \(d_{x^2-y^2}\) Bloch orbital of momentum \(-k\) emitting a virtual
phonon and scattering to a $d_{z^2}$ orbital of momentum $-k'$ and a $d_{z^2}$ orbital of momentum $k$ absorbing the phonon and scattering to a $d_{x^2-y^2}$ orbital of momentum $k'$. (34) and (35) define the phase convention of the $d_{x^2-y^2}$ and $d_{z^2}$ Bloch functions and the matrix element $U_{k,k'}$. The coupling $V_{k,k'}$ in (14) is calculated by projecting onto the above $d_{x^2-y^2}$, $d_{z^2}$ scattering.

Physically, what is accomplished is quite straightforward. The attractive coupling between two single electron states $k$, $-k$ in the same band or two different bands is due primarily to the attractive coupling of the $d_{x^2-y^2}$ orbital component of one electron with the $d_{z^2}$ component of the other electron. One reason that such a coupling may be dominant is due to the $d_{x^2-y^2}$ $k$ states localizing the electron charge in the plane, whereas the $d_{z^2}$ $-k$ state localizes the charge out of the CuO plane thereby reducing the Coulomb repulsion.

An attractive coupling mediated by projection onto the diagram in figure 5 is also possible for $(k \uparrow, -k \downarrow)$ pairs in the same band leading to a traditional BCS pairing term. Thus, one is faced with the possibility that BCS-like intra-band pairing may win out over IBP. This possibility is not realized for $k$ states near the band crossing point by the same kinematics that allows a band crossing to occur along the diagonals ($k_x = \pm k_y$). In order to have a large BCS-like pairing for a Cooper pair $(k \uparrow, -k \downarrow)$ in the same band with a $k$ state near the crossing point one requires a substantial amount of both $d_{x^2-y^2}$ and $d_{z^2}$ in the $k$ state. Near the band crossing point, the approximate $\sigma_d$ diagonal reflection symmetry precludes that leading to a suppression of BCS-like pairing by the above pairing mechanism. Also, because the U and L $k$ states are almost degenerate here, the system may further lower its energy by forming a pure $d_{x^2-y^2}$ and a pure $d_{z^2}$ state in order to maximize the pairing coupling. At $k$ points away from the diagonals, BCS-like pairing can occur and for arbitrary doppings, too.

Including BCS-like intra-band pairing by projection of figure 5 as we did for IBP is straightforward. Rather than diagonalizing a 2x2 matrix as we did in deriving (15) – (27), we must diagonalize a 4x4 matrix. This is not difficult to do and leads to more complicated quasiparticle energies than (23) and (24). To properly include BCS-like pairs, we should not restrict ourselves to the single diagram in figure 5. There are other combinations of inter-band to BCS-like pair scatterings that may become important.

Physically, what occurs is near the band crossing point on the diagonals, inter-band pairs are formed because one band is almost pure $d_{x^2-y^2}$ (with some O character) and the other band is almost pure $d_{z^2}$ (again with O character). Away from the Fermi surface touching point, only BCS-like pairs are kinematically allowed leading to standard BCS pairs for the $k$ states. Thus, one would expect to observe a gap in the photoemission for $k$ vectors along the $k_x = 0$ and $k_y = 0$ directions. This is observed for angle resolved photoemission (ARPES) on Bismuth 2212 although the observed Fermi surface crossing along $\Gamma M ((0,0) - (\pi,0))$ has been questioned by Campuzano et al as due to a $k$ vector shifted by the superlattice translation $(0.21\pi, 0.21\pi)$.

We also expect a crossover region in the Brillouin zone where inter-band pairs change over to BCS-like pairs. Because IBP is only strong at the crossing point along $k_x = k_y$, the crossover region should occur close to the diagonals. For BCS-like pairs $(k, -k)$, one would...
see a gap $\Delta$ in ARPES at this $k$ vector. On the diagonal at the touching point, one would again see a gap from (23) and (24). Slightly away from the diagonal while there are still inter-band pairs, (23) and (24) are still valid and at least one of these excitations has energy less than the gap. Thus, ARPES should see the “smallest gap” slightly off the diagonals $k_x = \pm k_y$ rather than on the diagonals. We have not yet calculated the size of this effect to determine whether present experimental resolution can see this effect.

Owing to the separation of the pairs along the diagonal into one band with no $d_{x^2-y^2}$ character and the other with no $d_{z^2}$ character, pairs are most strongly formed here than at any other $k$ point. This suggests that the dominant contribution to the Josephson tunneling current will come from IBP along the diagonals and we assume this is true unless such a current is rigorously zero. One can foresee that such a symmetry argument will be applied to inter-band tunneling in the c-axis direction making the contribution zero, thereby obtaining the “s-wave” result of Dynes$^{13}$ et al.

Let,

$$
\phi_{U,k} = A_{U,k} d_{x^2-y^2,k} + B_{U,k} d_{z^2,k} + \text{other terms},
$$

(36)

$$
\phi_{L,k} = A_{L,k} d_{x^2-y^2,k} + B_{L,k} d_{z^2,k} + \text{other terms},
$$

(37)

where $\phi_{U,k}$ and $\phi_{L,k}$ are the band wavefunctions and $A_k, B_k$ are the projections onto the Bloch functions in (34), (35). Then,

$$
a_{U,k}^\dagger = A_{U,k} d_{x^2-y^2,k}^\dagger + B_{U,k} d_{z^2,k}^\dagger + \cdots,
$$

(38)

$$
a_{L,k}^\dagger = A_{L,k} d_{x^2-y^2,k}^\dagger + B_{L,k} d_{z^2,k}^\dagger + \cdots,
$$

(39)

and

$$
d_{x^2-y^2,k}^\dagger = A_{U,k}^* a_{U,k}^\dagger + A_{L,k}^* a_{L,k}^\dagger + \cdots,
$$

(40)

$$
d_{z^2,k}^\dagger = B_{U,k}^* a_{U,k}^\dagger + B_{L,k}^* a_{L,k}^\dagger + \cdots.
$$

(41)

The pairing Hamiltonian term is,

$$
U_{k'k}(d_{x^2-y^2,k'}^\dagger d_{z^2,k^*}^\dagger d_{x^2-y^2,k}^\dagger d_{z^2,k'^*}^\dagger + d_{x^2-y^2,k'}^\dagger d_{z^2,k^*}^\dagger d_{x^2-y^2,k}^\dagger d_{z^2,k'^*}^\dagger).
$$

(42)

Projecting onto (14),

$$
V_{k'k} = (A_{U,k'} B_{L,-k'})^* (A_{U,k} B_{L,-k}) U_{k'-k} + (B_{U,k'} A_{L,-k'})^* (B_{U,k} A_{L,-k}) U_{-k'k} +
$$

$$
(A_{U,k'} B_{L,-k'})^* (B_{U,k} A_{L,-k}) U_{k'k} + (B_{U,k'} A_{L,-k'})^* (A_{U,k} B_{L,-k}) U_{-k'k}.
$$

(43)

Under the phase change in (10) and (11),

$$
A_{U,L,k} \rightarrow e^{i\Theta_{U,L}(k)} A_{U,L,k},
$$

(44)

14
$B_{U,Lk} \rightarrow e^{i\Theta_{U,L}(k)} B_{U,Lk},$ \hspace{1cm} (45)

and thus $V_{k'k}$ transforms as (12).

