REDUCED PAIRING HAMILTONIAN FOR INTERATOMIC TWO-ELECTRON EXCHANGE IN LAYERED CUPRATES

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A detailed Linear Combination of Atomic Orbitals (LCAO) tight-binding model is developed for the layered High-Temperature Superconductor (HTSC) cuprates. The band structure of these materials is described using a $\sigma$-band Hamiltonian employing Cu4$s$, Cu3$d_{x^2-y^2}$, O2$p_x$ and O2$p_y$ atomic orbitals. The Fermi level and the shape of the resulting Fermi surface are fitted to recent Angle Resolved Photon Emission Spectroscopy (ARPES) data to realistically determine the dispersion in the conduction band. Electron-electron interactions and, ultimately, Cooper pairing is obtained by introducing a Heitler-London, two-electron exchange between adjacent orbitals within the CuO2 plane. Finally, using the LCAO wavefunctions determined by the band structure fit, the Bardeen-Cooper-Schrieffer (BCS) type kernel is derived for interatomic exchange.

Keywords: layered superconductors

1. Introduction

Since the first discovery in 1986, the high-temperature superconducting cuprates have attracted great attention. There is a wealth of experimental data about this unusual family of materials which we shall not attempt to review here. Rather we will mention only two lines of inquiry: the Angle Resolved Photoemission Spectroscopy (ARPES) or Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS) experiments to determine the normal state band structure, and the ARPES measurements of the gap in the superconducting state. From these experiments there are quantitative results for the shape of the Fermi surface and the angular dependence of the superconducting gap around this surface, both of which can be compared in detail to any proposed theoretical model.

The quantity of theoretical work on the cuprates is similarly large, but can be roughly divided into two camps: one has made considerable effort to realistically model the band structure of the materials, from first principles where possible, whilst the other has concentrated on correlation effects by using idealized “toy” models of the Hubbard and t-J types. Whilst both of these camps have made considerable progress in their own fields, there has been surprisingly little overlap between the two. In particular, the band structures employed in the studies of correlations are rarely more sophisticated than the inclusion of nearest- or next-
nearest-neighbour hoppings on a square lattice, and bear little resemblance to either the measured or predicted band structures.

It is the purpose of this paper to analyze microscopic interatomic two-electron exchange processes which could be useful to understand the nature and origin of the superconducting correlations in the cuprate materials. As it is now almost universally accepted that it is the physics of the CuO$_2$ planes, the common feature of all the cuprates, which gives the materials such extraordinary properties our efforts will focus on the properties of these planes and we will omit the effects of extraneous, material-dependent details such as the presence of CuO chains, orthorhombic distortions, double planes, etc. Having devised a model we will fit recent experimental data to the single-particle sector, so that it accurately describes the band structure, and then we will proceed to derive an analytic expression for the BCS-type kernel, or pairing potential, $V(p, p')$. We will leave the solution of the resulting gap equation, and comparison to experiment, to a later date.

2. Model

In this work we attempt to understand the physics of the CuO$_2$ plane using a relatively simple, idealized, tight-binding model, within the Linear Combination of Atomic Orbitals (LCAO) approximation. To this end we consider only the four atomic orbitals coming from the Cu3$d_{x^2-y^2}$, Cu4$s$ and O2$p_{\sigma}$ states. Denoting the positions of the Cu, O$_x$ and O$_y$ atoms by $R_{Cu}$, $R_x$ and $R_y$ respectively, the in-plane lattice constant by $a_0$ and the unit cell index by $n = (n_x, n_y)$, the LCAO wavefunction reads:

$$\psi_{LCAO}(r) = \sum_{n,\alpha} \left[ D_{n\alpha} \psi_{Cu3d_{x^2-y^2}}(r - na_0 - R_{Cu}) + S_{n\alpha} \psi_{Cu4s}(r - na_0 - R_{Cu}) \right. \\
+ \left. X_{n\alpha} \psi_{O2p_\sigma}(r - na_0 - R_x) + Y_{n\alpha} \psi_{O2p_\sigma}(r - na_0 - R_y) \right],$$

where $\Psi_{n\alpha} = (D_{n\alpha}, S_{n\alpha}, X_{n\alpha}, Y_{n\alpha})$ is the vector of amplitudes for the $n$th unit cell. With each of these quantities is associated a Fermion operator satisfying the usual anticommutation relations $\{X_{n\alpha}, X_{m\beta}^\dagger\} = \delta_{nm} \delta_{\alpha\beta}$, $\{X_{n\alpha}, Y_{m\beta}^\dagger\} = 0$, etc. We use these operators to analyze exchange processes in the CuO$_2$ planes.

