Electron Pairing in High-T_c Superconductors

Weicheng Lv
Department of Physics
University of Illinois at Urbana-Champaign

May 4th, 2006

Abstract

In high-T_c cuprate superconductors, the pairing state of electrons is still spin-singlet, as in conventional BCS superconductors. But the orbital part of the wavefunction, order parameter or gap function, has a $d_{x^2-y^2}$ symmetry, rather than the isotropic s-wave symmetry. This exotic symmetry has been confirmed by various experiments, especially the phase-sensitive ones. But the underlying mechanism of d-wave pairing remains controversial. Investigations on Hubbard model provide some ideas.

1 Introduction

Since its discovery in 1986 (Bednorz and Müller), high-T_c cuprate superconductivity has always been a heated topic in condensed matter physics. Throughout these 20 years, great experimental and theoretical efforts are made in this field. But the theory of High-T_c superconductivity remains unclear. In this essay, I will focus on the unconventional electron pairing in cuprates, which is the key to superconductivity.

As we know, in conventional superconductors (described by BCS theory), electron-phonon interaction will result in an effective attraction between two electrons, which are of opposite spin and momentum. At low temperature, this attraction exceeds the Coulomb repulsion. So at the ground state, electrons will form a condensate of spin-singlet pairs - Cooper pairs. This condensate can be described by a complex order parameter $\Psi(\mathbf{r})$ (Landau-Ginzberg), which is proportional to the energy gap $\Delta(\mathbf{r})$. In momentum space, we will have $\Psi(\mathbf{k}) \sim \Delta(\mathbf{k})$. The energy gap $\Delta(\mathbf{k})$ of BCS superconductors is isotropic in **k**-space, meaning it has the same amplitude and phase in all directions.

In the unconventional superconductors - cuprates, the situations are more complicated. The *integer flux quantum effect* observed in SQUID experiments confirmed electrons still form pairs. Andreev-reflection demonstrated farther that the paired electrons have opposite spin and momentum. So the pairing state in cuprates is still spin-singlet. As the energy gap $\Delta(\mathbf{k})$ corresponds to the orbital parts of wave functions of paired electrons, it must be symmetric in **k**-space. This restricts the candidate pairing states to s-wave and d-wave. Early experiments seemed to favor the s-wave pairing. But theoretic workers also proposed the $d_{x^2-y^2}$ state starting from the strong on-site Coulomb repulsion. The significant differences of $d_{x^2-y^2}$ wave from s-wave are the existence of nodes and the sign change with a direction rotation of $\pi/2$. In mid 1990s, d-wave was shown to be dominant in cuprates by several carefully designed phase-sensitive experiments.

The essay is organized as follows. In Sec.2, we start from the general consideration of ODLRO and symmetry breaking. By group representation theory, a set of candidate pairing states is proposed. Then several phase-sensitive experiments are presented in Sec.3 to confirm the $d_{x^2-y^2}$ symmetry. Finally, in Sec.4, we try to explore the origin of d-wave symmetry in Hubbard model.

2 Candidate pairing states

2.1 ORLRO (off-diagonal long-range order) and symmetry breaking

The existence of ODLRO is a general property of all superconductors. We can express it as the particle correlation function

$$\rho(\mathbf{r}, \mathbf{r}') = \langle \psi^\dagger_\alpha(\mathbf{r}) \psi^\dagger_\beta(\mathbf{r}) \psi_\alpha(\mathbf{r}') \psi_\beta(\mathbf{r}') \rangle \tag{1}$$

where $\psi^\dagger_\alpha(\mathbf{r})$ and $\psi_\alpha(\mathbf{r})$ are field operators for creating and annihilating a particle at position $\mathbf{r}$ with momentum and spin state α. Electrons in Cooper pairs have opposite spin and momentum, $\alpha = -\beta$. With the limit of $|\mathbf{r} - \mathbf{r}'| \to \infty$, the correlation function is written as

$$\rho(\mathbf{r}, \mathbf{r}') = \langle \psi^\dagger_\downarrow(\mathbf{r}) \psi^\dagger_\uparrow(\mathbf{r}) \rangle \langle \psi_\downarrow(\mathbf{r}') \psi_\uparrow(\mathbf{r}') \rangle \tag{2}$$