Now every cuprate space group includes the inversion operator. We define the origin from which $\mathbf{R}$ in (34) and (35) is defined as a point of inversion. With this choice it is easy to see that the coefficients $A_{U,Lk}, B_{U,Lk}$ must always satisfy $A_k^* B_k = \text{real}.$

In general, the electron-phonon matrix element that appears at each vertex in the Feynman diagram in figure 5 is the sum of terms of the form,

$$i(\epsilon_{q\lambda} \cdot \mathbf{q}) V_{\lambda q}(c_{q\lambda} + c_{-q\lambda}^\dagger) \int e^{i\mathbf{q} \cdot \mathbf{r}} d_{x^2-y^2}^* v_{\lambda}(r) d_{x^2-y^2}(r) d\tau,$$ \hspace{1cm} (46)

where $\lambda$ is the phonon polarization and $\mathbf{q}$ is its momentum. $c_{q\lambda}$ is the destruction operator and $V_{\lambda q}$ is the Fourier transform of the phonon potential and $\epsilon_{q\lambda}$ is the polarization vector. Inversion symmetry guarantees $V_{\lambda-q} = V_{\lambda q},$ $V_{\lambda q}$ is always real and also that the integral in (46) over the electron states is real.

Using (34) and (35), the integral in (46) is,

$$\int e^{i\mathbf{q} \cdot \mathbf{r}} d_{x^2-y^2}^* v_{\lambda}(r) d_{x^2-y^2}(r) d\tau = \int e^{i\mathbf{q} \cdot \mathbf{R}'} e^{i\mathbf{k} \cdot \mathbf{R}} d_{x^2-y^2} v_{\lambda}(r-R') d_{x^2-y^2}(r-R).$$ \hspace{1cm} (47)

Taking the largest contribution to be when $R' = R,$

$$\int e^{i\mathbf{q} \cdot \mathbf{r}} d_{x^2-y^2}^* v_{\lambda}(r) d_{x^2-y^2}(r) d\tau = \int e^{i\mathbf{q} \cdot \mathbf{r}} d_{x^2-y^2} v_{\lambda}(r) d_{x^2-y^2}(r)d\tau.$$ \hspace{1cm} (48)

Plugging this back into (46), we see that the product of the two electron-phonon matrix elements due to the two vertices in figure 5 is always positive with the phase convention defined in (34), (35) where the origin of $\mathbf{R}$ is an inversion center. With BCS-like pairing, time reversal symmetry of the Cooper pairs is sufficient to guarantee the product of the two vertices is always mod-squared and thus positive.

Therefore, with our definitions of the $d_{x^2-y^2},$ $d_{x^2-y^2}$ Bloch functions, we may take the total coupling $U_{k'k}$ from figure 5 to be s-like,

$$U_{k'k} = \begin{cases} 
-V, & |\epsilon_k^{(U,L)} - \mu| < \hbar \omega_D \text{ and } |\epsilon_{k'}^{(U,L)} - \mu| < \hbar \omega_D, \\
0, & \text{otherwise},
\end{cases}$$ \hspace{1cm} (49)

leading to,

$$V_{k'k} = (-V)(A_{k'}B_{L-k'} + B_{k'}A_{L-k'})^*(A_kB_{L-k} + B_kA_{L-k}).$$ \hspace{1cm} (50)

The reason we have chosen the above range of $k', k$ values for non-zero pairing is seen by considering the relevant Feynman diagram in figure 5. The value is,
\[
\frac{1}{2} \left[ \frac{1}{[\epsilon_{k'}^{(U)} - \epsilon_k^{(L)}]^2 - \hbar^2 \omega^2} \right] + \frac{1}{[\epsilon_{k'}^{(L)} - \epsilon_k^{(U)}]^2 - \hbar^2 \omega^2} \right].
\]

\[
(A_{Uk'}B_{L-k'} + B_{Uk'}A_{L-k'})^*(A_{Uk}B_{L-k} + B_{Uk}A_{L-k})M^2,
\]

where \(M^2\) is a real positive number. If the constraints in (49) are satisfied, then the term in brackets is negative.

### D. Inter-Band Josephson Tunneling

In BCS theory, a Cooper pair is of the form \(\phi_{k \uparrow} \phi_{-k \downarrow}\) and transforms into itself under the operation of time reversal. For pairing across two distinct bands as we propose, the pair \(\phi_{Uk \uparrow} \phi_{L-k \downarrow}\) transforms into \(\phi_{Lk \uparrow} \phi_{U-k \downarrow}\) and not into itself under time reversal. Of course, the full Hamiltonian remains time reversal invariant. This key difference alters the standard Josephson tunneling in a subtle yet dramatic way that leads to a new interpretation of the macroscopic phase of superconductors.

