# $\hat{H} = -\sum_{\langle ij \rangle} J\mathbf{S}_i \cdot \mathbf{S}_j$ and $|\Psi\rangle_{BCS}$
## aka Magnetism and superconductivity

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December 2023

## 1 Ferromagnetic theory

As we know there exist many type of interactions operating between different magnetic moments which lead to different ground states such as ferromagnetism, antiferromagnetism, helical order ecc. A ferromagnet has a spontaneous magnetization even without external magnetic field. We now that all the magnetic properties mainly come from exchange interaction (double or super). The proper Hamiltonian for ferromagnetism in presence of external field is:

$$\hat{H} = -\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_{j} \mathbf{S}_j \cdot \mathbf{B}$$

so the Heisenberg model plus the Zeeman energy. In order to solve this problem we make the following hypothesis:

$$\mathbf{B}^i_{mf} = -\frac{2}{g\mu_B} \sum_{j} J_{ij}\mathbf{S}_j$$

this is the molecular field felt by the i-th site in the crystal. The exchange interaction between the i-th spin and its neighbours is:

$$-2\sum_{j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j = -2\mathbf{S}_i \cdot \sum_{j} J_{ij}\mathbf{S}_j = g\mu_B \mathbf{S}_i \cdot \mathbf{B}_{mf}$$

The total Hamiltonian becomes:

$$\hat{H} = g\mu_B \sum_{i} \mathbf{S}_i \cdot \mathbf{B}_{mf} + g\mu_B \sum_{j} \mathbf{S}_j \cdot \mathbf{B}$$

$$\hat{H} = g\mu_B \sum_{i} \mathbf{S}_i \cdot (\mathbf{B} + \mathbf{B}_{mf})$$

The molecular field felt by all magnetic moments measures the effect of magnetization. It can be expressed by:

$$\mathbf{B}_{mf} = \lambda\mathbf{M}$$

Finally, the hypothetical Hamiltonian for our system is:

$$\hat{H} = g\mu_B \sum_{i} \mathbf{S}_i \cdot (\mathbf{B} + \lambda\mathbf{M})$$

At low temperature , the magnetic mean field can align the magnetic moments even without external magnetic field. At higher temperature thermal fluctuation begin to progressively destroy the magnetization. This model is known as Weiss Model. We can use the quantum model for paramagnetic material:

$$\frac{M}{M_s} = B_J(y) \qquad y = \frac{g_J\mu_B J}{k_B T}(B + \lambda M)$$

At low $y$, we can approximate the Brillouin function as:

$$B_J(y) = \frac{J+1}{3J}y + o(y^3)$$

therefore in case of zero external magnetic field we can make some predictions. First consider the system of magnetization and y value:

$$\begin{cases} M = n\mu \cdot B_J(y) \\ y = \frac{g_J\mu_B J}{k_B T}\lambda M \to M(y) \end{cases}$$

We can see that, exists a critical value of $T$ for which the solution is triple degenerate. This corresponds to the case for which the slope of the Brillouin function is proportional to the slope of the straight line:

$$\frac{J+1}{3J} = \frac{k_B T_c}{\lambda\mu g_J\mu_B J}$$

and remember that the magnetization at saturation is :

$$M_s = n\mu_B g_J J$$

we have:

$$T_c = \frac{g_J\mu_B(J+1)\lambda n\mu}{3k_B} = \frac{n\lambda\mu_{eff}^2}{3k_B}$$

$$\mu_{eff} = g_J\mu_B\sqrt{J(J+1)}$$

We can also calculate the magnetic susceptibility. In the case of small B at high temperature the Brillouin function can be linearized:

$$\frac{M}{M_s} = \frac{k_B T_c}{\lambda\mu g_J\mu_B J} \cdot \frac{g_J\mu_B J}{k_B T}(B + \lambda M)$$

$$\frac{M}{M_s} = \frac{g_J\mu_B(J+1)}{3k_B}\left(\frac{B+\lambda M}{T}\right)$$

If we multiply and divide by $\lambda M_s$ we can use the expression of $T_c$:

$$\frac{M}{M_s} = \frac{T_c}{\lambda M_s}\left(\frac{B+\lambda M}{T}\right)$$

$$\frac{M}{M_s} - \frac{M T_c}{M_s T} = \frac{T_c B}{T\lambda M_s}$$

$$\frac{M}{M_s}\left(1 - \frac{T_c}{T}\right) = \frac{T_c}{T} \cdot \frac{B}{\lambda M_s}$$

$$\frac{M}{M_s}\frac{T-T_c}{T_c} = \frac{B}{\lambda M_s}$$

$$\frac{M}{M_s} = \frac{B T_c}{\lambda M_s}\frac{1}{T-T_c}$$

Remember that $M = \chi H$ and $B = \mu_o H$ therefore $\chi = \mu_o M/B$:

$$\chi = \lim_{B\to 0}\frac{\mu_o}{B}\frac{B T_c}{\lambda}\frac{1}{T-T_c} \propto \frac{1}{T-T_c}$$

known as **Curie Weiss law**.

In the case of external magnetic field, the phase transition is removed since there exists a finite magnetization for any value of temperature. We can demonstrate that $M \propto B^{1/3}$.

The molecular field comes from the exchange interaction. If we consider only the z neighbours, from the expression of $\mathbf{B}_{mf}$:

$$M = n\mu_B g_s S_i$$

$$\lambda M = \frac{2}{g_s\mu_B}z J_{ex} S_i$$

and so the field parameter is:
$$\lambda = \frac{2zJ_{ex}}{n\mu_B^2 g_s^2}$$
$$T_c(J_{ex}) = \frac{ng_J^2\mu_B^2 J(J+1)\lambda}{3k_B} = \frac{ng_J^2\mu_B^2 J(J+1)}{3k_B} \cdot \frac{2zJ_{ex}}{n\mu_B^2 g_s^2} = \frac{2zJ_{ex}J(J+1)}{3k_B}$$

Our discussion so far has the hypothesis of $L = 0$ and $J = S$. This works well for most of the 3d ions because the quenching of angular momentum. In 3d transition metals the crystal field is much stronger than the spin-orbit interaction and the third Hund's law doesn't hold. For 4f ions, the orbitals are much less extended so the crystal field term is negligible. The typical eigenfunctions associated to octahedral potential can be expressed by real functions. The ground state $|0\rangle$ is real function while the orbital momentum is a pure imaginary operator $-i\mathbf{r} \times \nabla$. The expected value of $\hat{\mathbf{L}}$ can take just one value for the ground state:

$$\langle 0| \hat{\mathbf{L}} |0\rangle = 0$$

So for the 3d TM the $\hat{\mathbf{S}}$ is a good quantum number. If now we consider the 4f TM $\hat{\mathbf{S}}$ is no more conserved and we must consider the sum of spin and orbital momentum $\hat{\mathbf{J}}$. The component of $\hat{\mathbf{S}}$ which is parallel to $\hat{\mathbf{J}}$ is conserved. We can demonstrate that this value is $(g_J - 1)\hat{\mathbf{J}}$. The interaction Hamiltonian is then:

$$\hat{H} = -\sum_{ij}(g_J - 1)^2 J_{ij}\mathbf{J}_i \cdot \mathbf{J}_j$$

The molecular parameter and the critical temperature is

$$\lambda = \frac{2zJ_{ex}}{n\mu_B^2 g_J^2}(g_J - 1)^2$$

$$T_c(J_{ex}) = \frac{2zJ_{ex}J(J+1)}{3k_B}(g_J - 1)^2$$

# 2 Antiferromagnetism

For negative exchange interaction, $J < 0$, we have antiferromagnetic ordering. It is better for the nearest neighbour moments to lie antiparallel. The molecular field can be expressed on the two sublattices:

$$B_+ = -\lambda|M|_-$$
$$B_- = -\lambda|M|_+$$

and the magnetization, using the usual Brillouin function:

$$M_\pm = M_s B_J\left(\frac{g_j\mu_B J|\lambda|M_\mp}{k_B T}\right)$$

We can find the critical temperature, defined as Neel temperature:

$$T_N = \frac{n|\lambda|\mu_{eff}^2}{3k_B}$$

We can evaluate the effect of a strong magnetic field placed parallel to the magnetizations. We can observe experimentally that above a critical field, called spin-flop field, the system snaps into another configuration where the angle between the external magnetic field and the magnatization directions is $\theta$ and $\phi$. Let us consider the energy associated to this type of system:

$$E = -MB\cos(\theta) - MB\cos(\phi) + AM^2\cos(\theta + \phi) - \frac{1}{2}\Delta(\cos^2(\theta) + \cos^2(\phi))$$

The first two terms are related to Zeeman splitting, second one to the exchange coupling and the last one models the magnetic anisotropy. Two possible configuration:

- $\theta = 0$ and $\phi = \pi$, perfect antiferromagnetism with energy:

$$E = -AM^2 - \Delta \qquad \text{doesn't depend on } B$$

- $\theta = \phi$, the energy is:

$$E = -2MB\cos(\theta) + AM^2\cos(2\theta) - \Delta\cos^2(\theta)$$

One minima can be cal$\partial E/\partial\theta = 0$ (ignoring the anisotropy term):

$$\theta_{min} = \arccos(\frac{B}{2AM})$$

The system decides to stay in the normal configuration until the external magnetic field reaches the critical field such that:

$$E_{AFM} > E_{SF}(\theta)$$

An interesting magnetic order is the "Helical order". We consider the nearest neighbours and the next nearest neighbours ($J_1$ and $J_2$). We use the Heisenberg Hamiltonian:

$$E = -2NJ_1 S \cdot S \cos(\theta) + J_2 S \cdot S \cos(2\theta)$$

and it is minimized for $\partial E/\partial\theta = 0$:

$$(J_1 + 4J_2\cos(\theta))\sin(\theta) = 0$$

$$\cos(\theta) = -\frac{J_1}{4J_2} \qquad \text{stable configuration for } |J_1| < 4|J_2|$$

## Interesting case of $D = 1$ and $d = 1$

We start from the Heisenberg Hamiltonian for one dimensional lattice and two possible value of the spins, $1/2$ and $-1/2$. The Hamiltonian (called Ising model), is:

$$\hat{H} = -2J\sum_{i=1}^{N} S_i \cdot S_{i+1}$$

The ground state is that for $S = 1/2$. If we add a small perturbation on the chain, for example one spin is reversed $\Delta S = 1/2 + 1/2$, the cost will be $E = J\Delta S = J$. Since this defect is delocalized along the chain (every site is the same), the entropy is $S = k_B \ln N$ and the Helmoltz free energy diverges:

$$S \to \infty \qquad F = E - TS \to -\infty$$

we can conclude that no long range appears for $T > 0$.

# 3    Pauli paramagnetism and Stoner criterion

Let now consider magnetism in metals. From an inspection of iron magnetic properties we see that the relative magnetic momentum is $2.2\mu_B$ so the usual description doesn't hold. We start from a free electron model:

$$E(k) = \frac{\hbar^2 k^2}{2m^*}$$

The number of state per unit wave number is simply $1/8\pi^3$ per unit volume. We can calculate the density of states in k space, that is:

$$g(k)dk = 4\pi k^2 \frac{1}{8\pi^3} dk$$

In the energy space we must have:

$$g(E)dE = g(k)dk$$

and therefore we can differentiate the expression for the energy $dE = \hbar^2 k/m^* dk$ to calculate $g(E)$, including the spin degeneracy:

$$g(E) = g(k) \cdot \frac{dk}{dE} = 2\frac{k^2}{2\pi^2} \cdot \frac{m^*}{\hbar^2 k} = \frac{1}{2\pi^2}(\frac{2m^*}{\hbar^2})^{3/2}\sqrt{E}$$

As usual we can now calculate the density of electrons by integrating over $[0; E_F]$ for $T = 0K$:

$$n = \int_0^{E_F} g(E)dE$$

In the general case we must take in account the Fermi distribution and we have:

$$n = \int_0^{\infty} \frac{1}{e^{\frac{E-\mu}{k_B T}} + 1} g(E)dE$$

The density of state at the Fermi vector is:

$$g(E_F) = g(k_F)(\frac{dk}{dE})_{k=k_F} = \frac{m^*}{\hbar^2 \pi^2}k_F$$

The density of electron from the k-space is simply:

$$n = \int_0^{k_F} \frac{k^2}{\pi^2}dk = \frac{1}{3\pi^2}k_F^3$$

and therefore:

$$k_F^3 = 3\pi^2 n$$

The electron are doubly degenerate because of the spin. An external magnetic filed breaks this degeneracy into two subbands separated by $2 \cdot \mu_B B$. The density of electrons with spin-up is $n_\uparrow = \frac{1}{2}g(E_F)\mu_B B$ and $n_\downarrow = \frac{1}{2}g(E_F)\mu_B B$. The Zeeman splitting is defined as:

$$\Delta E = -\mu_o \vec{H} \cdot \vec{\mu} \qquad \mu = -\mu_B B m_j$$

The net result is:

$$M = \mu_B(n_\uparrow - n_\downarrow) = g(E_F)\mu_B^2 B$$

The related susceptibility, defined as $M = \chi B/\mu_o$:

$$\chi_P = \frac{M}{B}\mu_o = \mu_o \mu_B^2 g(E_F)$$

Since:

$$n = \int g(E)dE \rightarrow g(E) = \frac{dn}{dE} \rightarrow g(E_F) = \frac{dn}{dE}|_{E=E_F} = \frac{3}{2}\frac{n}{E_F}$$

$$\chi_P = \mu_o \mu_B^2 \cdot \frac{3}{2}\frac{n}{E_F}$$

Note that the expression of Pauli paramagnetism is temperature independent since with started neglecting the Fermi smearing at $E_F$. The Pauli paramagnetism is much more weaker the the paramagnetism in insulators since only the electrons near Fermi surface play a role.

We want now to talk about ferromagnetism in metals. The magnetic moment in iron is a non-integer value. This can not be understand on the basis of localized moments. We start developing the theory of itinerant ferromagnetism. In the frame of Weiss model, we can say that exists a molecular field felt by any atom in the metal.