In superconductors, ODLRO denotes the onset of superconducting state

$$\rho(\mathbf{r}, \mathbf{r}') \begin{cases} = 0 & T > T_c \\ \neq 0 & T \leq T_c \end{cases} \tag{3}$$

Thus, the ODLRO corresponds to a non-vanishing expectation value of local pair amplitude $\langle \psi_\downarrow(\mathbf{r}') \psi_\uparrow(\mathbf{r}') \rangle$. It is consistent with the claim about the Landau-Ginzberg order parameter $\Psi(\mathbf{r})$ we made before. In momentum space, we will have $\langle c_\mathbf{k} c_{-\mathbf{k}} \rangle \sim \Psi(\mathbf{k}) \sim \Delta(\mathbf{k})$.

ODLRO exists in all kinds of superconductors. So the energy gap $\Delta(\mathbf{k}) \sim \langle c_\mathbf{k} c_{-\mathbf{k}} \rangle$ is well-defined in high-T_c superconductors, although there is no correspondence between $\Delta(\mathbf{k})$ and quasi-particle excitation spectrum. $\Delta(\mathbf{k})$ does describe the pairing the state in cuprates.

The onset of ODLRO is always accompanied by some kind of symmetry breaking. We know that without magnetic field, the normal to superconducting phase transition is of second order. Thus the symmetry breaking should be continuous at transitions. We can use ODLRO, order parameter $\Psi(\mathbf{k})$, energy gap $\Delta(\mathbf{k})$ as a measure of symmetry breaking in the superconducting phase.

The symmetry group describing the superconducting state H must be a subgroup of the whole symmetry group G describing the normal state:

$$G = X \otimes R \otimes U(1) \otimes T \tag{4}$$

and

$$H \subseteq G \tag{5}$$

where X is the symmetry group of crystal lattice, R is the symmetry group of spin rotation, $U(1)$ is the global gauge symmetry and T is the time reversal symmetry. As we know, in BCS superconductors, $U(1)$ is spontaneously broken in superconducting phase. In cuprates, one or more symmetries, in addition to $U(1)$ are broken at T_c. The degree of symmetry breaking is reflected in the symmetry property of gap function $\Delta(\mathbf{k})$. According to Landau theory of second-order phase transition, the order parameter describing the transition must transform according to one of the irreducible representation of symmetry group of high-temperature phase. We can expand $\Delta(\mathbf{k})$ by the basis function $\chi_\mu^j(\mathbf{k})$ of the irreducible representation Γ^j of group G:

$$\Delta(\mathbf{k}) = \sum_{\mu=1}^{l_j} \eta_\mu \chi_\mu^j(\mathbf{k}) \tag{6}$$

where l_j is the dimensionality of Γ^j. For simplicity, we can assume that $\Delta(\mathbf{k})$ transforms as the identity representation of R and T. Thus we can take G to be given by $X \otimes U(1)$.

2.2 Structure of cuprates and candidate pairing symmetry

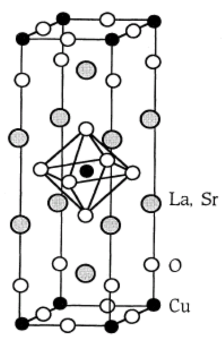


Figure 1: Crystal structure of $La_{2-x}Sr_xCuO_4$

First let's look at the lattice structure of cuprates (Figure 1). As we can see, $La_{2-x}Sr_xCuO_4$ are tetragonal crystals. They have CuO_2 planes, seperated by layers of other atoms. In general, CuO_2 plane is a common property of all cuprates. It is believed that the superconductivity process mainly occurs in CuO_2 planes. And other layers function as charge reservoirs, providing electrical carriers (electrons or holes). Thus the gap function $\Delta(\mathbf{k})$

is restricted to the k_x-k_y plane. Its symmetry should reflect the symmetry of Cu-O lattice.