This model can be conveniently split into two parts; a non-interacting part describing the single-electron band structure and an interacting part describing the effects of electron-electron interactions. We consider each of these in turn below.

2.1. Tight-binding band structure

When the differential overlap of the orbitals is neglected, the non-interacting, single-electron Hamiltonian can be parameterized by three atomic energies, $\epsilon_s$, $\epsilon_d$ and $\epsilon_p$, and three hopping integrals, $t_{sp}$, $t_{pd}$ and $t_{pp}$, corresponding to the transitions Cu4$s$ ↔ O2$p_\sigma$, O2$p_\sigma$ ↔ Cu3$d_{x^2-y^2}$ and O2$p_x$ ↔ O2$p_y$ respectively. In second-
quantization notation, the resulting Bloch-Hückel-like Hamiltonian reads

$$
\hat{H}_{BH} = \sum_{n\alpha} \left\{ \hat{D}_{n\alpha} \left[ \epsilon_d \hat{D}_{n\alpha} - t_{pd} \left( -\hat{X}_{n\alpha} + \hat{X}_{(n + 1, n_\beta)\alpha} - \hat{Y}_{n\alpha} + \hat{Y}_{(n + 1, n_\beta)\alpha} \right) \right] \\
+ \hat{S}_{n\alpha} \left[ \epsilon_s \hat{S}_{n\alpha} - t_{sp} \left( -\hat{X}_{n\alpha} + \hat{X}_{(n + 1, n_\beta)\alpha} - \hat{Y}_{n\alpha} + \hat{Y}_{(n + 1, n_\beta)\alpha} \right) \right] \\
+ \hat{X}_{n\alpha} \left[ \epsilon_p \hat{X}_{n\alpha} - t_{sp} \left( -\hat{D}_{n\alpha} + \hat{D}_{(n, n_\beta + 1)\alpha} \right) - t_{sp} \left( -\hat{S}_{n\alpha} + \hat{S}_{(n, n_\beta + 1)\alpha} \right) \\
- t_{pp} \left( \hat{X}_{n\alpha} - \hat{X}_{(n - 1, n_\beta)\alpha} - \hat{X}_{(n, n_\beta + 1)\alpha} + \hat{X}_{(n - 1, n_\beta + 1)\alpha} \right) \right] \right\} 
$$

(2)

This Hamiltonian is diagonalized by introducing the Bloch states $$\hat{\Psi}_{p\alpha} = (\hat{D}_{p\alpha}, \hat{S}_{p\alpha}, \hat{X}_{p\alpha}, \hat{Y}_{p\alpha})$$. The elements of these states are defined by the relation

$$
\hat{\Psi}_{n\alpha} = \left( \begin{array}{c}
\hat{D}_{n\alpha} \\
\hat{S}_{n\alpha} \\
\hat{X}_{n\alpha} \\
\hat{Y}_{n\alpha}
\end{array} \right) = \frac{1}{\sqrt{N}} \sum_{p} e^{i \phi_p} \left( \begin{array}{c}
\hat{D}_{p\alpha} \\
\hat{S}_{p\alpha} \\
e^{i \phi_a} \hat{X}_{p\alpha} \\
e^{i \phi_b} \hat{Y}_{p\alpha}
\end{array} \right),
$$

(3)

where $$N$$ is the number of unit cells, and the two phases are $$\phi_a = \frac{1}{2}(p_x - \pi)$$ and $$\phi_b = \frac{1}{2}(p_y - \pi)$$. The Hamiltonian can now be expressed in the more compact form

$$
\hat{H}_{BH} = \sum_{p\alpha} \hat{\Psi}_{p\alpha}^\dagger H_p \hat{\Psi}_{p\alpha},
$$

(4)

where the Hamiltonian matrix is

$$
H_p = \left( \begin{array}{cccc}
\epsilon_d & 0 & t_{pd} s_x & -t_{pd} s_y \\
0 & \epsilon_s & t_{sp} s_x & t_{sp} s_y \\
t_{pd} s_x & t_{sp} s_x & \epsilon_p & -t_{pp} s_x s_y \\
-t_{pd} s_y & t_{sp} s_y & -t_{pp} s_x s_y & \epsilon_p
\end{array} \right).
$$

(5)

Here, for the sake of convenience, we have adopted the shorthand notation of Andersen et al. $$s_x = 2 \sin(p_x/2)$$, $$s_y = 2 \sin(p_y/2)$$.

