Superconductivity and BCS Theory

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- Introduction
- Electron-phonon interaction, Cooper pairs
- BCS wave function, energy gap and quasiparticle states
- Predictions of the BCS theory
- Limits of the BCS gap equation: strong coupling effects
Introduction: conductivity in a metal

- **Drude theory**: metals are good electrical conductors because electrons can move nearly freely between the atoms in solids

\[
\sigma = \frac{ne^2 \tau}{m}
\]

- \( \sigma \) - conductivity
- \( n \) - density of conduction electrons
- \( e \) - electron charge
- \( m \) - effective mass of conduction electrons
- \( \tau \) - average lifetime for the free motion of electrons between collision with impurities, other electrons, etc

\[
\rho = \sigma^{-1} = \frac{m}{ne^2 \tau}
\]

\( \rho \) - resistance

\[
\langle \mathcal{P} \rangle \sim T^2 \sim T^5
\]

- \( \langle \mathcal{P} \rangle \) - average energy per electron

\[
\tau^{-1} = \tau_{\text{imp}}^{-1} + \tau_{\text{el-el}}^{-1} + \tau_{\text{el-ph}}^{-1}
\]

- \( \tau_{\text{imp}} \) - lifetime due to impurities
- \( \tau_{\text{el-el}} \) - lifetime due to elastic collisions
- \( \tau_{\text{el-ph}} \) - lifetime due to inelastic collisions

\[
\rho = \rho_0 + aT^2 + bT^5 + \ldots
\]

- \( \rho_0 \) - residual resistance

**Firstly observed in mercury (Hg) below 4K by Kamerlingh Onnes in 1911**
Introduction: Superconducting Materials

**KNOWN SUPERCONDUCTIVE ELEMENTS**

- BLUE = AT AMBIENT PRESSURE
- GREEN = ONLY UNDER HIGH PRESSURE

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_c$ (K)</th>
</tr>
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<tbody>
<tr>
<td>Nb</td>
<td>9.25</td>
</tr>
<tr>
<td>Pt</td>
<td>0.0019</td>
</tr>
<tr>
<td>Hg</td>
<td>4.2</td>
</tr>
<tr>
<td>Nb$_3$Sn</td>
<td>18</td>
</tr>
<tr>
<td>Nb$_3$Ge</td>
<td>23</td>
</tr>
</tbody>
</table>

*common feature of many elements*

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Introduction: Superconducting Materials

High-\( T_c \) layered cuprates (1986) Bednorz Müller

Borocarbide superconductors discovered in 2001

Heavy-fermion superconductors

Possible triplet superconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_c ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgBa(_2)Ca(_2)Cu(<em>3)O(</em>{8+\delta})</td>
<td>138</td>
</tr>
<tr>
<td>YBa(_2)Cu(<em>3)O(</em>{7})</td>
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</tr>
<tr>
<td>La(<em>{1.85})Sr(</em>{0.15})CuO(_4)</td>
<td>39</td>
</tr>
<tr>
<td>YNi(_2)B(_2)C</td>
<td>17</td>
</tr>
<tr>
<td>MgB(_2)</td>
<td>38</td>
</tr>
<tr>
<td>CeCu(_2)Si(_2)</td>
<td>0.65</td>
</tr>
<tr>
<td>UPt(_3)</td>
<td>0.5</td>
</tr>
<tr>
<td>Na(_{0.3})CoO(_2)-1.3H(_2)O</td>
<td>5</td>
</tr>
<tr>
<td>Sr(_2)RuO(_4)</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Introduction: Basic Facts ⇒ Meissner-Ochsenfeld Effect

What does it mean to have $\rho = 0$?

$$E = \rho \, j$$

1) $E = 0$, $j$ is finite inside all points of superconductors
2) From the Maxwell equation:
   $$\nabla \times E = -\frac{\partial B}{\partial t} = 0$$

- Below $T_c$ the magnetic field does not penetrate into superconductor (if we start from $B=0$ in the normal state)
- if above $T_c$ there some magnetic field $B \neq 0$, then below $T_c$ it is expelled out of the system ⇒ Meissner effect

Superconductors are perfect diamagnets!
Introduction: Basic Facts ⇒ Type I and type II superconductivity

What happens for the large magnetic field?