Cuprates, such as $La_{2-x}Sr_xCuO_4$ have a tetragonal crystal structure. The Cu and O atoms form square lattice. It has a symmetry of C_{4v}. In other cuprates with a orthorhombic structure, such as YBCO, The CuO_2 planes take the form of rectangular lattice with a symmetry of C_{2v}. The structures and corresponding symmetry operations of these two are shown in Figure 2.

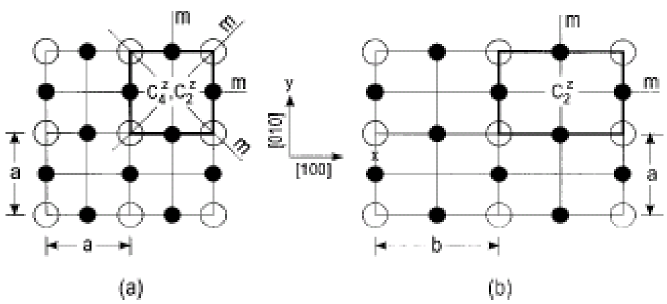


Figure 2: A schematic of CuO_2 planes: (a)square; (b)rectangular.

Here we will concentrate our study on square lattice. The group C_{4v} consists of the following symmetry operation elements: mirror reflections (m) with respect to lines $x = 0$, $y = 0$ and $x = \pm y$; a fourfold (C_4) and a two-fold (C_2) rotation about the c-axis. By subtracting C_4 and reflections along the diagonals, we get the C_{2v} symmetry group of rectangular lattice. According to the group representation theory, we arrive at the following candidate pairing states for C_{4v} (Figure 3). The actual pairing states will be

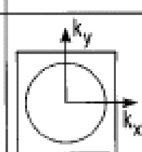
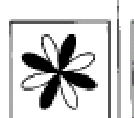
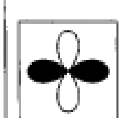
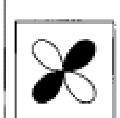
Group-theoretic notation	A_{1g}	A_{2g}	B_{1g}	B_{2g}
Order parameter basis function	constant	$xy(x^2-y^2)$	x^2-y^2	xy
Wave function name	s-wave	g	$d_{x^2-y^2}$	d_{xy}
Schematic representation of $\Delta(k)$ in B.Z.				

Figure 3: Candidate states for C_{4v} symmetry: black and white represent opposite signs of order parameter.

determined by experiments.

3 Phase-sensitive experiments

In this section, we will concentrate on experimental confirmation of $d_{x^2-y^2}$ pairing in cuprates. In short, we need to make distinctions between two leading candidate states: anisotropic s-wave and $d_{x^2-y^2}$ wave. Their order parameter (energy gap) is expressed as:

$$[d_{x^2-y^2} \text{ wave}]\Delta(\mathbf{k}) = \Delta_0[\cos(k_x a) - \cos(k_y a)] \tag{7}$$

$$[\text{anisotropic } s\text{-wave}]\Delta(\mathbf{k}) = \Delta_0[\cos(k_x a) - \cos(k_y a)]^4 + \Delta_1 \tag{8}$$

They, along with the isotropic s-wave, are drawn in Figure 4.

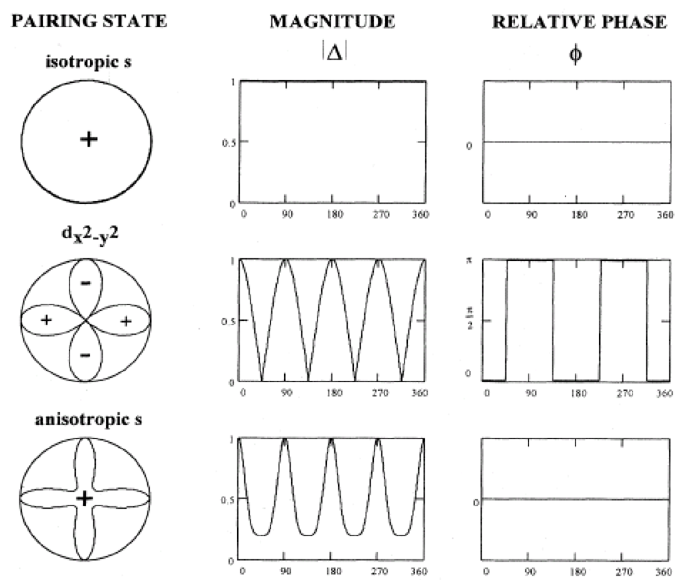


Figure 4: Magnitude and phase of superconducting order parameter as a function of $\mathbf{k}$.