The spectrum of this model is determined by the solutions of the Heisenberg equation of motion, $$i \hbar d_t \hat{\Psi}_{p\alpha} = [\hat{\Psi}_{p\alpha}, \hat{H}_{BH}]$$, which is equivalent to solving for the LCAO amplitudes:

$$
(H_p - \epsilon I) \Psi_{p\alpha} = 0.
$$

(6)

This matrix equation is easily solved. The four eigenvalues are determined from the secular equation

$$
\det (H_p - \epsilon I) = A(\epsilon) xy + B(\epsilon)(x + y) + C(\epsilon) = 0
$$

(7)
in which \( x = \sin^2(p_x/2) \), \( y = \sin^2(p_y/2) \) and the coefficients are

\[
\mathcal{A}(\epsilon) = 16 \left( 4t_{pd}^2 t_{sp}^2 + 2t_{sp}^2 t_{pp}^2 \varepsilon_d - 2t_{pd}^2 t_{pp} \varepsilon_s - t_{pp}^2 \varepsilon_d \varepsilon_s \right), \quad (8)
\]

\[
\mathcal{B}(\epsilon) = -4\varepsilon_p \left( t_{sp}^2 \varepsilon_d + t_{pd}^2 \varepsilon_s \right), \quad (9)
\]

\[
\mathcal{C}(\epsilon) = \varepsilon_d \varepsilon_s \varepsilon_p^2. \quad (10)
\]

In the above, the energies \( \varepsilon_d \), \( \varepsilon_s \) and \( \varepsilon_p \) are measured relative to their respective atomic levels: \( \varepsilon_d = \epsilon - \varepsilon_d \), \( \varepsilon_s = \epsilon - \varepsilon_s \) and \( \varepsilon_p = \epsilon - \varepsilon_p \).

To each of the four solutions of equation (7) there corresponds an eigenvector \( \Psi_p^B \), where, the band index, labels the solutions. The general (unnormalized) form for the eigenvector is

\[
\psi_p^B = \begin{pmatrix} D_p^B \\ S_p^B \\ X_p^B \\ Y_p^B \end{pmatrix} = \begin{pmatrix} -\varepsilon_s \varepsilon_p^2 + 4\varepsilon_p t_{sp}^2 (x+y) - 32t_{pp} t_{sp}^2 xy \\ -4\varepsilon_p t_{sp} t_{pd} (x-y) \\ -\varepsilon_s \varepsilon_p - 8t_{sp}^2 \varepsilon_y x \\ (\varepsilon_p \varepsilon_x - 8t_{sp}^2 \varepsilon_y) t_{pd} y \end{pmatrix} \quad (11)
\]

where \( t_{sp}^2 = t_{sp}^2 - \varepsilon_s t_{pp}/2 \), and \( \varepsilon_d \), \( \varepsilon_s \) and \( \varepsilon_p \) are understood to depend on the appropriate value of \( \epsilon \), which in turn depends upon \( p \) and the model parameters. We denote the normalized eigenvector with a tilde: \( \tilde{\psi}_p^B = \psi_p^B / |\psi_p^B| \).

### 2.2. Heitler-London interaction

The second-quantized Heitler-London interaction Hamiltonian describes the interatomic two-electron exchange between the copper and oxygen orbitals.

It comprises three parts corresponding to Cu4s ↔ O2p\(_x\), O2p\(_y\) ↔ Cu3d\(_{x^2-y^2}\) and O2p\(_x\) ↔ O2p\(_y\) exchanges with transition amplitudes \( J_{sp} \), \( J_{pd} \) and \( J_{pp} \) respectively:

\[
\hat{H}_{HL} = \hat{H}_{sp} + \hat{H}_{pd} + \hat{H}_{pp}, \quad (12)
\]

where,

\[
\hat{H}_{sp} = -\frac{J_{sp}}{2} \sum_{\alpha,\beta} \sum_n \left[ \hat{S}_n^{\dagger} \hat{X}_n^{\dagger} \hat{S}_n \hat{X}_n + \hat{S}_n^{\dagger} \hat{Y}_n^{\dagger} \hat{S}_n \hat{Y}_n \alpha \beta \right] + \hat{S}_{(n+1,n+1)}^{\dagger} \hat{X}_{(n+1,n+1)}^{\dagger} \hat{S}_{(n+1,n+1)} \hat{X}_{(n+1,n+1)} \alpha \beta \quad (13)
\]

\[
\hat{H}_{pd} = -\frac{J_{pd}}{2} \sum_{\alpha,\beta} \sum_n \left[ \hat{D}_n^{\dagger} \hat{X}_n^{\dagger} \hat{D}_n \hat{X}_n + \hat{D}_n^{\dagger} \hat{Y}_n^{\dagger} \hat{D}_n \hat{Y}_n \alpha \beta \right] + \hat{D}_{(n+1,n+1)}^{\dagger} \hat{X}_{(n+1,n+1)}^{\dagger} \hat{D}_{(n+1,n+1)} \hat{X}_{(n+1,n+1)} \alpha \beta \quad (14)
\]