Let try to make the heuristic argument more rigorous. Suppose we take some electrons near the Fermi surface (within $\delta E$) with spin down and place them into the spin up band. The density of electrons moved will be $1/2 g(E_F)\delta E$. They increase in energy by $\delta E$ and therefore the system has an higher energy:

$$\Delta E_{KE} = \frac{1}{2}g(E_F)\delta E^2$$

Now we have a net magnetization and therefore we can calculate the molecular field energy:

$$\Delta E_{PE} = -\int_0^M \mu_o B_{mf} dM' = -\frac{1}{2}\mu_o \lambda M^2 = -\frac{1}{2}\mu_o \lambda(\mu_B(n_\uparrow - n_\downarrow))^2$$

In our discussion:

$$n_\uparrow = \frac{1}{2}n + \frac{g(E_F)\delta E}{2}$$

$$n_\downarrow = \frac{1}{2}n - \frac{g(E_F)\delta E}{2}$$

and the difference in population is:

$$\Delta n = g(E_F)\delta E$$

$$\Delta E_{PE} = -\frac{1}{2}\mu_o \lambda(\mu_B g(E_F)\delta E)^2$$

By defining the Coulomb parameter $U = \mu_o \mu_B^2 \lambda$:

$$\Delta E_T = \frac{1}{2}g(E_F)\delta E^2 - \frac{1}{2}U(g(E_F)\delta E)^2$$

$$\Delta E_T = \frac{1}{2}g(E_F)\delta E^2(1 - Ug(E_F))$$

We have spontaneous magnetization if this last expression is negative. This is called Stoner criterion:

$$U \cdot g(E_F) > 1$$

Let us add the additional term related to an external magnetic field. We have that:

$$\Delta E_T = \frac{1}{2}g(E_F)\delta E^2(1 - Ug(E_F)) - M \cdot B$$

The first term is implicit quadratic in $M$:

$$M = \mu_B(N_\uparrow - N_\downarrow) = g_s \mu_B \Delta N$$

We can now minimize the energy and we find that:

$$\chi = \frac{\chi_P}{1 - Ug(E_F)}$$

called Stoner enhancement. We can calculate the Landau susceptibility $\chi_L$ as:

$$\chi_L = -\frac{\chi_P}{3}$$

Therefore the total susceptibility in the free electron gas is positive and paramagnetism is ever present. If we consider the effective mass is possible to find:

$$\chi = \chi_P[1 - \frac{1}{3}(\frac{m_e}{m^*})^2]$$

It follows that, in real material is possible to find metallic diamagnetism, for example in the case of bismuth.

# Neutron diffraction

Note that the actual structure of AFM materials must be probed using neutron diffraction. In the case of FM material the derivation of spin distribution is trivial.

If you want to study the periodicity of the lattice, you need to use diffraction. Using Bragg condition:

$$N\lambda = 2d\sin(\theta)$$

so we have constructive interference for few values of angle $\theta$ related to two parameter $d$ and $\lambda$. The beam is deflected by an angle $2\theta$. Basically we need to place the detector at angle $2\theta$ with respect to the incoming beam. Usually we don't know $2\theta$.

It can be demonstrate that Bragg's law is equivalent to the von Laue condition:

$$\mathbf{k} - \mathbf{k}' = \mathbf{Q}$$

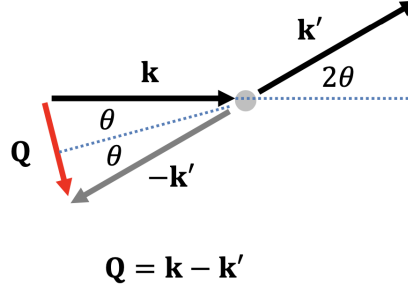where $\mathbf{Q}$ belongs to the reciprocal lattice.



Figure 1: Scattering event

So I have flux of something, elastically scattered by an ensemble of N scattering centers located at $\mathbf{R}_j$, with a rate:

$$R(2\theta, \phi) = \Phi| \sum_j f_j(\theta, \lambda) e^{-i\mathbf{Q}\cdot\mathbf{R}}|^2 d\Omega$$

where $f_j(2\theta, \phi)$ is the form factor. This expression is correct since we are dealing with neutrons which interacts with the nucleus. The cross-section is defined as:

$$\sigma = 2\pi \int_{2\theta=0}^{\pi} |f(2\theta, \phi)|^2 sin(2\theta) d(2\theta)$$

If $f_j$ is constant (same atoms), The square modulus expression can be written as:

$$|\sum_j e^{i\mathbf{Q}\cdot\mathbf{R}_j}|^2 \neq 0 \iff \mathbf{Q} \in \text{Reciprocal lattice}$$

For neutrons $f_j = 10^{-14}$. Note that neutrons have spin and therefore magnetic moment. For X-rays the form factor depends strongly on the number of electrons. For this reason we are not able to use x-rays for hydrogen since its cross section is really small.
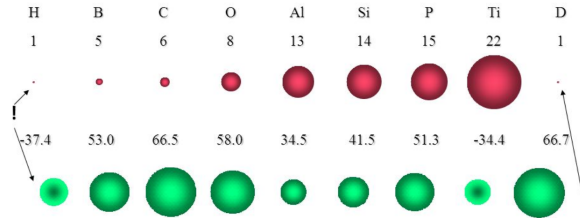


Figure 2: Different cross-section for X-rays and neutrons.

The scattering intensity is defined by the structure factor

$$F_{hkl} = \sum_n b_n e^{i[2\pi(hx+ky+lz)]}$$

from which we can also add the absorption term:

$$F_{hkl} = \sum_n b_n e^{i[2\pi(hx+ky+lz)]} e^{-W_n}$$

The main source of neutrons are nuclear reactors. The high energetic neutrons produced into the nucleus of the chamber are moderated using heavy water $D_2O$. Pipes are inserted to extract neutron for a given energy. Then to use this neutrons for scattering experiments, we select one energy using diffraction (of known material) and send them to the sample. We need to find the $2\theta$ angle for which we have constructive interference. Another possibility is to use powder. We send our monochromatic neutron beam. Since the crystals are randomly distributed, it is possible that one crystal is at the perfect angle $\theta$. We measure the diffracted angle ray $2\theta$ with a particular intensity and we can reconstruct the periodicity of the crystal.

# Bose Einstein Condensate

At the beginning of twelfth century, an Indian physicist Bose sent a letter to Einstein in which he developed a theory for the emission of black body radiation. He treated the electromagnetic field as a gas of identical particle. Einstein soon realized that the same method can be used for a gas of identical particle with mass. The key idea for quantum identical particle is that we can simply count the number of available state using combinatorics. If we have $N_s$ identical particles in $M_s$ states then the way in which the bosons can arrange is:

$$W_s = \frac{(N_s + M_s - 1)!}{N_s!(M_s - 1)!}$$

Let us take a gas of bosons in a volume $V$. The $\mathbf{k}$ values are quantized using periodic boundary condition. The quantum states contained in $d\mathbf{k}$ are then:

$$\frac{\#states(d\mathbf{k})}{d\mathbf{k}} = \frac{V}{(2\pi)^3}$$

Consider free particles with energy $\epsilon_k = \hbar^2 k^2/2m$, in three dimension the shell of radius $k_s$ with thickness $dk_s$ has:

$$M_s = 4\pi k_s^2 dk_s \frac{V}{(2\pi)^3} = g(\mathbf{k})d\mathbf{k}$$

Considering $g(\mathbf{k})d\mathbf{k} = g(\epsilon)d\epsilon$ we can calculate the DOS in energy space:

$$g(\epsilon) = \frac{m^{3/2}}{\sqrt{2}\hbar^3\pi^2}\sqrt{\epsilon}$$

In the limit of microcanonical ensemble, the occupation number of single particle states of energy $\epsilon_k$ is given by the Bose-Einstein distribution:

$$f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} - 1}$$

Unlike the classical ideal gas or the Fermi gas, Bose-Einstein ideal gas has a thermodynamic transition phase to the so called Bose-Einstein Condensate. This phase transition is driven by the particle statistics and not their interactions. Below a critical temperature $T_c$ part of the bosonic gas condensate and coexists with the normal bosonic gas. The ratio between the total density $n$ and the condensed one $n_o$ is given by:

$$\frac{n}{n_o} = 1 - (\frac{T}{T_c})^{3/2}$$

The condensed particles are not separated in space from the other by in momentum space. The condensed particles all occupy zero momentum state.

The density of particles is given by:

$$n = \int_0^\infty f_{BE}(\epsilon)g(\epsilon)d\epsilon$$

Since we usually know the density of particles and the temperature, this expression becomes an implicit equation in $\mu$. We can solve the integral:

$$n = (\frac{mk_BT}{2\pi\hbar^2})^{3/2}g_{3/2}(z)$$

where $z = e^{\beta\mu}$ and the function $g_{3/2}(z)$ is defined as:

$$g_{3/2}(z) = \sum_{p=1}^{\infty}\frac{z^p}{p^{3/2}}$$

At high T or low density, we can expand the function $g_{3/2}(z) \approx z + ...$ and we can express the chemical potential:

$$\mu \approx -\frac{3}{2}k_BTln(\frac{mk_BT}{2\pi\hbar^2n^{3/2}})$$

At $T_c$ (the previous approximation is not valid) the chemical potential becomes zero, i.e. the g-function becomes maximum:

$$T_c = (\frac{n}{2.612})^{2/3}\frac{2\pi\hbar^2}{k_Bm}$$

The zero energy state occupation is given by $f_{BE}(\epsilon_k = 0)$:

$$N_o = \frac{1}{e^{-\beta(\mu)} - 1}$$

therefore in the thermodynamic limit ($V \to \infty$ i.e. $N_o \to \infty$) the chemical potential is:

$$\mu \approx -k_BT\frac{1}{N_o} \approx 0$$

Below $T_c$ we must account separately the Bose condensate and the bosonic gas:

$$N = N_o + \sum_{\mathbf{k}\neq 0} f_{BE}(\epsilon_k)$$

As done before we calculate the particle density using the DOS excluding the $\mathbf{k} = 0$ point and we can obtain, for $T < T_c$:

$$n = n_o + 2.612(\frac{mk_BT}{2\pi\hbar^2})^{3/2}$$

$$\frac{n}{n_o} = 1 - (\frac{T}{T_c})^{3/2}$$

$$U = V \cdot \int \epsilon \cdot f_{BE}(\epsilon)g(\epsilon)d\epsilon$$

$$u = \frac{U}{N} = \frac{3}{2}k_BT \cdot \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

We can now calculate the specific heat for $T < T_c$ and obtain:

$$C_v \propto T^{3/2}$$

## 3.1 Realization of BEC

Two main possibilities: Magnetic trapping or laser cooling. In second one the atoms are slowed using photons from laser source. High energy atoms absorb the photon along a particular direction. For conservation of momentum, the excited atom slow down because of recoil. The subsequent emission happens on random direction therefore the total effect is to slow down the atomic gas. The Doppler effect causes a shift in the frequency of light emitted or absorbed by an atom depending on its velocity relative to the observer. In laser cooling, the cooling mechanism relies on the fact that atoms moving toward a laser beam experience a higher frequency (blue-shifted), while atoms moving away
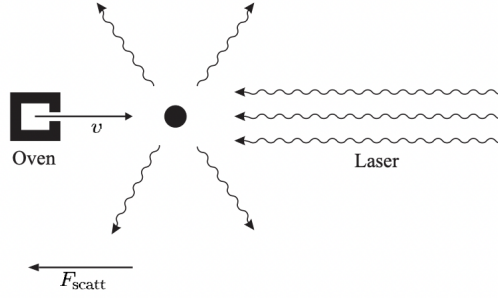
Figure 3: Laser cooling

experience a lower frequency (red-shifted). This differential frequency shift is used to selectively slow down the atoms in the direction of the laser beam. Therefore we can effectively select and slow down blue shifted atoms.

In order to create BEC we need to neglect inter-atomic interactions (remember that BEC is a pure statistical condensate). The first demonstration of BEC has been obtained in 1995 with $^{87}Rb$. Note that it has a very large mass, with respect He, and therefore we expect a very low critical temperature $T_c$ since $T_c \propto 1/m$. It has one unpaired electron in the s shell and the only other contribution to the total spin comes from the nucleus.

## Superfluid

From classical description we can derive that a particle has a momentum of order:

$$p = (2mk_BT)^{1/2}$$

Quantum mechanically, particles have a typical De Broglie wavelength $\lambda = h/p$, and therefore a thermal De Broglie wavelength of:

$$\lambda_{dB} = (\frac{2\pi\hbar}{mk_BT})^{1/2}$$

Quantum effects arise when the lattice parameter is in the order of $\lambda_{dB}$. In order to obtain superfluid phase we need a substance which doesn't solidify until very low temperature. For example, let us consider Ne. Gas phase condense at $27K$ and freeze at $24K$. Atomic mass is $20m_p$ and therefore $\lambda_{dB} \approx 0.07nm$. This value is not comparable with its lattice constant, therefore we can exclude superfluidity. If now consider He at low pressure it doesn't solidify but remains liquid. However it becomes liquid only at $4K$. This arise from its low well potential ($\epsilon_o = 1.03eV$). At $4K$ the $\lambda_{dB}$ becomes comparable with it lattice constant. But why is it that liquid He doesn't crystallize? Because quantum fluids have zero point motion. Their kinetic energy is different from zero even at absolute zero temperature. Let us consider the Einstein phonon model. The zero point energy for the oscillator is:

$$E_o = \frac{3}{2}\hbar\omega_o$$

Therefore the quantization of levels into the Lennard-Jones potential gives a frequency:

$$\omega_o = \sqrt{\frac{4k}{m}}$$

In the case of He, the zero point energy is $7meV$, therefore it corresponds to a thermal energy of $70K$, which tends to maintain liquid phase.