Early experiments, such ARPES, only measure the magnitude of gap function (so as referred to magnitude-sensitive tests). Although they did give a highly anisotropic picture of order parameter, they cannot distinguish the anisotropic s-wave from $d_{x^2-y^2}$ wave.

Investigating on Figure 4, we find that the two states are clearly distinguished by their phases. The s-wave has a uniform phase, while the d-wave exhibits discontinuous jumps of π at (110) lines. This observation is the fundamental of the several following phase-sensitive experiments, which provide direct evidence of d-wave pairing in cuprates.

3.1 DC SQUID interference

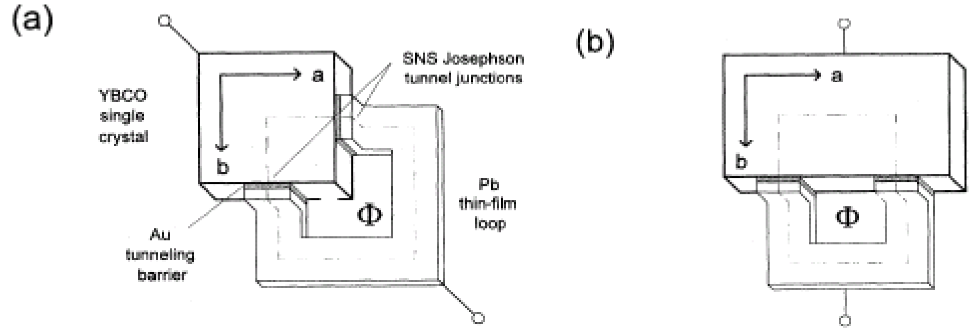


Figure 5: Design of *dc* SQUID experiments: (a) corner SQUID to determine the relative phase between orthogonal directions. (b) edge SQUID used a control sample.

The experiment setup is shown in Figure 5. We build Josephson junctions on two orthogonal faces of a high-T_c superconductor single crystal (YBCO). The two junctions are connected by a loop of a conventional s-wave superconductor. This circuit form a two-junction interferometer that can be used to study the pairing symmetry.

According to *dc* Josephson effect, the supercurrent in a Josephson junction satisfies

$$I = I_c \sin\gamma \tag{9}$$

where I_c is called the critical supercurrent, the maximum current with a zero voltage bias, and γ is the gauge-invariant phase difference

$$\gamma = \varphi_L - \varphi_R + \frac{2\pi}{\Phi_0}\int_L^R (A)\cdot \mathbf{d}l \tag{10}$$

where Φ_0 is the flux quantum $\pi\hbar c/e$.

So, in the above *dc* SQUID, we'll have

$$I = I_{ca}\sin\gamma_a + I_{cb}\sin\gamma_b \tag{11}$$

subject to the phase constraints

$$\gamma_a - \gamma_b + 2\pi\frac{\Phi}{\Phi_0} + \delta ab = 0 \tag{12}$$

where Φ is the magnetic flux in the loop and δ_{ab} is the intrinsic phase shift inside the YBCO. If we neglect the loop's self inductance, then $\Phi = \Phi_{ext}$. Further we assume that $I_{ca} = I_{cb} = I_0$ By simple calculation, we find

$$I_c(\Phi_{ext}) = 2I_0|\cos(\pi\Phi_{ext}/\Phi_0 + \delta_{ab}/2)| \tag{13}$$

If YBCO has s-wave symmetry, $\delta_{ab} = 0$ and the circuit is the same as an ordinary dc SQUID. The critical current I_c has the maximum value for zero applied field. In contrast, for $d_{x^2-y^2}$ symmetry, $\delta_{ab} = \pi$. Thus, at zero flux, I_c is the minimum 0.

