2 Superconductivity

2.9 Unconventional superconductor

2.9.3 $d$-wave superconductor

Another interesting class of unconventional superconductor are those with very high transition temperatures.

In the 1980s, a breakthrough was made with the discovery of Cuprate superconducting materials with transition temperature up to $\sim 140k$. It was soon realized that superconductors with such high Tc cannot be described by the BCS theory because phonon cannot generate such strong attractive interactions. The exact mechanism of high Tc superconductors remains a topic of debate until today. Among the few less controversial features of high Tc superconductors is the pairing symmetry.

A large class of high Tc Superconductors were found in Cuprate compounds. Even though these are bulk materials, they have a layered structure with each layer being a two dimensional plane containing copper and oxygen. The coupling between the layers are very weak. Therefore, we can effectively treat the system as two dimensional. The Copper Oxygen plane has square lattice symmetry with one copper atom per each lattice site and one oxygen atom per each link.

Experimental evidence has shown that Cooper pairs in high Tc superconductors are in spin singlet states. Correspondingly, the order parameter $\Delta_k$ has to have even angular momentum. On a lattice, the Fermi surface is not entirely a circle, a better way to express $\Delta_k$ is as a function of $k$ instead of the angle $\theta$ on the Fermi surface. And the symmetry breaks down from full rotation symmetry to that of the square lattice and the order parameter forms a representation of this reduced symmetry.
Figure 1: Copper-Oxygen plane in Cuprate. Blue dots are Copper atoms and green dots are oxygen atoms.

Possible forms of $\Delta_k$ in the singlet pairing channel include

\[
\begin{align*}
\Delta_k &= \Delta, & (s) \\
\Delta_k &= \Delta(\cos k_x + \cos k_y)/2, & (s^-) \\
\Delta_k &= \Delta(\cos k_x - \cos k_y)/2, & (d_{x^2-y^2}) \\
\Delta_k &= \Delta \sin k_x \sin k_y, & (d_{xy})
\end{align*}
\]

which are all symmetric under $k \rightarrow -k$. The first case corresponds to a uniform over the Fermi surface and is naturally called the $s$-wave pairing. The second case is not quite rotationally invariant. In fact, it has nodal points at $k_x \pm k_y = \pm \pi$. It is still considered to be a subclass of $s$-wave pairing because when $k$ is small, $\Delta_k$ is approximately a constant ($\Delta$). Only when the Fermi surface is large and we take into account the restriction imposed by the lattice structure do we have this possibility of gap closing in $s$-wave pairing.

The third case is one possible form of $d$ wave pairing. The name $d_{x^2-y^2}$ comes from the fact that when $k$ is small, $\Delta_k$ is approximated by $\frac{-1}{4} \Delta (k_x^2 - k_y^2)$. If we have a circular Fermi surface, then $\Delta_k$ on the Fermi surface is proportional to $\cos^2 \phi - \sin^2 \phi = \cos 2\phi = (e^{i2\phi} + e^{-i2\phi})/2$. Therefore, this $\Delta_k$ belongs to the class of $d$ wave pairing and is labeled as $d_{x^2-y^2}$. The pairing gap closes at $k_x = \pm k_y$ and the gapless nodes always exists no matter how small the Fermi surface is.

The fourth case is another possible form of $d$ wave pairing. When $k$ is small, $\Delta_k$ is approximately $\Delta k_x k_y$. On a spherical Fermi surface, this is proportional to $2 \sin \phi \cos \phi = \sin 2\phi = \frac{i}{2} (e^{-i2\phi} - e^{i2\phi})$, hence a $d$ wave.

Given a material, like the Cuprate, how to distinguish between these pairing possibilities? First of all, the first case of uniformly gapped while the latter three all have gapless points. Therefore, by measuring the low energy density of states (through measurement of for example specific heat), one can distinguish between the first and the next three cases. Moreover, the $d$ wave pairing functions have different symmetry than the $s$ wave ones – under $\pi/2$ rotation in the $x - y$ plane, $d$ wave gets a minus sign while the $s$ wave does not. The two $d$ wave pairing functions are very similar. They only differ in the location of the nodal points. A straight forward way to distinguish them is through ARPES – Angle Resolved Photo Emission Spectroscopy, which is able to measure not only the energy but also the momentum of photo excited electrons hence mapping out the low energy spectrum. Another interesting approach is to use Josephson junctions. For unconventional superconductors whose pairing function is different at different locations on the Fermi surface, the properties of the junction would depend on the orientation of the crystal making up the junction.
This provides another way to tell the difference between different pairing functions.

Experimental evidence strongly suggests that in Cuprate, the actual pairing function is of the $d_{x^2−y^2}$ type. But what does this pairing symmetry tell us about the pairing mechanism, i.e. what leads to the formation of the Cooper pairs? The answer to this question is not entirely clear. It is generally expected that strong electron-electron correlation is responsible for the pairing in Cuprates, which can be seen from the generic phase diagram of Cuprate superconductors (and many other high Tc superconductors).

\begin{equation}
H = - \sum_{\langle i,j,\sigma \rangle} t_{ij} c_{i,\sigma}^\dagger c_{j,\sigma} + h.c. + U \sum_i n_{i\uparrow} n_{i\downarrow}
\end{equation}

In the undoped limit, if we look at the band structure of the copper-oxygen plane, we will see that the conduction band is half filled. Usually that means the system would be metallic. Instead, Cuprates are insulators and it is well understood that this originates from the strong electron-electron repulsion such that the system enters the Mott insulating state with one electron per lattice site (exactly half filling). Now as an Mott insulator, even though the electrons do not move any more, they can still interact in the spin channels. And it is known that in a Mott insulator the induced spin interaction is of the anti-ferromagnetic form and on an un-frustrated square lattice, anti-ferromagnetic order is formed and remains a stable phase with finite increase of temperature and doping.

The two directions of doping corresponds to adding extra electrons and adding extra holes. With finite doping, the system becomes metallic which is susceptible to the formation of Cooper pairs and a superconducting dome appears. If we keep increasing the doping, the superconductivity is killed and the system becomes a normal metal (Fermi liquid). But the phase diagram also contains other parts whose nature has been under intense debate. There is a Pseudogap part with small density of states. A popular theory is that in the Pseudogap phase there are pre-formed Cooper pairs but their phase fluctuate so much there is no symmetry breaking yet. The pre-formed Cooper pairs opens up a gap on part of the Fermi surface, reducing it to Fermi arcs. Another phase at a higher doping is the strange metal (non-Fermi liquid) phase. It is called ‘strange’ because of its unusual properties. For example, the resistivity at low temperature scales as $T$ instead of $T^2$ as in a usual metal.

It is believed that the fundamental model describing all these phases is the simple Fermi Hubbard model
Although the model looks very simple, it is extremely difficult to analyze. The study regarding its phase diagram and its relation to high Tc superconductor is still an ongoing project in condensed matter research today.

### 2.9.4 Particle Hole symmetry

The BdG Hamiltonian of superconductors has a special property called the ‘Particle Hole Symmetry’. Consider, for example, the Hamiltonian of the 1D Majorana chain which in terms of momentum modes takes the form

$$
H = \frac{1}{2} \sum_k \begin{pmatrix} c_k & c_{-k} \end{pmatrix} \begin{pmatrix} 2t \cos k - \mu & \Delta \sin k \\ \Delta^* \sin k & -2t \cos k + \mu \end{pmatrix} \begin{pmatrix} c_k \\ c_{-k}^\dagger \end{pmatrix}
$$

(6)

If we call the $2 \times 2$ matrix for each $k H(k)$, then the particle hole symmetry is manifested as

$$
\sigma_x H^*(k) \sigma_x = -H(-k)
$$

(7)

which implies that the eigenvalues of $H(k)$ and that of $H(-k)$ come in opposite pairs. So if we look at the spectrum of $H$ as a whole, it comes in opposite pairs. This does not mean that each energy level of the system is doubly degenerate. Instead, it is due to the redundancy in writing down the Hamiltonian.

This symmetry has concrete meaning when we consider the spectrum on an open chain. There, we cannot decompose into momentum eigenmodes any more, but we can still identify a ‘particle hole symmetry’ which acts as

$$
CH^*C = -H
$$

(8)

The spectrum hence still comes in pairs. But if there is one level that is at exactly zero energy, this level cannot be moved away, guaranteeing the stability of the Majorana zero mode in the Majorana chain.

### 3 Symmetry Protected Topological Phase

Having discussed the Majorana chain model, a similar picture can help us understand topological phases in a more general interacting setting.

#### 3.1 Haldane phase in 1D

The spin 1 chain with anti-ferromagnetic Heisenberg interaction provides the first and simplest example of symmetry protected topological order. Consider the Hamiltonian

$$
H = \sum_i \vec{S}_i \cdot \vec{S}_{i+1}
$$

(9)

where $\vec{S}$ is the spin 1 operator

$$
S^x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},
S^y = \frac{i}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix},
S^z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}
$$

(10)
This Hamiltonian has a rich symmetry, including spin rotation and time reversal ($\vec{S} \rightarrow -\vec{S}$).

What is the ground state like? For classical spin, anti-ferromagnetic interaction leads to Neel order, with spins ordered as $\uparrow\downarrow\uparrow\downarrow\ldots$. In 1D quantum chains, long range order cannot survive and usually gets reduced to power law decaying correlation. This is what happens in anti-ferromagnetic Heisenberg spin $1/2$ chain, which is known to be gapless. For the spin $1$ chain, it was thought to be gapless as well until Haldane pointed that it should actually be gapped. Moreover, as we are going to see below, it has symmetry protected topological order!

The Heisenberg model is very hard to solve and the existence of a gap remained a controversy for quite some time. On the other hand, exact ground state can be found for a slightly modified Hamiltonian proposed by Affleck, Kennedy, Lieb and Tasaki (AKLT).

$$H = \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + \frac{1}{3} \left( \vec{S}_i \cdot \vec{S}_{i+1} \right)^2$$  \hspace{1cm} (11)