\[
\hat{H}_{pp} = -\frac{J_{pp}}{2} \sum_{\alpha,\beta} \sum_n \left[ \hat{X}_n^{\dagger} \hat{Y}_n^{\dagger} \hat{X}_n \hat{Y}_n + \hat{X}_n^{\dagger} \hat{Y}_n^{\dagger} \hat{X}_n \hat{Y}_n \alpha \beta \right] + \hat{X}_{(n+1,n+1)}^{\dagger} \hat{Y}_{(n+1,n+1)}^{\dagger} \hat{X}_{(n+1,n+1)} \hat{Y}_{(n+1,n+1)} \alpha \beta \quad (15)
\]
The complexity of this expression is greatly simplified by moving to the Bloch basis defined in equation (3). In this momentum-space representation it is more natural to label the fermionic operators by the band index, \( B \), than by the orbital index. Accordingly we separate these indices by writing

\[
\hat{\Psi}_{p\alpha} = \sum_B \tilde{\Psi}_B^{p\alpha} \hat{c}_B^{p\alpha},
\]

(16)

where \( \tilde{\Psi}_B^{p\alpha} \) is the normalized LCAO eigenvector coming from the band structure and \( \hat{c}_B^{p\alpha} \) is the annihilation operator for an electron in the \( B \)-band with momentum \( p \) and spin \( \alpha \). In what follows, we will drop the band-index and focus solely on the strongly hybridized \( d \)-band which contains the Fermi level.

3. BCS Theory

Moving to the Bloch basis and substituting for \( \hat{\Psi}_{p\alpha} \) leads to the momentum-space representation of the Heitler-London interaction term. At this point we have made no approximations, aside from neglecting completely filled or empty bands, and the representation is exact. However, the resulting Hamiltonian is too complicated for us to proceed further without approximations. The simplest course we can take is to make the mean-field or BCS approximation whereby fluctuations about the homogeneous, currentless equilibrium state are ignored. This leads to a simplified form of the Hamiltonian:

\[
\hat{H}_{HL} = \frac{1}{2N} \sum_{\alpha\beta} \sum_{pp'} \hat{c}_{p\beta}^{\dagger} \hat{c}_{p\alpha}^{\dagger} V(p, p') \hat{c}_{-p\alpha} \hat{c}_{p\beta}
\]

(17)

where the BCS pairing-potential is

\[
V(p, p') = \left[ J_{sp} \tilde{S}_p \tilde{S}_{p'} + J_{pd} \tilde{D}_p \tilde{D}_{p'} \right] \left[ W_{xx'} \hat{X}_p \hat{X}_{p'} + W_{yy'} \hat{Y}_p \hat{Y}_{p'} \right] - \frac{J_{pp}}{2} \hat{X}_p \hat{X}_p' W_{xx} W_{yy} \hat{Y}_p \hat{Y}_{p'}
\]

(18)

Here we have introduced a new notation:

\[
W_{xx'} = c_x c_x' - s_x s_x' = 4 \cos \left( \frac{p_x + p_x'}{2} \right)
\]

(19)

\[
W_{yy'} = c_y c_y' - s_y s_y' = 4 \cos \left( \frac{p_y + p_y'}{2} \right)
\]

(20)

Note that \( W_{xx'} \) and \( W_{yy'} \) are sums of separable terms, which is to say that the \( p_x \) and \( p_x' \) dependencies can be factored out. Thus \( V(p, p') \) is also a sum of separable terms.

For a sufficiently strong, attractive potential, and a low enough temperature, the BCS Hamiltonian gives rise to a superconducting condensate of Cooper pairs with zero center-of-mass momentum. Following the BCS prescription we obtain the
following self-consistent expression for the superconducting gap:

\[
\Delta(p) = -\frac{1}{N} \sum_{p'} V(p, p') \frac{\tanh \left( \frac{E(p')}{2T} \right)}{2E(p')} \Delta(p'),
\]

(21)

where the quasiparticle energies are \( E(p) = \sqrt{\xi^2(p) + |\Delta(p)|^2} \), and \( \xi(p) = \epsilon(p) - \mu \) is the normal state energy in the \( d \)-band relative to the chemical potential or Fermi energy.

4. Discussion

In this paper we derived the matrix elements of different interatomic two-electron exchange processes and obtained the corresponding gap equation. The analysis demonstrates that the \( B_{1g} \) symmetry of the order parameter, required for the description of the ARPES and Josephson data for the gap, cannot be obtained by considering only interatomic interactions. We thus arrive at the conclusion that other exchange processes should be found and taken into account to explain the pairing interaction in the cuprates, if we wish to follow the traditional BCS scheme.

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