In the case of superfluid He, the specific heat at low temperature has a first order transition at $T_c$ and it is usually called lambda point. The behaviour of $c_V$ is perfectly in agreement with a theoretical model called *three dimensional XY-model*. The main point is that, multiple physical systems end up having identical set of critical exponent. In the case of He II $\alpha = -0.009$. Each point of the phase of system is characterized by a unit vector $\hat{n}$ characterized by a phase $\theta$ with respect to a direction. In superfluid phase all these vectors are aligned as in the case of magnetization.
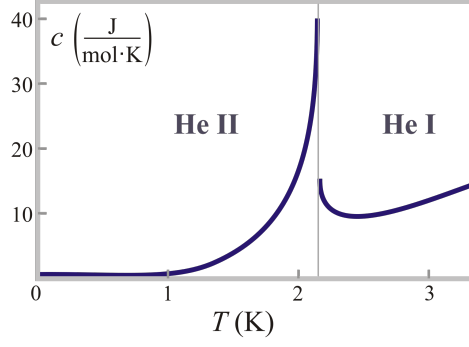
Figure 4: Lambda transition

We postulate the existence of a macroscopic wave function. Suppose to a have the superfluid phase in a region of He fluid. It correspond to a condensate into the wave function $\psi_o(\mathbf{r})$, such that:

$$n_o = |\psi_o(\mathbf{r})|^2$$

represent the density of particles in the condensate. Generally speaking, the wave function is a complex number, so can take.

$$\psi_o(\mathbf{r}) = |\psi_o(\mathbf{r})|e^{i\theta(\mathbf{r})} = \sqrt{n_o}e^{i\theta(\mathbf{r})}$$

We have superflow whenever $\theta(\mathbf{r})$ is not constant. The current density is then defined as:

$$\mathbf{j}_o = \frac{\hbar}{2mi}(\psi_o(\mathbf{r})^*\nabla\psi_o(\mathbf{r}) - \psi_o(\mathbf{r})\nabla\psi_o(\mathbf{r})^*)$$

and considering the previous expression for the ,macroscopic wave function we obtain:

$$\mathbf{j}_o = \frac{\hbar}{m}n_o\nabla\theta$$

Hence the average velocity is:

$$\mathbf{v}_s = \frac{\hbar}{m}\nabla\theta$$

Typical flow velocity for normal fluid in cylindrical tube of length L and radius R is:

$$\frac{\Delta P}{L} \approx \frac{\eta v}{R^2}$$

In an experiment Kapista found that $\Delta P = 0$ whatever the flow velocity. This mean that the superfluid must have viscosity zero. Other experiment found finite viscosity, for example the case of inertia of oscillatory stack of disks. The total inertia will depend on two contributes, the disks themselves and the fluid between the disk. Experiments showed that a just fraction of He II contributes to the inertia. The two-fluid model is then developed:

$$n = n_s + n_n$$

At temperature near to $0K$ it was empirical found that:

$$n_s(T) \approx n - AT^4$$

while close to the critical temperature:

$$\begin{cases} n_s = B(T_c - T)^v, & T < T_c \\ n_s = 0 & T > T_c \end{cases}$$

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The two-fluid model has some important consequences. First of all the superfluid component acts like one many body quantum state and, therefore, doesn't carry any entropy. All heat transfer is due to normal fluid:

$$\mathbf{Q} = Ts\mathbf{v}_n$$

Let us connect two tanks with small cylinder in which the normal fluid cannot flow due viscosity. There will be flow of particle but not flow of heat, i.e. the temperature difference remains constant.

Let us be more formal. From the Gibbs free energy we can find that the chemical potential depends on two variables:

$$d\mu = -sdT + vdP$$

We can integrate this expression between two points $(0,0)$ and $(T^*, P^*)$:

$$\mu(T, P) = \mu_o - \int_0^{T^*} s(T,P)dT + \int_0^{P^*} v(0,P)dP$$

The second integral is simply $vP$ while the first one is harder to solve. It is something that has the dimension of volume times pressure which we call fountain pressure.
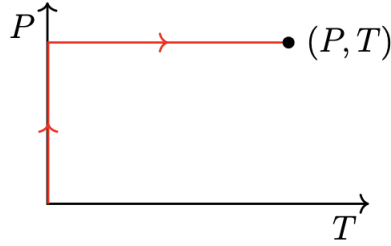


Figure 5: (T,P) plane.

$$\mu = \mu_o + vP - vP_f(T)$$

From Newton's law:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla(\rho g z + \mu(P, T))$$

For $\Delta z = 0$, neglecting the constant term we have:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla(\Delta P)$$

We therefore have motion from 1 to 2, for $\Delta P = 0$, if $\Delta P_f > 0$. But it is monotonically increasing in T, so:

$$\Delta P_f > 0 \qquad if \qquad T_2 > T_1$$

We have seen that the superflow velocity can be expressed with the gradient of something. It means that has a potential, i.e. it is irrotational. We calculate the circulation of $v_s$ along close circuit:

$$\kappa = \oint \mathbf{v}_s \cdot d\mathbf{r} \rightarrow \text{independent on the path}$$

After a full circulation (one lap):

$$\kappa = \frac{\hbar}{m}\Delta\theta$$

The macroscopic wave function is a coherent state, i.e. with well defined. After one lap the wave function must be the same:

$$\psi(\mathbf{r}) = \psi(\mathbf{r})e^{i\Delta\theta}$$

and therefore:

$$\Delta\theta = 2\pi n$$

The superflow is then quantized:

$$\kappa = \frac{\hbar}{m}2\pi n$$

# BCS Theory

During the 50's Bardeen, Cooper and Schrieffer published the first microscopic theory of superconductivity. This theory was able predict correctly some properties of superconductors (SC). First of all, the theory correctly explained the isotope effect:

$$T_c \propto M^{-\alpha} \tag{1}$$

where $M$ is the mass of the isotope. In the original paper the constant $\alpha$ was around 0.5. This prediction is correct for Zn, Hg and Pb. However it doesn't hold for other elements. The second main prediction regards the creation of an energy gap in the density of states at Fermi energy. As we'll see, the small gap has width $2\Delta$ and it is correctly corroborated by experiments.
BCS theory built three major insights:

- Sometimes exists an effective attractive force between electrons.

- Electrons form a pair, which constitutes a bosonic state.

- All the electrons near $E_F$ pair up and "fall" to the same wavefunction.

## Development of theory

In order to successfully describe superconductivity let take a strong correlated material. The first interaction that arise from electrons is obviously the Coulomb interaction:

$$V(\mathbf{r} - \mathbf{r}') = \frac{e^2}{4\pi\epsilon_o|\mathbf{r} - \mathbf{r}'|} \tag{2}$$

Electrons moving in a Fermi liquid, as in metal, are considered as quasiparticles. By considering electrons and their surrounding exchange correlation hole, it turns out that Coulomb interaction is reduced by screening. An example of this effect is the so called Thomas Fermi model. Secondly electrons interact with each other via their interaction with phonons. The phonons can be interpreted deformation of the lattice. They can be considered as quantum harmonic oscillators of wave vector $\mathbf{q}$ and mode $\lambda$. Such displacements in crystal lattice induce a modulation (of wavelength $2\pi/q$) of electron charge density. An electron moving through the crystal lattice will experience this periodic modulation and undergo diffraction.

If initial state is a Bloch state $\psi_{n\mathbf{k}}$ after the diffraction it can be in the state $\psi_{n'\mathbf{k}'}$. The extra momentum is provided by the phonon of momentum $\mathbf{q}$. Note that, the phonon can be created $\mathbf{q}$ and also annihilated $-\mathbf{q}$. Therefore we can transfer the momentum to another electron by annihilating the phonon. This construction is represented in figure (6).
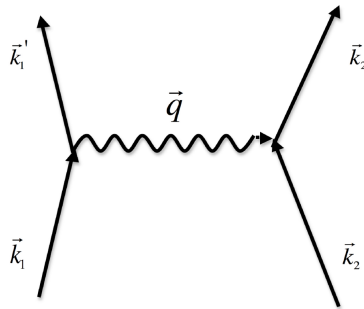


Figure 6: Feynman diagram of e-p interaction.

This can be seen as an electron-electron interaction mediated by the excitation of crystal lattice, i.e. phonon. The net effect is to transfer a momentum $\hbar\mathbf{q}$ from one electron to another. It turns out to be in the following form:

$$V_{eff}(\mathbf{q},\omega) = |g_{\mathbf{q}\lambda}|^2 \frac{1}{\omega^2 - \omega_{\mathbf{q}\lambda}^2} \qquad (3)$$

where the phonon has frequency $\omega_{\mathbf{q}\lambda}$. The matrix element $|g_{\mathbf{q}\lambda}|^2$ represent the probability of electron scattering from $\mathbf{k}$ to $\mathbf{k}+\mathbf{q}$

Migdal had demonstrated that the vertex term $g_{\mathbf{q}\lambda}$ depends on the effective mass of the electron and the mass of ions:

$$g_{\mathbf{q}\lambda} \approx \sqrt{\frac{m}{M}}$$

Since this ratio is in the order of $10^{-4}$, the electron-phonon coupling is really small. Nevertheless the analytic treatment of BCS is still impossible. For this reason an approximation is introduced. We first neglect the dependence of the interaction on the wave vector $\mathbf{q}$ and the phonon branch, replacing $\mathbf{q}$ by an effectively average over all values of $\mathbf{q}$. The $\omega_{\mathbf{q}}$ is replaced by $\omega_D$, the Debye frequency and $g_{\mathbf{q}\lambda}$ by $g_{eff}$. The effective interaction between the electrons due exchange of phonon is then:

$$V_{eff}(\mathbf{q},\omega) = |g_{eff}|^2 \frac{1}{\omega^2 - \omega_D^2}$$

From this expression we can see that the potential becomes attractive when the phonon frequency $\omega < \omega_D$.

We are only interested in electrons with energy within $k_B T$ from $E_F$. Usually in superconductive regime we have that $\hbar\omega_D >> k_b T$. Therefore we assume that:

$$V_{eff}(\mathbf{q},\omega) = -|g_{eff}|^2$$

Let us now perform a *Gedankenexperiment* by adding two additional electron state just above $E_F$, $[\mathbf{k}_1, E(\mathbf{k}_1)]$ and $[\mathbf{k}_2, E(\mathbf{k}_2)]$. A week attractive potential is given by $V_{eff}$, and this pair of electrons can continually interacts by exchange phonons. The wave vector of these electrons can change but their sum must be conserved:

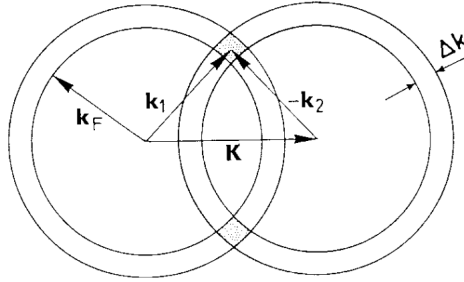$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1^{'} + \mathbf{k}_2^{'} = \mathbf{K}$$



Figure 7: $\Delta k = \hbar\omega_D$, image from [1]

The attractive interaction, which happens only within $\hbar\omega_D$ form $E_F$, is described by the shaded areas in figure (8). This area is maximum for $K = 0$. It follows that the maximum attraction is given for:

$$\mathbf{k}_1 = -\mathbf{k}_2$$

Another path to arrive at the same result is the following. Cooper noted that the interaction is attractive only near the Fermi surface. We can ask ourselves what is the effect of this attraction for just a pair of electrons outside the Fermi sphere. He found that they form a bound state. This should be unexpected since two electrons in free space

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would not bind with the same attractive force. At zero Kelvin, all the states below $k_F$ are occupied. If now we add two electrons they will interact through electron-phonon interaction. The two particles wave function is:

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = e^{i\mathbf{k}_{cm}\cdot\mathbf{R}_{cm}}\gamma(\mathbf{r}_1 - \mathbf{r}_2)\phi^{spin}_{\sigma_1,\sigma_2}$$

The energy is minimized for $\mathbf{k}_{cm} = 0$ therefore for $\mathbf{k}_1 = -\mathbf{k}_2$ By solving the two bodies problem:

$$-\frac{\hbar}{2m}(\nabla_1^2 + \nabla_2^2)\Psi + V(\mathbf{r}_1, \mathbf{r}_2)\Psi = (\epsilon + 2E_F^o)\Psi$$

considering pairs of k-values such that:

$$E_F^o < \frac{\hbar^2 k^2}{2m} < E_F^o + \hbar\omega_D$$

and a two bodies state:

$$\Psi(\mathbf{r}_1 - \mathbf{r}_2) = \sum_{\mathbf{k}} f(\mathbf{k})e^{-i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)}$$

where $f(\mathbf{k})$ becomes zero outside the attractive domain, we obtain:

$$\epsilon = \frac{2\hbar\omega_D}{1 - \exp(\frac{2}{V_o Z(E_F^o)})}$$

We have considered the electron-phonon interaction constant in the attractive regime, denoted with $V_o$, and we have taken only 1/2 of the density state at the Fermi energy because the formation of pairs:

$$Z(E_F^o) = D(E_F^o)/2$$

In the case of very weak interaction, $V_o Z(E_F^o) << 1$, the energy associated is given by:

$$\epsilon \approx -2\hbar\omega_D \cdot \exp(-\frac{2}{Z(E_F^o)V_o})$$

Thus a bound state does exist!

Therefore the initial Fermi-sea is unstable in the sense that exist state with lower energy. An high density of pairs by which the system try to archive a lower energy are formed. This new ground state is the superconducting state. Now on, with take in consideration only singlet state $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ and $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$. The scattering from $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ to $(\mathbf{k}'\uparrow, -\mathbf{k}'\downarrow)$ mediated by $V_{kk'}$ leads to energy reduction of Cooper pair formation. The total energy reduction is not simply the sum over single pair formation. One must seek the minimum of total energy of the whole system for all possible configurations, taking in account the kinetic one electron component and the energy reduction due electron-phonon interaction. Note that, we must have an increase of energy above $E_F^o$ associated to an increase of kinetic energy. The probability that the pair $(\mathbf{k}\uparrow, -\mathbf{k}\downarrow)$ is occupied is given by $w_k$. The kinetic energy is:

$$E_{kin} = 2\sum_k w_k\xi_k \qquad \xi_k = E_{(}\mathbf{k}) - E_F^o)$$

Let us define the pair creation operator:

$$\hat{P}_{\mathbf{k}}^+ = c_{\mathbf{k}\uparrow}^+ c_{-\mathbf{k}\downarrow}^+$$

It simply creates a pair electron state with zero total momentum with opposite spin. Schrieffer wrote down a coherent state many body wave function (that can be written as a ground state time an operator):

$$|\Psi\rangle_{BCS} \propto \exp(\sum_{\mathbf{k}} \alpha_k \hat{P}_{\mathbf{k}}^+)|0\rangle$$

where $|0\rangle$ is the state with no electron at all in the band of Bloch states at Fermi energy. Can be demonstrated that:

$$[\hat{P}_{\mathbf{k}}^+, \hat{P}_{\mathbf{k}'}^+] = 0$$

and so, if we take $\mathbf{k} = \mathbf{k}'$ we have the following condition:

$$(\hat{P}_{\mathbf{k}}^+)^2 = 0$$

Using Pauli exclusion principle, if we expand the exponential we must neglect quadratic and higher term and so we can write:

$$|\Psi\rangle_{BCS} \propto \prod_{\mathbf{k}} (1 + \alpha_{\mathbf{k}} \hat{P}_{\mathbf{k}}^+) |0\rangle$$

Normalizing we arrive to the BCS states:

$$|\Psi\rangle_{BCS} = \prod_{\mathbf{k}} (u_{\mathbf{k}} + v_{\mathbf{k}} \hat{P}_{\mathbf{k}}^+) |0\rangle$$

where:

$$u_{\mathbf{k}} = \frac{1}{1 + |\alpha_{\mathbf{k}}|^2}$$

$$v_{\mathbf{k}} = \frac{\alpha_{\mathbf{k}}}{1 + |\alpha_{\mathbf{k}}|}$$

such that:

$$|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$$

So now we have an expression of may-body wave function for the electron pairs and we can use $v_k$ and $u_k$ as variational parameters to minimize the energy. Let take the bra-ket of the Hamiltonian on the BCS state:

$$\langle \Psi_{BCS} | \hat{H} | \Psi_{BCS} \rangle = E$$

Differentiating with respect the variational parameter $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ leads to write the following system:

$$\begin{cases} (\epsilon_{\mathbf{k}} - \mu) u_{\mathbf{k}} + \Delta v_{\mathbf{k}} = E_{\mathbf{k}} u_{\mathbf{k}} \\ \Delta^* u_{\mathbf{k}} - (\epsilon_{\mathbf{k}} - \mu) v_{\mathbf{k}} = E_{\mathbf{k}} v_{\mathbf{k}} \end{cases}$$

It can be shown that, the solution is given by:

$$E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + |\Delta|^2} \qquad \xi_{\mathbf{k}} = \epsilon_{\mathbf{k}} - \mu$$

where $\Delta$ is called BCS gap parameter and it is essentially defined as:

$$\Delta = |g_{eff}|^2 \sum_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}}^*$$

After some calculation, evaluating the eigenvector $v_k$ and $u_k$, we arrive to the BCS equation:

$$\Delta = |g_{eff}|^2 \sum_{\mathbf{k}} \frac{\Delta}{2 E_{\mathbf{k}}}$$

Integrating (instead of summing) on attractive interaction region, we can write the Delta parameter as:

$$|\Delta| = 2 \hbar \omega_D e^{-1/V_o \cdot Z(E_f^o)}$$

All discussion made until now are valid for $T = 0K$. By adding small excitation due to finite temperature we can use the developed theory of BCS at $0K$. From this we can obtain the gap parameter in function of the temperature. After some calculation we can derive the gap equation for finite temperature:

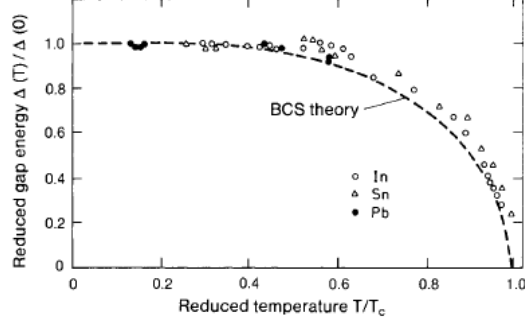$$\Delta = |g_{eff}|^2 \sum_{\mathbf{k}} \frac{\Delta}{2 E_{\mathbf{k}}} tanh(\frac{E_{\mathbf{k}}}{2 k_B T})$$

Figure 8: BCS gap in function of T, image from [1]

In the limit of $\Delta \to 0$ one can obtain:

$$k_B T_c = 1.13 \cdot \hbar \omega_D \exp(-\frac{1}{V_o Z(E_F^o)})$$

In the limit of $T \to 0K$ one can retrieve the value of the gap parameter:

$$2\Delta(0) = 3.52 \cdot k_B T_c$$

It is easy to demonstrate that, the BCS ground state is invariant (in square modulus) to the presence of current which carries out a phase term:

$$|\Psi(\mathbf{K} \neq 0, \mathbf{r})|^2 = |\Psi(\mathbf{K} = 0, \mathbf{r})|^2$$

The consequences of creation of coherence state are shown in the Josephson effect. Consider two superconductors separated by a weak link. the two separated SC phases are described by GL order parameter which can be simplified by an amplitude term and a phase term. Josephson was able to find the current flowing in the junction:

$$I = I_c sin(\theta_L - \theta_R)$$

where the two phases are related to the macroscopical wave function, i.e. the GL order parameter. If a finite voltage is applied across the junction, the macroscopic wave function becomes time dependent:

$$i\hbar \frac{\partial \psi_R(t)}{\partial t} = -2eV_R \psi_R(t)$$

$$i\hbar \frac{\partial \psi_L(t)}{\partial t} = -2eV_L \psi_L(t)$$

Josephson demonstrated that an increasing in voltage leads to a phase shift:

$$\Delta \theta = \Delta \theta_o + \frac{2eV}{\hbar} t$$

and the current becomes:

$$I = I_c sin(\Delta \theta_o + \frac{2eV}{\hbar} t)$$

which oscillates with frequency:

$$\nu = \frac{2eV}{\hbar}$$

The theory developed so far can be used to characterize Superconducting Quantum Interference Device (SQUID). Suppose we have a SC ring in which there are two weak links. At each junction, the current is defined by the Josephson formula:

$$I = I_c sin(\Delta \theta_1) + I_c sin(\Delta \theta_1)$$

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If the two junction are balanced (the critical current are the same) and a small current is applied, we expect a constant phase difference across the junction:

$$\Delta\theta = arcsin(\frac{I}{2I_c})$$

This is no longer true in case of external magnetic field. Using gauge invariance we find that the phase difference is not the same:

$$\Phi = \int \mathbf{B} \cdot d\mathbf{S} = \frac{2e}{\hbar}\int \nabla\theta \cdot d\mathbf{r} = \frac{2e}{\hbar}(\Delta\theta_1 - \Delta\theta_2)$$

The two phase difference for the junctions are linked to the flux of magnetic field:

$$\Delta\theta_1 = \Delta\theta + \frac{\pi\Phi}{\Phi_o}$$

$$\Delta\theta_2 = \Delta\theta - \frac{\pi\Phi}{\Phi_o}$$

Replace these value in the equation for the current we obtain:

$$I = 2I_c sin(\Delta\theta)cos(\frac{\pi\Phi}{\Phi_o})$$

$$I_c = I_o|cos(\frac{\pi\Phi}{\Phi_o})|$$

By measuring the critical current, is possible to measure the magnetic field with a precision of $10^{-10}T$.

## Unconventional p-wave SC

Usually the vast majority of superconductors are in the spin-singlet state, i.e. the spatial function has even parity

$$\phi(\mathbf{k}) = \phi(-\mathbf{k})$$

while the spin factor has odd parity to ensure antisymmetrization of the total pair wave function. It is also possible to construct a spin-triplet state where the spatial function is odd. The pair state will be:

$$|\psi(\mathbf{k})\rangle = \phi_{11}(\mathbf{k})|\uparrow\uparrow\rangle + \phi_{12}(\mathbf{k})|\uparrow\downarrow + \downarrow\uparrow\rangle + \phi_{22}(\mathbf{k})|\uparrow\uparrow\rangle$$
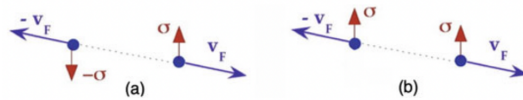


Figure 9: Singlet and triplet states

For odd parity of spacial function, the spin-triplet state has to be represented by three components described by the vector $\mathbf{d}(\mathbf{k})$.

The gap parameter which can constitute the order parameter can be expressed using the the d-vector.

$$|\Delta_{\mathbf{k}}|^2 = \frac{1}{2}tr(\hat{\Delta}_{\mathbf{k}}^{\dagger}\hat{\Delta}_{\mathbf{k}}) = |\mathbf{d}(\mathbf{k})|^2$$

It defines the anisotropy of superconduction linked to non equal quantization axis symmetry ($l \neq 0$). This means that all spin-triplet superconductor are unconventional superconductor.

The anisotropy of spin-triplet state for $l = 1$ defines the p-wave superconductors such as $UPt_3$. In this case the d-vector can be expressed as:

$$\mathbf{d}(\mathbf{k}) = \frac{\Delta_o}{k_F}(k_x \pm k_y)\hat{z}$$

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In the frame of group theory, we can represent the $\mathbf{d(k)}$ on the basis of irreducible representations of the point group symmetry. We express the three components of d-vector on these eigenfunctions of symmetry operation:

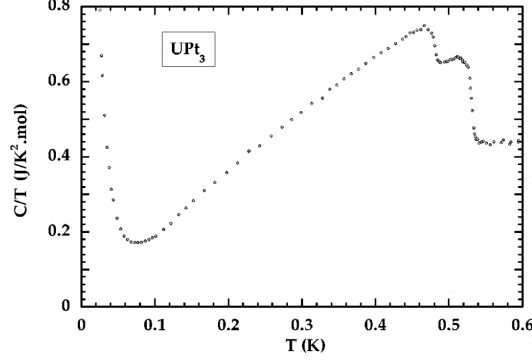$$d_i(\mathbf{k}) = \sum_{\Gamma m} b_{\Gamma m i} f_{\Gamma i}(\mathbf{k})$$



Figure 10: Two peaks seems to be correlated to two nonzero components of order parameter, image from [2].

As we can see from the specific heat of $UPt_3$ we have two phase transition temperatures. It is believed that these correspond to two different gap components becoming nonzero. Actually they may come from a doubly degenerate representation, i.e. the two gap components belong to the same irreducible representation.

| | | |
|---|---|---|
| $E_{1u}$ ($\Gamma_5^-$) | $\hat{z}k_x, \hat{z}k_y$ ; <br> $k_z\hat{x}, k_z\hat{y}$ | $\mathrm{Re}[f_+(\vec{k})]\hat{z}$, $\mathrm{Im}[f_+(\vec{k})]\hat{z}$; <br> $\mathrm{Re}[f_z(\vec{k})\hat{r}_+]$, $\mathrm{Im}[f_z(\vec{k})\hat{r}_+]$; <br> $\mathrm{Re}[f_+(\vec{k})^2\hat{r}_-]f_z(\vec{k})$, $\mathrm{Im}[f_+(\vec{k})^2\hat{r}_-]f_z(\vec{k})$; <br> $\mathrm{Re}[f_-(\vec{k})^5]\hat{z}$, $\mathrm{Im}[f_-(\vec{k})^5]\hat{z}$; <br> $\mathrm{Re}[f_-(\vec{k})^4\hat{r}_-]f_z(\vec{k})$, $\mathrm{Im}[f_-(\vec{k})^4\hat{r}_-]f_z(\vec{k})$; <br> $\mathrm{Re}[f_-(\vec{k})^6\hat{r}_+]f_z(\vec{k})$, $\mathrm{Im}[f_-(\vec{k})^6\hat{r}_+]f_z(\vec{k})$; |
| $E_{2u}$ ($\Gamma_6^-$) | $\hat{x}k_x - \hat{y}k_y, \hat{x}k_y - \hat{y}k_x$ <br> $\hat{z}(k_x^2 - k_y^2)k_z, \hat{z}k_xk_yk_z$ | $\mathrm{Re}[f_+(\vec{k})\hat{r}_+]$, $\mathrm{Im}[f_+(\vec{k})\hat{r}_+]$; <br> $\mathrm{Re}[f_+(\vec{k})^2]f_z(\vec{k})\hat{z}$, $\mathrm{Im}[f_+(\vec{k})^2]f_z(\vec{k})\hat{z}$; <br> $\mathrm{Re}[f_+(\vec{k})^3\hat{r}_-]$, $\mathrm{Im}[f_+(\vec{k})^3\hat{r}_-]$; <br> $\mathrm{Re}[f_-(\vec{k})^3\hat{r}_-]$, $\mathrm{Im}[f_-(\vec{k})^3\hat{r}_-]$; <br> $\mathrm{Re}[f_-(\vec{k})^4]f_z(\vec{k})\hat{z}$, $\mathrm{Im}[f_-(\vec{k})^4]f_z(\vec{k})\hat{z}$; <br> $\mathrm{Re}[f_-(\vec{k})^5\hat{r}_+]$, $\mathrm{Im}[f_-(\vec{k})^5\hat{r}_+]$; |

Figure 11: Character table for $D6_h$ point group.

# References

[1] H. Ibach and H. Lüth. *Solid-State Physics: An Introduction to Principles of Materials Science*. Advanced texts in physics. Springer Berlin Heidelberg, 2009.

[2] Robert Joynt and Louis Taillefer. The superconducting phases of upt 3. *Reviews of Modern Physics*, 74(1):235, 2002.