The experiment results are shown below (Figure 6). We see that $d_{x^2-y^2}$ symmetry dominates in the pairing state of YBCO.

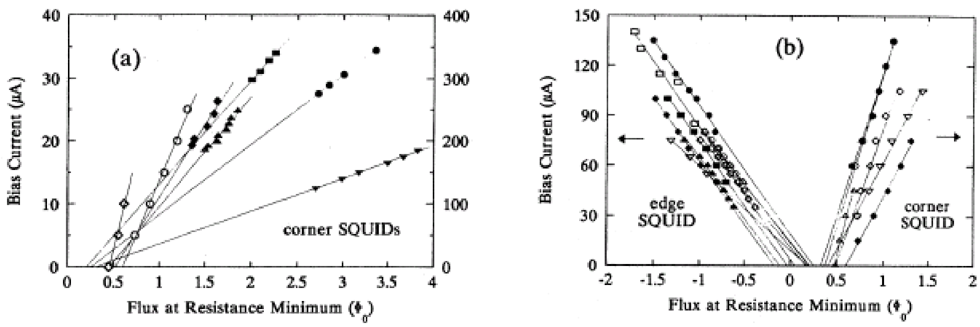


Figure 6: Results for dc SQUID experiments: (a) Extrapolation to zero bias current for different samples: an intercept of $\Phi/2$ indicates a $d_{x^2-y^2}$ symmetry. (b) Comparison of corner SQUID and edge SQUID: edge SQUID extrapolates to zero, while corner SQUID extrapolates to $\Phi/2$

3.2 Single Josephson junction modulation

Consider a rectangular junction with length L, W, D in $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ direction respectively. D is the thickness between two superconductors. Applying a magnetic field B in $\mathbf{y}$ direction, we can choose the vector potential $\mathbf{A}$ as $A_z = Ax$. By using Eq.(10), and integrating from $-L/2$ to $L/2$ in $\mathbf{x}$ direction, we finally get the supercurrent

$$I_s = J_0 \frac{\sin(\pi\Phi/\Phi_0)}{(\pi\Phi/\Phi_0)} \sin(\varphi_R - \varphi_L) \tag{14}$$

where $J_0 = j_0 LW$, j_0 is the current density, and $\Phi = BLD$ is the magnetic flux through the junction. Thus the critical current

$$I_c(\Phi) = J_0 \left|\frac{\sin(\pi\Phi/\Phi_0)}{(\pi\Phi/\Phi_0)}\right| \tag{15}$$

We test the pairing symmetry on the corner junction. Then the tunneling is partly into a-c face and partly into b-c face. The magnetic field is applied along the c-direction. If we have s-wave pairing, I_c satisfies the same equation as Eq. (15), featuring the maximum at zero applied field. For d-wave symmetry, the critical current modulates as

$$I_c(\Phi) = J_0 \left| \frac{\sin^2(\pi\Phi/2\Phi_0)}{(\pi\Phi/2\Phi_0)} \right| \tag{16}$$

Thus at zero flux, $I_c = 0$

It's claimed this single-junction modulation approach has great practical advantages over the *dc* SQUID tests, because it avoids a lot of complicated issues in data interpretation. The results are shown in Figure 7. The dip in the corner junction test is a strong evidence for $d_{x^2-y^2}$ pairing.