- **Type I** superconductor: the magnetic field remains zero until suddenly the superconductivity is destroyed, \( H_c \).
- **Type II** superconductor: there are two critical fields, \( H_{c1} \) and \( H_{c2} \).

Magnetic field enters in the form of vortices \((H_{c1} < H < H_{c2})\).

- **Abrikosov** vortices.
Microscopic BCS Theory of Superconductivity

First truly microscopic theory of superconductivity!
(Bardeen-Cooper-Schrieffer 1957)

Three major insights:

(i) The effective forces between electrons can sometimes be attractive in a solid rather than repulsive

(ii) „Cooper problem“ ⇒ two electrons outside of an occupied Fermi surface form a stable pair bound state, and this is true however weak the attractive force

(iii) Schrieffer constructed a many-particle wave function which all the electrons near the Fermi surface are paired up
BCS theory: the electron-electron interaction (i)

**Bare electrons** repel each other with electrostatic potential:

\[ V(r - r') = \frac{e^2}{4\pi\varepsilon_0 |r - r'|} \]

In a metal we are dealing with **quasiparticles** (electron with surrounding exchange-correlated hole)

\[ V(r - r') = \frac{e^2}{4\pi\varepsilon_0 |r - r'|} e^{-|r - r'|/r_{TF}} \]

Thomas-Fermi screening \( r_{TF} \) reduces substantially the repulsive force
Electrons move in a solid in the field of positively charged ions.

Due to vibrations, the ion positions at $R_i$ will be displaced by $\delta R_i$.

Such a displacement means the creation of phonons $\Rightarrow$ a set of quantum harmonic oscillators.

Modulation of the charge density and the effective potential $V_1(r)$ for the electrons.
BCS theory: the electron-phonon interaction (Fröhlich 1950) (i)

\[ \delta V_1(r) = \sum_i \frac{\partial V_1(r)}{\partial R_i} \delta R_i \]

with wavelength \(2\pi/q\)

\[ \Psi_{nk}(r) \Rightarrow \Psi_{n'k-q}(r) \]

with emission of phonon

\[ \Psi_{mk}(r) \Rightarrow \Psi_{m'k+q}(r) \]

with absorption of phonon

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Effective interaction of electrons due to exchange of phonons

\[ V_{\text{eff}}(q, \omega) = \left| g_{q\lambda} \right|^2 \frac{1}{\omega^2 - \omega_{q\lambda}^2} \]

\( g_{q\lambda} \) is a constant of electron-phonon interaction

\( \omega_{q\lambda} \) is a phonon frequency

\( m \sim \frac{m}{M} \Rightarrow \) small number
Effective interaction of electrons due to exchange of phonons

\[ V_{\text{eff}}(\omega) = \left| g_{\text{eff}} \right|^2 \frac{1}{\omega^2 - \omega_D^2} \]

- \( g_{\text{eff}} \) is an effective constant of electron-phonon interaction
- \( \omega_D \) is a typical Debye phonon frequency

For \( \omega < \omega_D \) and low temperatures

\[ V_{\text{eff}}(\omega) = -\left| g_{\text{eff}} \right|^2, \quad |\omega| < \omega_D \]

\[ |\varepsilon_{k_i} - \varepsilon_F| < \hbar \omega_D \]

\[ \xi \] coherence length
What is the effect of the attraction just for a single pair of electrons outside of Fermi sea:

**Trial two-electron wave function**

\[ \Psi(r_1, \sigma_1, r_2, \sigma_2) = e^{ik_{cm} R_{cm}} \varphi(r_1 - r_2) \chi_{\sigma_1, \sigma_2}^{\text{spin}} \]
\[ \Psi(r_1, \sigma_1, r_2, \sigma_2) = -\Psi(r_2, \sigma_2, r_1, \sigma_1) \]

1) \( k_{cm} = 0 \), Cooper pair without center of mass motion
2) Spin wave function

**Spin singlet (S=0)**

\[ \chi_{\sigma_1, \sigma_2}^{\text{spin}} = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right) \]