Consider first the case of Josephson tunneling of a BCS-like Cooper pair on one side of a junction to a BCS-like pair on the other side of the junction. We will neglect all factors in the expression for the supercurrent \(J\) contributing only to the magnitude and not to the phase of \(J\). The phase of the pair tunneling matrix element for the transfer of a \((k \uparrow, -k \downarrow)\) pair to a \((p \uparrow, -p \downarrow)\) pair is contained in the product of two single-electron tunneling matrix elements, \(T_{kp}\) and \(T_{-k-p}\) and the product of the two gap functions, \(\Delta_k^*\) and \(\Delta_p^*\) on either side of the junction. This leads to supercurrent,\(^18\)

\[
J \propto T_{kp}T_{-k,-p}\Delta_k\Delta_p^* = |T_{kp}|^2\Delta_k\Delta_p^*.
\]

In this expression, \(T_{kp}\) is the matrix element for the transfer of a single electron of momentum \(k\) to an electron of momentum \(p\), \(T_{-k,-p}\) is the corresponding matrix element for transferring the \(-k\) electron to \(-p\) and \(\Delta_k, \Delta_p^*\) are the gap functions on the two sides of the junction. By overall time reversal symmetry, \(T_{-k,-p} = T_{kp}^*\). Thus, the supercurrent is completely controlled by the phases of the superconducting gap functions on each side of the junction. The phases of the gap functions \(\Delta, \Delta'\) are determined by the symmetry of the pairing interactions for each superconductor. Thus, for all BCS-like pairing models, Josephson tunneling gives direct information of the symmetry of the gap.

For IBP, the situation is dramatically different. Suppose we tunnel from an inter-band superconductor to a BCS superconductor. With Cooper pairing across bands, the matrix element for transferring a momentum \(k\) electron in the U band to a momentum \(p\) electron on the other side of the junction, \(T_{kp}^{(U)}\), is different from the matrix element for transferring a \(-k\) electron in the L band to a \(-p\) electron on the other side of the junction, \(T_{-k,-p}^{(L)}\). Although, \(T_{-k,-p} = T_{kp}^*\) and \(T_{-k,-p} = T_{kp}^*\) by overall time reversal symmetry, the phase part of the pair transfer matrix element is of the form,
In the case of inter-band pairing, the symmetry of the pairing interactions and the orbital character of the band wavefunctions both contribute to the overall tunneling phase. Under a redefinition of the single band wavefunctions (10), (11),

\[ T_{kp}^{(U,L)} \rightarrow e^{i\Theta_{U,L}(k)} T_{kp}^{(U,L)}, \]  

and from the gap equation (26),

\[ \Delta_k \rightarrow e^{-i[\Theta_{U}(k)-\Theta_{L}(k)]} \Delta_k, \]  

leading to no change in \( J \). Note also that the above result is independent of the phase convention of the band orbitals on the BCS side of the junction because if an electron of momentum \( p \) is multiplied by a phase factor \( e^{i\theta} \), then the phase of the \(-p\) electron is multiplied by \( e^{-i\theta} \).

Remember that as we argued in the previous section, we take the dominant supercurrent to be due to the inter-band Cooper pairs near the diagonal crossing points unless the contribution is rigorously zero.

Let us apply our new relation (53) for the supercurrent to the four key Josephson tunneling experiments on YBCO. The first one by Wollman et al on a YBCO-Pb corner junction is the simplest. We have shown that the phase of the supercurrent is independent of the choice of single particle wavefunctions. In this experiment, tunneling occurs along the two perpendicular Cu-O bond directions in the CuO planes of YBCO (x and y axes) which are connected by a Pb wire. Pb is a BCS s-wave superconductor. A phase difference of \( \pi \) implies a d-wave gap, whereas no phase difference implies an s-wave gap. A d-wave result is obtained.

Let \( T_{kp}^{(U,L)}(x) \) be the matrix element for tunneling a k electron in the U or L band to a p electron in Pb along the x-axis. Choose the phase convention on the k states such that a 90° \( (C_4) \) rotation of the wavefunction for k is equal to the wavefunction for momentum \( C_4 k \). Then, we must have \( T_{C_4 k, C_4 p}^{(U,L)}(y) = T_{kp}^{(U,L)}(x) \). From (36) and (37), our phase convention gives,

\[ A_{U,L}(C_4 k) = -A_{U,L}(k), \]  
\[ B_{U,L}(C_4 k) = +B_{U,L}(k). \]  

Using the gap equation and the expression (50) for \( V_{k'k} \),

\[ \Delta_k = \Delta(A_{Uk}B_{L-k} + B_{Uk}A_{L-k})^*. \]  

Hence,

\[ \Delta_{C_4 k} = -\Delta_k, \]
leading to the result,

\[ J(C_k \to C_p) = -J(k \to p). \]  

Therefore, our IBP model also gives an observed “d-wave” gap.

For the tri-crystal model of Tsuei\(^3\) et al, we use the fact that for \( k \) near the Fermi surface touching point, \( \phi_{Uk} \) has almost no \( d_{z^2} \) character and \( \phi_{Lk} \) has almost no \( d_{x^2-y^2} \) character or vice versa. For such a \( k \) vector, \( B_{Uk} \approx 0, A_{Lk} \approx 0 \) (or \( A_{Uk} \approx 0, B_{Lk} \approx 0 \)) and we can take the phase convention \( A_{Uk}, B_{Lk} \) real with \( A_{Uk} > 0, B_{Lk} > 0 \) (or \( B_{Uk} > 0, A_{Lk} > 0 \)). With this convention, \( \Delta_k \) is real and \( \Delta_k > 0 \).

Suppose a \( d_{x^2-y^2} \) orbital on one side of the grain boundary tunnels predominantly into a \( d_{z^2} \) state on the other side of the boundary and thus \( d_{z^2} \) on one side goes predominantly to \( d_{z^2} \) on the other side. Then, the matrix element for \( d_{x^2-y^2} \to d_{z^2} \) is proportional to \( \cos 2\theta \cos 2\phi \) where \( \theta \) and \( \phi \) are the orientations of the \( x \) and \( y \) axes in the CuO planes with respect to the grain boundary. Similarly, the \( d_{z^2} \to d_{z^2} \) matrix element has no orientation dependence and is thus constant.

Suppose instead, that the dominant tunneling is \( d_{x^2-y^2} \to d_{z^2} \) and \( d_{z^2} \to d_{x^2-y^2} \). In this case, one matrix element is proportional to \( \cos 2\theta \) and the other is proportional to \( \cos 2\phi \) leading the pair tunneling product \( \cos 2\theta \cos 2\phi \) as before.

Taking the product of the various factors in (53), we see that the phase controlling the current is the same as to be expected from a \( d_{x^2-y^2} \) gap as is observed.

For the c-axis YBCO-Pb tunneling of Dynes\(^{13}\) et al, an analysis similar to the YBCO corner junction case shows that the inter-band pairs do not contribute to the current. We still expect to see current due to the BCS-like pairs in this case.