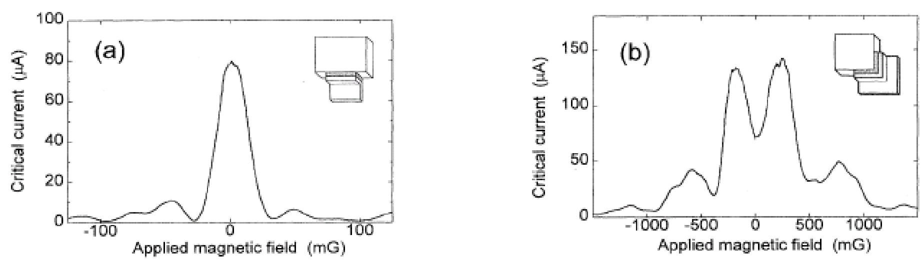


Figure 7: Results for single-junction modulation experiments: (a) edge junction; (b) corner junction

In fact, we can think of the single-junction modulation as an analogue of one-slit diffraction in optics. And Eq.(15) is just the formula of Fraunhaufer diffraction. Similarly, the previous *dc* SQUID is just like two-slit interference.

3.3 Half-integer flux quantum effect

We know that the magnetic flux is quantized in superconductors. It follows directly from Ginzberg-Landau equation.

$$\Phi = \int_S \mathbf{B} \cdot d\mathbf{S} = n\Phi_0 \tag{17}$$

But an odd number of π shifts will spontaneously generate a half-integer flux quantization.

$$\Phi = (n + 1/2)\Phi_0 \tag{18}$$

This is called *half-integer flux quantum effect.*

By MBE techniques, Tsuei *et al.* firstly fabricated a YBCO ring made up of segments with different orientations. And they observed this half-integer flux quantization in this ring, which is the strongest evidence for $d_{x^2-y^2}$ pairing so far.

4 Theory work on Hubbard model

Hubbard model is believed to capture the essence of strong correlated electrons in cuprates. It is expressed as

$$H = -\sum_{i,j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i} n_i \tag{19}$$

where $t_{ij} = t$ if (i, j) are the nearest-neighbor sites and zero otherwise, U is the one-site Coulomb repulsion, and μ is the chemical potential. Consider the retarded Green function

$$\langle\langle c_{i\uparrow}; c_{j\downarrow}\rangle\rangle = \theta(t-t')\langle\{c_{i\uparrow}(t), c_{j\downarrow}(t')\}\rangle \tag{20}$$

where $\theta(t - t')$ is the Heaviside function, and $\{A, B\}$ denotes the anticommutator. Its equation of motion is

$$\omega\langle\langle c_{i\uparrow}; c_{j\downarrow}\rangle\rangle = \langle\{c_{i\uparrow}, c_{j\downarrow}\}\rangle + \langle\langle[c_{i\uparrow}, H]; c_{j\downarrow}\rangle\rangle \tag{21}$$

where H is the Hamiltonian defined in Hubbard model Eq.(19), and $[A, B]$ denotes the commutator. Calculate the commutator

$$[c_{i\sigma}, H] = U n_{i-\sigma} c_{i\sigma} + \sum_{j} t_{ij} c_{j\sigma} \tag{22}$$

$$[n_{i-\sigma} c_{i\sigma}, H] = U n_{i-\sigma} c_{i\sigma} + \sum_{j} t_{ij}(n_{i-\sigma} c_{j\sigma} + c^{\dagger}_{i-\sigma} c_{j-\sigma} c_{i\sigma} - c^{\dagger}_{j-\sigma} c_{i-\sigma} c_{i\sigma}) \tag{23}$$

So this equation of motion will not be closed. It involves infinite higher-order Green functions. This is the intrinsic difficulty of strong correlation.

What facilitates our calculation is to introduce two new operators

$$\eta_{i\sigma} = c_{i\sigma} n_{i-\sigma} \quad \xi_{i\sigma} = c_{i\sigma}(1 - n_{i-\sigma}) \quad c_{i\sigma} = \eta_{i\sigma} + \xi_{i\sigma} \tag{24}$$

These two operators describe composite excitations: $\eta_{i\sigma}$ describe an electron restricted to move on sites already occupied by an electron with opposite spin, while $\xi_{i\sigma}$ requires no occupancy on the sites. The commutator of $\eta_{i\sigma}$ and $\xi_{i\sigma}$ with the interaction part of Hubbard Hamiltonian yields $-(\mu - U)\eta_{i\sigma}$ and $-\mu\xi_{i\sigma}$, respectively. So they can be used to diagonalize the $t = 0$ Hubbard model. If we use this basis to compute correlation functions, all higher-order corrections will be multiplied by a hopping term t. Thus, in the limit of $t/U \ll 1$, where high-T_c superconductivity occurs, we can treat the kinetic energy as a perturbation. By this strong-coupling expansion, we will be able to calculate the correlation functions.

Due to the page limit here, I cannot go to the detailed computations performed in ref. 6, 8, 9. What they find is that the traditional correlation function, $\langle c_{i\uparrow}c_{j\downarrow}\rangle$ does not determine the pairing gap in 2D Hubbard model. Rather

$$\theta_{ij} = \langle c_{i\uparrow}c_{i\downarrow}n_{j\tau}\rangle = \langle \eta_{ij\uparrow}\eta_{ij\downarrow}\rangle \tag{25}$$

is the relevant anomalous correlation function that determines the $d_{x^2-y^2}$ pairing. Here $\eta_{ij\sigma}$ is defined as

$$\eta_{ij\sigma} = c_{i\sigma}n_{j\tau} \tag{26}$$

where (i, j) are nearest-neighbor sites.

One of their results regarding $d_{x^2-y^2}$ symmetry is shown below (Figure 8). It clearly shows the d-wave symmetry.

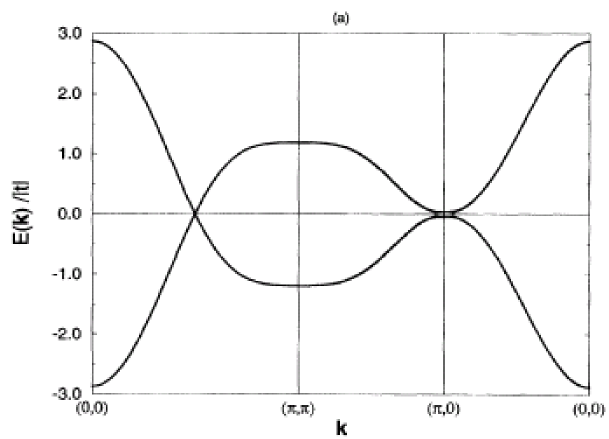


Figure 8: The energy spectrum of the Hubbard two bands

5 Final remarks

By now, we've shown, both theoretically and experimentally, a predominant d-wave pairing symmetry in high-T_c superconductors, namely cuprates. But there exists an inconsistency between the traditional correlation function $\langle c_{i\uparrow}c_{j\downarrow}\rangle$ and the anomalous correlation function θ_{ij} we introduced in Sec.4. Does this mean the pairing actually occurs between composite particles rather than the electrons? Present work seems to favor so. Moreover, this anomalous pairing requires that a double-occupied site neighbors a single-occupied site and the double occupancy will be shared between the two sites.

After 20 years of discovery, the mechanism of high-T_c superconductivity remains unsettled. In this systems, antiferromagnetism, pairing, spin-density-wave, charge-density wave, quantum phase transition all occur. There is no accepted analytical methodology. It is still a big challenge for physics researchers.

References

[1] D.J. Van Harlingen, Rev. Mod. Phys. **67,** 515 (1995)

[2] J. Annett, N. Goldenfeld and A. Leggett, cond-mat/9601060

[3] C.C. Tsuei and J.R. Kirtley, Rev. Mod. Phys. **72,** 969 (2000)

[4] Z.X. Shen *et al.* Phys. Rev. Lett. **70,** 1553 (1993)

[5] E. Dagotto, Rev. Mod. Phys. **66,** 763 (1994)

[6] T.D. Stanescu, I. Martin and P. Phillips, Phys. Rev. B **62,** 4300 (2000)

[7] L.M. Roth, Phys. Rev. **184,** 451 (1967)

[8] S. Avella *et al.* Int. J. Mod. Phys. B **12,** 81 (1998)

[9] J. Beenen and D.M. Edwards, Phys. Rev. B **52,** 13636 (1995)

[10] G.D. Mahan, *Many-Particle Physics* (2000)