**Spin triplet (S=1)**

\[ \chi_{\sigma_1, \sigma_2}^{\text{spin}} = \frac{1}{\sqrt{2}} \left( |\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle \right) \]
3) Orbital part of the wave function

Spin singlet  \( \varphi(r_1 - r_2) = +\varphi(r_2 - r_1) \) even function

Spin triplet  \( \varphi(r_1 - r_2) = -\varphi(r_2 - r_1) \) odd function

\( \varphi(r_1 - r_2) = f(|r_1 - r_2|)Y_{lm}(\theta, \phi) \)

BCS: For the spin singlet state and s-wave symmetry a substitution of the trial wave function in Schrödinger equation  \( H\Psi = E\Psi \)

\(-E = 2\hbar \omega_D e^{-1/\lambda}, \quad \lambda = |g_{\text{eff}}|^2 N(\varepsilon_F)\)

\(\lambda\) - electron-phonon coupling parameter

Bound state exists independent of the value of \(\lambda\) !!!
Whole Fermi surface would be unstable to the creation of such pairs

Pair creation operator

\[ \hat{P}_k^+ = c_{k \uparrow}^+ c_{-k \downarrow}^+ \]

\[ [\hat{P}_k, \hat{P}_k^+] \neq 1 \]

\[ [\hat{P}_k^+, \hat{P}_k^+] = 0 \]

\[ (\hat{P}_k^+)^2 = 0 \]

Cooper pairs are not bosons!

\[ |\Psi_{BCS}\rangle = \prod_k (u_k^* + v_k^* P_k^+) |0\rangle \]

\( u_k \) and \( v_k \) are the normalizing coefficients (parameters)

\[ \langle \Psi_{BCS} | \Psi_{BCS} \rangle = 1 \]

\[ |u_k|^2 + |v_k|^2 = 1 \]

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BCS wave function: variational approach at T=0

\begin{align*}
\text{minimize} \quad & E = \langle \Psi_{BCS} | \hat{H} | \Psi_{BCS} \rangle \\
\text{with} \quad & \langle \hat{N} \rangle = \text{const}
\end{align*}

\begin{align*}
\hat{H} &= \sum_{k,\sigma} \varepsilon_k c_{k\sigma}^+ c_{k\sigma} - \left| g_{\text{eff}} \right|^2 \sum_{k,k'} c_{k\uparrow}^+ c_{-k\downarrow}^+ c_{-k'\downarrow} c_{k'\uparrow} \\
E &= \sum_k \varepsilon_k \left( \left| v_k \right|^2 - \left| u_k \right|^2 + 1 \right) - \left| g_{\text{eff}} \right|^2 \sum_{k,k'} v_k^* u_{k'}^* u_k^* v_k \\
N &= \sum_k \left( \left| v_k \right|^2 - \left| u_k \right|^2 + 1 \right) \\
\left| u_k \right|^2 + \left| v_k \right|^2 &= 1
\end{align*}
BCS wave function: variational approach at $T=0$ (iii)

Minimization with Lagrange multipliers $\mu$ and $E_k$

$$0 = \frac{\partial E}{\partial u_k^*} - \mu \frac{\partial N}{\partial u_k^*} + E_k u_k$$

$$0 = \frac{\partial E}{\partial v_k^*} - \mu \frac{\partial N}{\partial v_k^*} + E_k v_k$$

$$E_k u_k = (\varepsilon_k - \mu) u_k + \Delta v_k$$

$$E_k v_k = \Delta^* u_k - (\varepsilon_k - \mu) v_k$$

$$\Delta = \left| g_{eff} \right|^2 \sum_k u_k v_k^*$$

$$\pm E_k = \pm \sqrt{(\varepsilon_k - \mu)^2 + |\Delta|^2}$$

$$\left| u_k \right|^2 = \frac{1}{2} \left( 1 + \frac{\varepsilon_k - \mu}{E_k} \right)$$

$$\left| v_k \right|^2 = \frac{1}{2} \left( 1 - \frac{\varepsilon_k - \mu}{E_k} \right)$$

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The BCS energy gap and quasiparticle states (iii) are given by:

$$\Delta = \left| g_{\text{eff}} \right|^2 \sum_k \frac{\Delta}{2E_k} \quad \Rightarrow \quad \left| \Delta \right| = 2\hbar \omega_D e^{-1/\lambda}$$

This equals to the binding energy of a single Cooper pair at T=0.