For the hexagonal YBCO tunneling of Lim\(^{14}\) et al, the situation is different from the tri-crystal YBCO in one very important manner. Here a hexagonal MgO layer is placed on the LaAlO\(_3\) substrate and then YBCO is grown onto the sample. The hexagonal MgO causes YBCO to grow above it with its planar \( x, y \) axes rotated 45\(^\circ\) from the angle of the YBCO grown directly over the LaAlO\(_3\) substrate. Thus, we expect a misalignment of the CuO planes across the six junctions complicating the matrix elements for single particle tunneling. Unfortunately, we have been unable to find a convincing argument telling us whether inter-band or BCS-like pairs dominate the single electron matrix elements in this case.

### III. NORMAL STATE NMR AND TRANSPORT

#### A. NMR

Armed with our parameters for the relevant bands and the criteria derived from IBP that the optimal doping is when the two Fermi surfaces touch, it is very easy to compute the normal state nmr and transport properties using standard expressions for the nmr and the Bloch-Boltzmann equation for the transport. It is quite satisfying that not only can we understand qualitatively the numerous anomalous features of the nmr and transport as due
to the character of the bands at this very special doping, but quantitatively the numbers are respectable.

The key normal state nmr features\(^5-11\) a theory for the cuprates must explain are: 1.) the difference in the relaxation rate curves with temperature \(T\) for the Cu and O nuclei in the plane, 2.) the similar Knight shifts (KS) at the two sites, 3.) the similarity of the O relaxation rate over \(T\) and the KS, 4.) the lack of \(T\) dependence of the KS for optimally doped YBCO\(_7\) and a monotonic increasing \(T\) dependence of the KS for optimally doped LaSrCuO and underdoped YBCO\(_{6.63}\), 5.) the strictly monotonic decreasing Cu relaxation rate over \(T\) for optimally doped YBCO\(_7\) and the initially increasing and then decreasing Cu relaxation rate over \(T\) for underdoped YBCO\(_{6.63}\) and optimally doped LaSrCuO, and 6.) the large anisotropy of the Cu relaxation rate for magnetic fields in the plane and along the \(z\)-axis.

Figure 2 shows the two band Fermi surfaces at optimal doping. The electron-like band centered at \(k = (0, 0)\) is the U(pper) band and the hole-like surface centered around \((\pi, \pi)\) is the L(ower) band. Both bands are occupied at \(k = (0, 0)\) and unoccupied at \((\pi, \pi)\).

Figure 3 shows the density of states for the two bands. The first thing to notice is that at the Fermi energy \(\epsilon_F\), the L band has the lower density of states. We expect that this band predominantly carries the current and being hole-like will give a Hall coefficient with the correct sign. The large peak in the density of states of the U band at an energy a little larger \((\approx 0.06\) eV\) than \(\epsilon_F\) is due to the saddle point singularity at \((\pi, 0), (0, \pi)\) for the U band. The width of the peak is due primarily to the overall strength of the \(z\)-axis couplings. This width is very sensitive to the details of the structure. This sensitivity controls the \(T\) dependence of the KS. The other aspects of the density of states are robust.

Considering first the Cu spin relaxation, the two relevant orbitals are \(d_{x^2-y^2}\) and \(d_{z^2}\). Because there is no orbital relaxation between these orbitals regardless of the magnetic field direction, the relevant relaxation is dipole-dipole. We will neglect here the core polarization relaxation which we expect will not change the qualitative conclusions. The relaxation rate for a \(z\)-axis magnetic field is given by,

\[
{\ ^{63}W_z} = 2\left(\frac{2\pi}{\hbar}\right)\left(\gamma_e\gamma_h\hbar\right)^2 \int d\epsilon f(\epsilon)(1 - f(\epsilon))\left(\frac{1}{r^3}\right)^2 \left[ W_{\text{dip}}^{z}(\epsilon) + W_{\text{orb}}^{z}(\epsilon) \right],
\]

\[
W_{\text{dip}}^{z}(\epsilon) = \left(\frac{1}{7^2}\right) \left[ 6N_{d_{x^2-y^2}}(\epsilon)N_{d_{z^2}}(\epsilon) + N_{d_{x^2-y^2}}(\epsilon)N_{d_{x^2-y^2}}(\epsilon) + N_{d_{z^2}}(\epsilon)N_{d_{z^2}}(\epsilon) \right],
\]

\[
W_{\text{orb}}^{z}(\epsilon) = 0,
\]

where \(N(d_{x^2-y^2})(\epsilon)\) and \(N(d_{z^2})(\epsilon)\) are the total bare density of states at energy \(\epsilon\) and \(f(\epsilon)\) is the Fermi-Dirac function.

The relaxation rate for a planar field \(^{63}W_{xy}\) is identical to \(^{63}W_z\) above with \(W_{\text{dip}}^{z}\) and \(W_{\text{orb}}^{z}\) replaced with,
\[ W_{\text{dip}}^{xy} = \left( \frac{1}{T^2} \right) \left( \frac{5}{2} \right) \left[ N_{d_{2s-y^2}}(\epsilon) N_{d_{2s-y^2}}(\epsilon) + N_{d_z}(\epsilon) N_{d_z}(\epsilon) \right] + \left( \frac{3}{T^2} \right) N_{d_{2s-y^2}}(\epsilon) N_{d_z}(\epsilon), \]  

(64)

\[ W_{\text{orb}}^{xy} = 0, \]  

(65)

Figures 4(a, b) show the amount of orbital character of \( d_{x^2-y^2} \) and \( d_z^2 \) in the U and L bands. The total bare density of states for \( d_z^2 \), say, is the amount of orbital character of \( d_z^2 \) in the U band times the density of states of the U band \( N_U(\epsilon) \) plus a corresponding term for the L band. Figures 6(a – c) are plots of the bare density of states for each orbital due to each band and the total bare density of states. In all calculations of the mnr and Hall effect, the temperature dependence of chemical potential has been taken into account. \( \mu \) decreases about \( 5 \times 10^{-3} \) eV from \( T = 0 \) to \( T = 300K \). Finally, plots of \( ^{63}W_z/T \) and \( ^{63}W_{xy}/T \) are shown in figures 7(a, b) where we have used the value \( ^{21} \langle 1/r^3 \rangle = 6 \) a.u. The curves show the characteristic peak at a \( T \) value greater than \( T_c \) and the order of magnitude of the rate is consistent with experiment. With the above figures and expressions for the relaxation rates we can qualitatively see why the correct behavior is obtained.

There are two different ways an electron may relax a Cu nucleus: one by intra-band (U electron to U electron or L electron to L electron), or two, by the inter-band processes U to L and L to U. Due to the larger density of states of the U band, intra-band L to L relaxation is small. This leaves the relaxation rate to be determined by the U to U intra-band scattering and U to L (L to U) inter-band scattering. The U to U scattering leads to an increase of \( W/T \) due to the sharp increase in the U band density at the saddle point singularity. On the other hand, the contribution from the inter-band term must decrease due to the closeness of the Fermi energy to the very top of the L band and therefore the vanishing of the density of states. The competition of these two terms gives the final result shown. Regarding the Cu KS, only the U to U contribution and L to L contribution can appear because the KS comes from diagonal elements of the electron-nuclear Hamiltonian. The U to U KS contribution dominates the L to L KS contribution due to the larger density of states of the U band as before leading to a monotonically increasing KS if the hyperfine couplings have the correct sign. The sign of the couplings will be discussed later on, but we can now see that the Cu KS and \( W/T \) will have different temperature dependencies as observed.

It is pleasing to find that our calculated value for the relaxation rate has the correct order of magnitude (experimentally, \( ^{63}W_z/T \approx 20 \text{s}^{-1}\text{K}^{-1} \) at 100K versus our value of 7.2 \( \text{s}^{-1}\text{K}^{-1} \)). Our calculation has completely neglected the effects of the Cu 4s contact term and secondarily, the core polarization contribution. Also, our calculated percentage increase from 30K to the peak is about 3% versus an experimental increase of \( \approx 10 \rightarrow 20\% \) and the percentage decrease from the peak value to the 300K value is 15% versus the observed \( \approx 50\% \). In spite of these differences, the qualitative behavior is correct and this is the most important aspect given the level of calculation used in deriving the Hubbard model parameters.
As we can see from figures 7(a, b), the relaxation anisotropy of $\approx 3.4$ is not accounted for with the present model. What is missing here is a small amount of $d_{xy}$ orbital character in our bands. $d_{xy}$ is the next most unstable Cu orbital by ligand field theory after $d_{x^2-y^2}$ and $d_{z^2}$. Including some $d_{xy}$ character affects $W_{xy}$ dramatically because now orbital relaxation is permitted $W_{xy}^{orb} \neq 0$, whereas $W_{z}^{orb}$ remains zero. Including $d_{xy}$ makes,

$$W_{orb}^{xy}(\epsilon) = 4N_{d_{x^2-y^2}}(\epsilon)N_{d_{xy}}(\epsilon),$$  \hspace{1cm} (66)

$$W_{orb}^{z} = 0. \hspace{1cm} (67)$$

There are also additional terms due to $d_{xy}$ in the dipole-dipole terms (62), (64) but these are small and cannot account for the anisotropy. We neglect them here.

The coefficient of 4 in front of $W_{orb}^{xy}$ is about 30 times larger than the first coefficient in (62) and more than two orders of magnitude greater than the other coefficients in $W_{z}^{dip}$. Thus, $d_{xy}$ character on the order of a few percent will lead to a contribution to $W_{xy}$ as large as the dipole term leading easily to an anisotropy factor commensurate with experiment.

For the planar O sites, the relevant orbital is $p_{\sigma}$. The O 2s will be considered later. The lack of a second major O orbital near the Fermi surface and also the fact that at $(\pi, \pi)$ there is no mixing of antibonding (most unstable) $p_{\sigma}$ (symmetry $B_{1g}$) with $d_{z^2}$ ($A_{1g}$) are the differences between O and Cu that leads to the different spin relaxation rate temperature dependencies. Figure 4c shows the amount of $p_{\sigma}$ character on an O site at various energies. Figure 6c shows the $p_{\sigma}$ bare density of states due to the U and L bands and the total bare density of states.

We can see that the contribution to the bare density of states due to the L band $N_{L,p_{\sigma}}(\epsilon)$ is small compared to the U band term $N_{U,p_{\sigma}}(\epsilon)$ leading to a small contribution to the relaxation rate due to the L band. This is due to the L band k states near the Fermi energy being close to $(\pi, \pi)$. At $(\pi, \pi)$, $d_{z^2}$ couples to the neighboring $\sigma$ orbitals which must be in a bonding configuration. This bonding set of $\sigma$ orbitals is stabilized by the $t_{\sigma\sigma}$ term. Thus, to create the most unstable $d_{z^2}$ configuration at $(\pi, \pi)$, we cannot have a large amount of $p_{\sigma}$ character leading to the small value for $N_{L,p_{\sigma}}(\epsilon)$ near the Fermi energy.

There are three distinct directions for the magnetic field at the O site with different relaxation rates. These are the z-axis normal to the CuO planes, the $\sigma$ axis along the Cu-O bond direction, and the perpendicular axis $\perp$ normal to z and $\sigma$. With only the $p_{\sigma}$ to consider, the relaxation along $z$ and $\perp$ are equal, $^{17}W_{z} = ^{17}W_{\perp} \neq ^{17}W_{\sigma}$.

The expressions for $^{17}W_{z}$, $^{17}W_{\sigma}$ are of the same form as for Cu (61) with the crude approximation $<1/r^3> \approx 3$ a.u. determined by ab-initio calculations and $\gamma_n$ the gyromagnetic ratio of the $^{17}O$ nucleus. With only a $p_{\sigma}$ contributing, there is no orbital relaxation in any direction of the magnetic field,

$$^{17}W_{orb}^{z} = ^{17}W_{\sigma}^{orb} = ^{17}W_{orb}^{\perp} = 0. \hspace{1cm} (68)$$

The dipole-dipole relaxation term is,
A plot of the $^{17}W_\sigma$ relaxation is shown in figure 8. The others are simply 2.5 times larger. This relaxation is monotonic increasing due to the bare density of $p_\sigma$ due to the L band being small.