What about the excited states and finite temperatures? Consider the BCS state $|\Psi_{\text{BCS}}\rangle$ and small excitations relative to this state.

$$c_{k\uparrow}^+ c_{-k\downarrow}^+ c_{-k'\downarrow} c_{k\uparrow} \approx \left\langle c_{k\uparrow}^+ c_{-k\downarrow}^+ \right\rangle c_{-k'\downarrow} c_{k\uparrow} + c_{k\uparrow}^+ c_{k\downarrow}^+ \left\langle c_{-k'\downarrow} c_{k\uparrow} \right\rangle$$

The Hamiltonian $\hat{H}$ is:

$$\hat{H} = \sum_{k,\sigma} \left( \epsilon_k - \mu \right) c_{k\sigma}^+ c_{k\sigma} - \sum_k \left( \Delta^* c_{-k\downarrow} c_{k\uparrow} + \Delta c_{k\uparrow}^+ c_{-k\downarrow}^+ \right)$$
BCS energy gap and quasiparticle states

Unitary transformations: \[ U^+ \hat{H} U = \hat{H}_{\text{diag}} \]

\[ U = \begin{pmatrix} u_k & \nu_k^* \\ -\nu_k & u_k^* \end{pmatrix} \]

\[ \pm E_k = \pm \sqrt{(\varepsilon_k - \mu)^2 + |\Delta|^2} \]

new pair of operators:

\[ b_{k\uparrow} = u_k^* c_{k\uparrow} - \nu_k^* c_{-k\downarrow} \]

\[ b_{-k\downarrow}^+ = \nu_k c_{k\uparrow} + u_k c_{-k\downarrow} \]

\[ \hat{H}_{\text{diag}} = \sum_k E_k \left( b_{k\uparrow}^+ b_{k\uparrow} + b_{-k\downarrow}^+ b_{-k\downarrow} \right) \]

What is the physical meaning of these operators?

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BCS quasiparticle states

1) $b$ operators are fermionic:
\[
\{ b_{k\sigma}, b_{k'\sigma}' \} = \delta_{kk'} \delta_{\sigma\sigma'}, \{ b_{k\sigma}, b_{k'\sigma}' \} = 0, \{ b_{k'\sigma}', b_{k'\sigma}' \} = 0
\]

2) $b$ "particles" are not present in the ground state:
\[
b_{k\uparrow} \left| \Psi_{BCS} \right\rangle = 0
\]

3) The excited state corresponds to adding 1, 2, ... of the new quasiparticles to this state

4) $b$ –quasiparticle is superposition of an electron and a hole
\[
b_{k\uparrow} = u_k^* c_{k\uparrow} - v_k^* c_{-k\downarrow}^+
\]

5) The energy gap is $2\Delta$
**BCS gap equation at finite temperature: \( T_c \)**

\[
\langle b_{k\uparrow}^+ b_{k\uparrow} \rangle = f(E_k), \quad \langle b_{-k\downarrow}^+ b_{-k\downarrow} \rangle = 1 - f(E_k)
\]

allows to determine temperature dependence of the gap

\[
\Delta = \left| g_{\text{eff}} \right|^2 \sum_k \langle c_{-k\downarrow} c_{k\uparrow} \rangle
\]

\[
\Delta = \left| g_{\text{eff}} \right|^2 \sum_k \frac{\Delta}{2E_k} \tanh\left( \frac{E_k}{2k_B T} \right)
\]

\[
2\Delta(T = 0) = 3.52 k_B T_c
\]

\[
k_B T_c = 1.13 \hbar \omega_D \exp(-1/\lambda)
\]

\[
T_c \propto M^{-\frac{1}{2}}
\]

**Condensation energy**

\[
E_{\text{cond}} \approx \sum_k [\varepsilon_k - E_k] = -\frac{1}{2} N(\varepsilon_F) |\Delta|^2
\]

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Some thermodynamic properties

1) Specific heat discontinuity at \( T = T_c \)