There remains one orbital that can make a large contribution to the relaxation due to its large hyperfine coupling to the nucleus that we have not yet considered. That is the O 2s orbital. A very small amount of 2s can have a large effect on $^{17}W$ without making any change in our calculated band structure. At $(\pi, \pi)$, the L band has no $d_{x^2-y^2}$ character and by symmetry no 2s character either. Thus, similar to $N_{Lp_\sigma}(\epsilon)$, there is almost no contribution to the O 2s bare density $N_{2s}(\epsilon)$ due to the L band leading to the same monotonic increasing behavior as in figure 8. O 2s will make a large change to the absolute value of the relaxation rate. Without estimating the size of the 2s contribution, we cannot compare our answer in figure 8 to experimental data on LASCO. Without O 2s, the values in figure 8 are about an order of magnitude too small.\(^7\)

The KS on the O sites is due to the O 2s Fermi contact interaction, the $p_\sigma$ orbital dipole coupling and core polarization. In figure 9, we simply plot the KS,

$$K_\sigma = -2K_z = -2K_\perp = \left(\frac{8}{3}\right)\left(\frac{1}{\mu_B}\right)\mu_B^2 \int \left(-\frac{\partial f}{\partial \epsilon}\right) N_{p_\sigma}(\epsilon) d\epsilon,$$

(71)

due to the $p_\sigma$ dipole-dipole term. Since the 2s and core polarization shifts are isotropic, our curve may be compared to the axial KS, $K_{ax} = 2(K_\sigma - K_\perp)/3$. The monotonic increase in the shift is due to the sharp increase in the U band density of states above $\epsilon_F$ due to the saddle point singularity at $(\pi, 0), (0, \pi)$.

The KS involves only one factor of $N_{p_\sigma}(\epsilon)$ while the relaxation contains $N_{p_\sigma}(\epsilon)^2$. Thus, there is no way $^{17}W/T \propto K_\sigma$ is strictly possible, although from the figures, the agreement is not far off.

For the Cu KS, we need to introduce the effects of the Cu 4s orbital and the two $p_z$ orbitals above and below the Cu on the apical oxygens. Experimentally, the Cu KS for a z-axis field is T independent while for planar fields the shift is monotonic increasing with increasing T. As we discussed, the dominant contribution to the shift will come from the bare density of states for the orbitals from the U bands. If we can somehow show that the hyperfine couplings are positive for planar fields and zero for the z-axis field, then we should expect a curve similar to figure 9 for Cu KS.

The Cu KS along the z-axis and planar directions is the sum of,

$$^63K_\alpha = K_\alpha^{\text{dip}}(d_{x^2-y^2}) + K_\alpha^{\text{dip}}(d_{z^2}) + K_\alpha^{\text{contact}}(4s) + K_\alpha^{\text{cp}} + K_\alpha^{\text{dip}}(d_{z^2}, 4s),$$

(72)
where \( \alpha \) is the field direction \( z \) or planar, \( K^\text{dip}(d_{x^2-y^2}) \), \( K^\text{dip}(d_{z^2}) \) are the dipole shifts due to the \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals, \( K^\text{contact}(4s) \) is the Fermi contact shift, \( K^\text{cp} \) is the core polarization shift, and \( K^\text{dip}(d_{z^2}, 4s) \) is the dipole contribution due to the interference of \( d_{z^2} \) and 4s. The expressions for the first four terms are,

\[
K^\text{dip}_z(d_{x^2-y^2}) = -2K^\text{dip}_{xy}(d_{x^2-y^2}) = -\frac{8}{7} \left( \frac{1}{\sqrt{3}} \right)^2 \mu_B \int \left( -\frac{\partial f}{\partial \epsilon} \right) N_{d_{x^2-y^2}}(\epsilon)d\epsilon, \tag{73}
\]

\[
K^\text{dip}_z(d_{z^2}) = -2K^\text{dip}_{xy}(d_{z^2}) = \frac{8}{7} \left( \frac{1}{\sqrt{3}} \right)^2 \mu_B \int \left( -\frac{\partial f}{\partial \epsilon} \right) N_{d_{z^2}}(\epsilon)d\epsilon, \tag{74}
\]

\[
K^\text{contact}_z(4s) = K^\text{contact}_{xy}(4s) = \frac{16\pi}{3} |\psi_{4s}(0)|^2 \mu_B^2 \int \left( -\frac{\partial f}{\partial \epsilon} \right) N_{4s}(\epsilon)d\epsilon, \tag{75}
\]

\[
K^\text{cp} = K^\text{cp}_{xy} = -(2\alpha) \left( \frac{1}{\sqrt{3}} \right)^2 \mu_B \int \left( -\frac{\partial f}{\partial \epsilon} \right) [N_{d_{z^2-y^2}}(\epsilon) + N_{d_{z^2}}(\epsilon)]d\epsilon. \tag{76}
\]

We take the value \( \alpha = 0.33 \) (dimensionless) from Abragam and Bleaney.\(^{21}\) \( \psi_{4s}(0) \) is the value of the 4s orbital at the nucleus.

The \( d_{z^2}, 4s \) interference term is evaluated by taking the mean value of a band wavefunction at the Fermi surface with the dipole Hamiltonian. Let,

\[
\phi_k = A_k d_{x^2-y^2}k + B_k d_{z^2}k + C_k \psi_{4sk} + \ldots, \tag{77}
\]

where \( d_{x^2-y^2}k \), \( d_{z^2}k \) are defined in (34), (35) and \( \psi_{4sk} \) is defined similarly. Then,

\[
\langle \phi_k | H^\text{dip} | \phi_k \rangle = (-2\mu_B)(\gamma_{n}h)[I_x S_x + I_y S_y - 2I_z S_z].
\]

\[
\left\{ \left( -\frac{2}{7} \left( \frac{1}{\sqrt{3}} \right)^2 \right) |A_k|^2 + \left( \frac{2}{7} \left( \frac{1}{\sqrt{3}} \right)^2 \right) |B_k|^2 + \left( \frac{1}{\sqrt{5}} \right)^2 \left( \frac{1}{r^3} \right)_{z^2,s} (B^*_k C_k + B_k C^*_k) \right\}
\]

+ term involving \( (A^*_k C_k + A_k C^*_k) \),

\[
\left( \frac{1}{r^3} \right)_{z^2,s} = \int_0^{+\infty} r^2 dr R_{d_{z^2}}(r) \left( \frac{1}{r^3} \right)_{4s}(r), \tag{79}
\]

where \( I \) is the nuclear spin and \( R_{d_{z^2}}(r), R_{4s}(r) \) are the radial parts of the \( d_{z^2} \) and 4s orbitals respectively with normalizations,

\[
\int_0^{+\infty} r^2 dr R_{d_{z^2}}(r)^2 = \int_0^{+\infty} r^2 dr R_{4s}(r)^2 = 1. \tag{80}
\]

Averaging over the Fermi surface, the interference term \( A^*_k C_k + A_k C^*_k \) due to \( d_{x^2-y^2} \) and 4s becomes zero due to the different symmetries of \( d_{x^2-y^2} \) and 4s (\( B_{1g} \) and \( A_{1g} \)). The first two terms in (78) lead to \( K^\text{dip}(d_{x^2-y^2}) + K^\text{dip}(d_{z^2}) \) and the third term gives,
conductivity $\sigma$ no vacancies in the chains and one can expect more 3D dispersion from the current. The Hall coefficient $R$ of the Fermi energy at the crossing point, we take the L band as the primary carrier of $B$. Hall Effect and Resistivity shifts and O relaxation will become T independent. For optimally doped YBCO, $\pi$ and (0, $\pi$) saddle point singularity is sufficiently far away from the Fermi energy, then the shifts and O relaxation will become T independent. For optimally doped YBCO, there are no vacancies in the chains and one can expect more 3D dispersion from the $d_{z^2}$ orbital.

B. Hall Effect and Resistivity

Since the density of states for the L band is smaller than for the U band in the vicinity of the Fermi energy at the crossing point, we take the L band as the primary carrier of current. The Hall coefficient $R_H$ is the ratio of the transverse conductivity $\sigma_{xy}$ and the conductivity $\sigma$ squared. Using standard Boltzmann theory,\textsuperscript{22}

$$\sigma_{xy} = \left(\frac{m_e^2 \Omega_0}{\hbar}\right) \left(\frac{1}{\Omega}\right) \sum_k \left(- \frac{\partial f}{\partial \epsilon_k}\right) v_{k_y} \left[ v_{k_y} \frac{\partial}{\partial k_x} - v_{k_x} \frac{\partial}{\partial k_y} \right] v_{k_x},$$

where $<B^*_k C_k>$ is the mean value of $B^*_k C_k$ over the Fermi surface and $N(\epsilon)$ is the total density of states of the band. Depending on the sign of $<B^*_k C_k>$, the shift due to the interference term can be positive enhancing the field due to $d_{z^2}$, or negative decreasing the net magnetic field of $d_{z^2}$. The bare $d_{z^2}$ and $4s$ density of states from this band are $|B_k|^2 N(\epsilon)$ and $\langle |C_k|^2 \rangle N(\epsilon)$. Since only one power of $C_k$ appears in (81), $B^*_k C_k$ can be large although $\langle |C_k|^2 \rangle$ may be small.

The bare $d_{x^2-y^2}$ density of states is smaller than the $d_{z^2}$ density of states at the Fermi energy leading to a net positive shift from $K(d_{x^2-y^2}) + K(d_{z^2})$ along the z-direction and a net negative shift along the plane. $K^{contact}(4s)$ is isotropic and always positive.

At all $k$ vectors on the Fermi surface, the $d_{z^2}$ and $p_z$’s on the apical O form an antibonding combination leading to a larger amount of $4s$ character than one expects from a $d_{x^2-y^2}$ band. Thus, if the $d_{z^2}$, $4s$ interference term leads to a negative $<B^*_k C_k>$ that is sufficiently large, the net effect of $K(d_{x^2-y^2}) + K(d_{z^2}) + K(d_{z^2}, 4s)$ leads to a dipolar field which is negative in the z direction and positive along the plane. We shall assume that due to the charge donation of the apical O $p_z$ to the Cu $4s$, this is the case. With this assumption, we can see how the net shift on the Cu due to a z-axis field can add to zero while simultaneously leading to positive shifts for planar fields. In (72), the contribution to $K$ from the contact and core polarization terms should be a net isotropic positive value. Without the interference shift (81), there is no way the z-axis shift can add to zero. Figure 10 shows the T dependence of the z-axis shift of $K(d_{x^2-y^2})$ and $-K(d_{z^2})$. These curves have approximately the same T dependence as the O shift and $^{17}W/T$.

The above considerations also show why for fully doped YBCO, the T dependence of the shifts and $^{17}W/T$ are almost constant. If there is more dispersion in the z-direction of the $d_{z^2}$ orbital, then the saddle point peak in the U band density of states will be broadened. If the plateau is sufficiently broad to extend all the way to the Fermi energy or the (π,0) and (0, $\pi$) saddle point singularity is sufficiently far away from the Fermi energy, then the shifts and O relaxation will become T independent. For optimally doped YBCO, there are no vacancies in the chains and one can expect more 3D dispersion from the $d_{z^2}$ orbital.
\[ \sigma = m_e \Omega_0 \left( \frac{1}{\Omega} \right) \sum_k \left( -\frac{T_f}{\partial \epsilon_k} \right) v_k^2, \]  

\[ R_H = \left( \frac{\Omega_0}{q_c} \right) \frac{\sigma_{xy}}{\sigma^2}, \]

where \( m_e \) is the electron mass, \( \Omega_0 \) is the primitive unit cell volume \( \Omega_0 = 96 \text{ Å} \), \( \Omega \) is the total volume, \( q = -|e| < 0 \) is the electron charge, and \( c \) is the velocity of light. \( v_k = \nabla_k \epsilon_k / \hbar \) is the velocity. We have multiplied \( \sigma_{xy} \) and \( \sigma \) by the appropriate factors of \( m_e \) and \( \Omega_0 \) to make the expressions in (82) and (83) dimensionless and have neglected the scattering rate \( 1/\tau \) in these expressions because for \( R_H \), \( \tau \) does not appear. We may also define \( \sigma_{xy}(\epsilon) \) and \( \sigma(\epsilon) \) by replacing the Fermi-Dirac function \( -\partial f / \partial \epsilon_k \) by the delta function \( \delta(\epsilon_k - \epsilon) \) in (82) and (83). Then,

\[ \sigma_{xy} = \int \sigma_{xy}(\epsilon) \left( -\frac{T_f}{\partial \epsilon_k} \right) d\epsilon, \]  

\[ \sigma = \int \sigma(\epsilon) \left( -\frac{T_f}{\partial \epsilon_k} \right) d\epsilon. \]

Figure 11 is a plot of \( \sigma_{xy}(\epsilon) \) and \( \sigma(\epsilon) \) and figure 12 shows the temperature dependence of the Hall coefficient at optimal doping. The absolute magnitude of \( R_H \) is about ten times larger than observed values for LASCO, but the calculated percentage change of \( R_H \) from the 100K to 300K is \( \approx 40\% \) in good agreement with experiment\(^{12} \) (\( \approx 50\% \)).

These curves were calculated taking the small z-axis dispersion parameters \( T_{(0,0)}, T_{(\pi,0)}, \) and \( T_{(\pi,\pi)} \) in (31) – (33) to be zero. This was done to simplify the computation. \( \sigma_{xy}(\epsilon) \) changes very rapidly for energies higher than the Fermi energy at the band touching point, whereas the change in \( \sigma(\epsilon) \) is not as dramatic.

The abrupt change in \( \sigma_{xy}(\epsilon) \) is due to the two band crossing point. Near the Fermi energy of the crossing point, the repulsion of the two bands for non-diagonal \( k \) vectors strongly affects the shape of the two Fermi surfaces leading to a large curvature for the L band. At energies slightly higher than the Fermi energy, the L band surface is not affected by the presence of the U band and the Fermi surface becomes “small” leading to the reduced curvature. The overall T dependence of \( R_H \) is due to the combined T dependencies of both \( \sigma \) and \( \sigma_{xy} \) rather than solely due to \( \sigma_{xy} \) as one would expect from a first glance at figure 11. We can see that the presence of the two-band crossing point and the association of optimal superconductivity with this point is the root cause of the strong anomalous temperature dependence of the Hall coefficient.

There are several possible explanations for our calculated value for \( R_H \) being more than ten times too large. The most obvious one is the neglect of next-nearest neighbor hopping terms in our Hubbard model. The second cause is due to our 2D approximation to the band structure. A more detailed description than ours of the z-axis dispersion is required. The third reason is the neglect of the contribution from the electron-like surface of the U band.
Finally, more refined ab-initio calculations than the ones performed in the following paper on the CuO$_6$ complex embedded in the point charge field of LASCO will change the parameters used in our Hubbard model.

The resistivity due to scattering with phonons should be linear at the optimal doping for two reasons: 1.) the Fermi surface for the L band is “small”, and 2.) at optimal doping the electron current can strongly relax by scattering to a U electron state. At optimal doping, the U band Fermi surface touches the L band surface leading to nearby states in k space with very different currents. The T dependence of $\sigma$ complicates this scenario because $\sigma$ is proportional to the effective number of charge carriers in the band. It is unclear how the T dependence of the relaxation rate $1/\tau$ could cancel this dependence. If a full-blown 3D model was used instead of our 2D model with the third dimension included as a perturbation, we believe that the temperature dependence of $\sigma$ would become small while $\sigma_{xy}$ would remain very T dependent.

**CONCLUSIONS**

We have presented a model for superconductivity of the cuprates based on the idea that Cooper pairs are formed from electrons between two distinct bands. This leads naturally to associating optimal doping with a Fermi surface touching point of the two bands. We have postulated the character of the two bands to arise from $d_{x^2-y^2}$, $d_{z^2}$, $O_{p\sigma}$, and apical $O_{pz}$ orbitals. A Hubbard model for these bands is set-up and we calculate some normal state consequences of the model. With our model, many of the anomalous features of the normal state nmr, Hall effect, and resistivity are explained qualitatively and to varying degrees quantitatively. The primary reason for the anomalous normal state properties is due to the optimal doping being at the Fermi surface touching point.

We show that inter-band pairing alters the standard interpretation of Josephson tunneling. With inter-band pairs, the detailed nature of the single particle tunneling matrix elements plays a prominent role. We show that with this new piece of physics, three of the four Josephson tunneling experiments are explained by our model with a phonon mediated attractive coupling.

The parameters in the Hubbard model used in this paper are derived in the following paper by Perry and Tahir-Kheli from calculations on a CuO$_6$ cluster for La$_{2-x}$Sr$_x$CuO$_4$. We conclude there that contrary to band structure calculations where only one band with Cu $d_{x^2-y^2}$ and O $p\sigma$ character is found, two bands exist at the Fermi energy with the character described above.
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Table 1. Parameters in Hubbard Model in (eV).

| Parameter | Value   |
|-----------|---------|
| $\epsilon_{d_{x^2-y^2}}$ | -2.403  |
| $\epsilon_{d_{z^2}}$       | -2.092  |
| $\epsilon_{p_{\sigma}}$    | -6.122  |
| $\epsilon_{p_{z}}$         | -0.852  |
| $t_{x^2-y^2,\sigma}$       | 1.347   |
| $t_{z^2,\sigma}$           | 0.514   |
| $t_{\sigma\sigma}$         | 0.368   |
| $t_{\sigma\sigma a}$       | -0.041  |
| $t_{p_{\sigma},d_{z^2}}$   | 1.076   |
| $t_{p_{\sigma},\sigma}$    | 0.078   |
| $t_{p_{\sigma},p_{z}}$     | 0.493   |
**FIG. 1.** Dispersions of the U (solid line) and L (dashed line) bands.

**FIG. 2.** Fermi surfaces at various dopings. The short dashes is for optimal doping, the long dashes is underdoping, and the solid line is overdoping.

**FIG. 3.** Density of states of the U (solid line) and L (dashed line) bands near the optimal Fermi energy.

**FIG. 4a.** $d_{z^2}$ character of the U (solid line) and L (dashed line) bands.

**FIG. 4b.** $d_{z^2}$ character of the U (solid line) and L (dashed line) bands.

**FIG. 4c.** $p_\sigma$ character of the U (solid line) and L (dashed line) bands.

**FIG. 5.** Feynman diagram for the pairing term with matrix element $U_{k'k}$.

**FIG. 6a.** Bare density of states for $d_{z^2-y^2}$ for the U (solid line) and L (dashed line) bands and the total bare density of states (dotted line).

**FIG. 6b.** Bare density of states for $d_{z^2}$ for the U (solid line) and L (dashed line) bands and the total bare density of states (dotted line).
FIG. 6c. Bare density of states for $p_x$ for the U (solid line) and L (dashed line) bands and the total bare density of states (dotted line).

FIG. 7a. Spin relaxation rate over $T$ of Cu for a $z$-axis field.

FIG. 7b. Spin relaxation rate over $T$ of Cu for a planar field. The contribution of $d_{xy}$ is not included.

FIG. 8. Relaxation rate over $T$ for O with field along the Cu-O bond direction.

FIG. 9. $\sigma$ direction Knight shift due to $p_x$ band.

FIG. 10. $O \sigma$ direction Knight shift due to $p_x$ band.

FIG. 11. Plots of the L band $\sigma_{xy}(\epsilon)$ and $\sigma(\epsilon)$. Units are dimensionless.

FIG. 12. Temperature dependence of the L band Hall coefficient.