2\textsuperscript{nd} order phase transition \( \Rightarrow \) discontinuity of specific heat

\[
\frac{\Delta C}{C_n} \bigg|_{T=T_c} = \frac{C - C_n}{C_n} \bigg|_{T=T_c} = 1.43
\]

2) Key quantity: density of states

\[
N(E) = 2 \sum_k \delta(\omega - E_k)
\]
Predictions of the BCS theory

1) Paramagnetic susceptibility of the conduction electrons

\[ \chi(q \rightarrow 0, \omega \rightarrow 0) \propto N(\varepsilon_F) \rightarrow n_\uparrow - n_\downarrow \]

spin of Cooper Pairs \( S=0 \)

\[ \frac{1}{T_1T} \propto \left[ N(\varepsilon_F) \right]^2 \]

effect of coherence factors

\[ M = \chi H \]
Predictions of the BCS theory

2) Andreev scattering: electron in a metal

\[ \varepsilon_k - \varepsilon_F < \Delta \]

- An electron will be reflected at the interface.
- An electron will combine another electron and form Cooper pair.

\( e \) and \( h \) are exactly time reversed:

\[
\begin{align*}
-e & \Rightarrow e \\
-k & \Rightarrow -k \\
\sigma & \Rightarrow -\sigma
\end{align*}
\]
1) Even if $k$ is not a good quantum number

a) To reformulate the BCS theory in terms of field operators

$$\Psi_{i\uparrow}(\mathbf{r}), \quad \Psi_{i\downarrow}(\mathbf{r})$$

works for alloys

Non-magnetic impurities do not influence s-wave superconductivity

Anderson (1959)
Paramagnetic limit of superconductivity

Lack of inversion symmetry

1) Condensation energy vs polarization energy

\[ \Delta_q = \Delta_0 e^{iqr} \]
Predictions of the BCS theory: Josephson effect

1) Violation of U(1) gauge symmetry

\[ c_{k\uparrow} \Rightarrow c_{k\uparrow} e^{i\varphi} \]

\[ |\Psi_{BCS}\rangle \Rightarrow |\Psi_{BCS}\rangle e^{i2\varphi} \]

2) Coherent tunneling of a Cooper-pairs

Supercurrent between SC1 and SC2 due to phase coherent Cooper pair tunneling

\[ I = I_c \sin(\varphi_2 - \varphi_1) \]
Interplay of Coulomb repulsion and attraction: Anderson-Morel model

\[ V_{\vec{k}, \vec{k}'} = \frac{4\pi e^2}{q^2} = \frac{4\pi e^2}{q^2 \varepsilon(q, \omega)} \]

\[ V_{\vec{k}, \vec{k}'} = \frac{4\pi e^2}{q^2 (q')^2} + \frac{4\pi e^2}{q^2 + k^2_{TF} \omega^2 - \omega_q^2} \]

Coulomb repulsion is larger than attractive

\[ k_B T_c = 1.14 \hbar \omega_D \exp \left[ -\frac{1}{\lambda - \mu^*} \right] \]

\[ \mu^* = \frac{\mu}{1 + \mu \ln \left( \frac{W}{\hbar \omega_D} \right)} \]

\[ T_c \neq 0 \text{ even } \lambda < \mu \]
Strong coupling effects: Eliashberg theory

Assumption of BCS: $\lambda \ll 1$

for $\lambda = 0.2 \div 0.5$ the effect of electrons on phonons also has to be taken into account

- Phonon frequencies renormalize due to electrons
- Self-consistent inclusion of screened Coulomb repulsion between the electrons $\Rightarrow \mu^*$

$$k_B T_c = \frac{\hbar \omega_D}{1.45} \exp \left( \frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right)$$

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\alpha$</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.45</td>
<td>0.9</td>
</tr>
<tr>
<td>Pb</td>
<td>0.49</td>
<td>7.2</td>
</tr>
<tr>
<td>Mo</td>
<td>0.33</td>
<td>0.9</td>
</tr>
<tr>
<td>Os</td>
<td>0.2</td>
<td>0.62</td>
</tr>
<tr>
<td>MgB$_2$</td>
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<td>39</td>
</tr>
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</table>
Further reading: