BCS theory

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The BCS theory of superconductivity is successful in describing the main features of the Type-I superconductors. In this paper I will review the fundamental principles and results of this model, from the Cooper problem and its implications, to the formulation of the revolutionary theory.

Superconductors (SC) materials can be divided in two categories, known as Type-I and Type-II [1](we won't consider high temperature SC in this paper). The magnetic field vs. temperature (H-T) phase diagram of the Type-I superconductors is characterized by a first order phase transition curve $H_c(T)$ from the normal to the superconducting state, with a second order phase transition point at $H_c(T=0)$. This low temperature phase is known as the *Meissner-Ochsenfeld* phase [2], in which the electrical resistivity of the material is zero and all the magnetic field inside is screened out by surface supercurrents (*Meissner* effect). SC Type-II have two different phases: the Meissner phase below the $H_{c1}(T)$ curve, and the *mixed state* between $H_{c1}(T)$ and $H_{c2}(T)$, in which the resistivity of the material is zero, but the magnetic field is allowed to penetrate as quantized flux, in the form of an hexagonal lattice of vortices (*Abrikosov's lattice*) [3].

In 1950, Ginzburg and Landau [4] presented their theory of superconductivity, introducing the complex pseudowave-function ψ as an order parameter within Landau's general theory of second order phase transitions. The complex function ψ represents the macroscopic coherent state of the electrons in the superconducting phase. The same year of Abrikosov's paper, Bardeen, Cooper and Schrieffer [5] presented their microscopic theory of superconductivity for Type-I SC, the *BCS theory*. As opposed of the GL theory, it concentrates entirely on the excitations rather than on the superconducting electrons. The main facts that the BCS theory explains are (a) the formation of the *Cooper pairs* [6] of electrons and the origin of the attractive interaction, (b) a second order phase transition at the critical temperature T_c (H=0), (c) an electronic specific heat varying as $exp(-\Delta_0/k_BT)$ near T = 0 K as an evidence for an energy gap for individual particle-like excitations,(d) the dependence of T_c on isotopic mass, and (e) the effects associated with zero electrical resistivity and perfect diamagnetism.

FOCK SPACE AND OCCUPATION NUMBER REPRESENTATION

The wavefunction of an isolated electron is a function of its position $\mathbf{r}$ and spin variable s (up $\uparrow$ or down $\downarrow$). Using the short-hand notation $x \equiv (\mathbf{r}, s)$, the fermionic many-particle quantum state must be totally antisymmetric with respect to particle exchange: $\Psi(\dots x_i \dots x_k \dots) = -\Psi(\dots x_k \dots x_i \dots)$, with i=1 ... N. For a piece of solid, $N \sim 10^{23}$, so this function is practically intractable. First, consider the Slater determinants' representation: choose a complete set of orthonormal one-particle spinor-orbitals functions $\phi_{k\sigma}(x)$, select N of those orbitals, $\phi_{k_1\sigma_1}(x)$, $\phi_{k_2\sigma_2}(x)$, ...,$\phi_{k_N\sigma_N}(x)$, and form the determinant

$$\Phi_L(x_1 \dots x_N) = \frac{1}{\sqrt{N!}} det\|\phi_{k_i\sigma_i}(x_k)\| \qquad (1)$$

which has the right symmetry, and $L = (k_1\sigma_1, \dots, k_N\sigma_N)$ labels the orbital configuration. The complete N-fermion wavefunction may be represented as

$$\Psi(x_1 \dots x_N) = \sum_L C_L \Phi_L(x_1 \dots x_N) \qquad (2)$$

with certain coefficients C_L, $\sum_L |C_L|^2 = 1$. Now, if the number N is macroscopicaly large, it cannot be fixed at a single definite value in experiments due to emission and absorption of particles (*e.g.*, photons), and also it is technically useful to work with a grand canonical ensemble with variable N. In order to do so, we change our N-fixed Hilbert space by a Fock space: instead of specifying the multi-index L as a row of N indices $k_i\sigma_i$ we may denote a basis state by specifying the occupation numbers n_i (0 or 1) of all orbitals i:

$$|n_1 \dots n_i \dots\rangle, \qquad \sum_i n_i = N, \qquad (3)$$

and our previous determinantal state (1) is now represented as $|\Phi_L\rangle = |\phi_{k_1\sigma_1}, \phi_{k_2\sigma_2}, \dots, \phi_{k_N\sigma_N}\rangle$. Now, the simplest operators are those which provide just a transition between basis states (3) which are as close to each other as possible: those which differ in one occupation number only. The definition of these creation and annihilation operators for fermions, $\hat{c}^\dagger$ and $\hat{c}$, must have regard to the antisymmetry of the quantum states and to Pauli's exclusion principle. They are defined as

$$\hat{c}_i|\dots n_i \dots\rangle = |\dots n_i - 1 \dots\rangle n_i (-1)^{\sum_{j<i} n_j}, \quad (4)$$

$$\hat{c}_i^\dagger|\dots n_i \dots\rangle = |\dots n_i + 1 \dots\rangle (1 - n_i)(-1)^{\sum_{j<i} n_j}. \quad (5)$$

It is easily seen that these operators have all the needed properties, and do particularly not create non-fermionic

states (with occupation numbers different from 0 and 1). As oppose to the bosonic systems for which the creation and annihilation operators commute (*e.g.* for a harmonic oscillator $[\hat{a}_i, \hat{a}_j^\dagger] = \hat{a}_i\hat{a}_j^\dagger - \hat{a}_j^\dagger\hat{a}_i = \delta_{ij}$) the fermionic operators obey the key relations

$$[\hat{c}_i, \hat{c}_j^\dagger]_+ = \hat{c}_i\hat{c}_j^\dagger + \hat{c}_j^\dagger\hat{c}_i = \delta_{ij}, \tag{6}$$

$$[\hat{c}_i, \hat{c}_j]_+ = [\hat{c}_i^\dagger, \hat{c}_j^\dagger]_+ = 0. \tag{7}$$

The basis (3) of the Fock space is systematically generated out of a single basis vector, the *vacuum state* $|\rangle \equiv |0\ldots0\rangle$ (with $N = 0$) by applying $\hat{c}^\dagger$-operators. Within this representation, we can write a Hamiltonian with (possibly spin-dependent) pair interactions as

$$\hat{H} = \sum_{ij} \hat{c}_i^\dagger (k_i|h|k_j)\hat{c}_j + \frac{1}{2}\sum_{ijkl} \hat{c}_i^\dagger\hat{c}_j^\dagger (k_ik_j|w|k_kk_l)\hat{c}_k\hat{c}_l \tag{8}$$

where the first sum represents the independent particle energy, and the second is the two-particle term, split in the *direct* and *exchange* interaction integrals.

THE COOPER PROBLEM

A normal conducting Fermi liquid can be represented by a fermionic quasiparticle excitation spectrum which behaves as a gas of independent particles with excitation energies ϵ_k. The ground state of the system would be characterized by a ket with zero excitation number $|0\rangle$, for which all the orbitals with $\epsilon < \mu$ are occupied, and the rest, with $\epsilon > \mu$ are empty (μ is the chemical potential or Fermi energy). By adding a single electron with $\epsilon_{k_i} > \mu$ or a single hole with $\epsilon_{k_i} < \mu$, we change the state of the system to the $|k_i\sigma_i\rangle$ excited state, which is, as the ground state, an eigenstate of the Hamiltonian (8). Hence, the single particle excitation spectrum of our quasiparticle Hamiltonian $\hat{H}$ above the state $|0\rangle$ is just $\eta_k = |\epsilon_k - \mu|$.

Consider now a state with two excited particles $|k_1\sigma_1k_2\sigma_2\rangle$. For two excited electrons it can be seen [7] that the application of the quasiparticle Hamiltonian gives rise to a correlated pair state that is not an eigenstate of the Hamiltonian anymore. We try to find this pair state of lowest energy for two electrons, which we expect to have zero total momentum for the case of an isotropic metal:

$$\mathbf{k_2} = -\mathbf{k_1}, \qquad |\psi\rangle = \sum_{\mathbf{k}} a_k|\mathbf{k}\sigma, -\mathbf{k}\sigma'\rangle \tag{9}$$

where it is assumed a fixed combination of σ and σ'. We want this pair state $|\psi\rangle$ to be an eigenstate of $\hat{H}$, $\hat{H}|\psi\rangle = E|\psi\rangle$:

$$\hat{H}|\psi\rangle = \sum_{\mathbf{k}} \hat{c}_{\mathbf{k},\sigma}^\dagger\hat{c}_{-\mathbf{k},\sigma'}^\dagger|0\rangle 2\eta_k a_{\mathbf{k}} + \\ + \sum_{\mathbf{k},\sigma} \hat{c}_{\mathbf{k}+\mathbf{q},\sigma}^\dagger\hat{c}_{-\mathbf{k}-\mathbf{q},\sigma'}^\dagger|0\rangle w_{\mathbf{k},-\mathbf{k},\mathbf{q}}a_{\mathbf{k}}. \tag{10}$$

$\mathbf{q}$ is given by the selection rules for the scattering of two particles undergoing a change of momentum from $\mathbf{k}$ to $\mathbf{k} \pm \mathbf{q}$. From (10) we can get a relation of the eigenenergies and the coefficients a_k:

$$E(a_{k'} - a_{-k'}\delta_{\sigma\sigma'}) = 2\eta_{k'}(a_{k'} - a_{-k'}\delta_{\sigma\sigma'}) + \\ + \sum_{\mathbf{q}} w_{k'-q,-k'+q,q}(a_{k'-q} - a_{-k'+q}\delta_{\sigma\sigma'}) \tag{11}$$

Due to the isotropy of the problem, we expect the solution to be angular momentum eigenstate, hence a_k should have a definite parity. We can see that there are non-trivial solutions for some specific cases:

- for even parity, $a_{-k} = a_k$, non-trivial if $\delta_{\sigma\sigma'} = 0$ ($\sigma' = -\sigma$), *i.e.* for total spin equal zero;
- for $\delta_{\sigma\sigma'} = 1$ ($\sigma' = \sigma$), non-trivial if $a_{-k} = -a_k$ which corresponds to an odd-parity angular momentum state.

The first case could have $L_T = 0$ ($s - wave$) and $S_T = 0$ (*e.g.* electron-pairs in a superconductor), while the second, $L_T = 1$ ($p - wave$) and $S_T = 1$ (*e.g.* ^3He).

For the singlet case, assume $a_{\mathbf{k}} = a_k Y_{lm}(\mathbf{k}/k)$ with even l. The scattering coefficient expands as $w_{k',-k',k-k'} = \sum_{lm} \lambda_l w_k^l w_{k'}^{l*} Y_{lm}(\mathbf{k}) Y_{lm}^*(\mathbf{k}')$, in which negative (positive) λ_l corresponds to an attractive (repulsive) interaction. This yields

$$1 = \lambda_l \sum_k |w_k^l|^2 \frac{1}{E_{lm} - 2\eta_k} \equiv \lambda_l F(E_{lm}). \tag{12}$$

The sought lowest pair energy corresponds to the lowest solution of $F(E_{lm}) = 1/\lambda_l$ (Fig. 1). If $\lambda_l > 0$, then the lowest solution E_{lm} is positive and the ground state $|0\rangle$ of the normal metal is stable. But if at least one λ_l-value is negative (attractive interaction), then there is unavoidably a negative solution E_{lm}: the excited pair has negative energy and the normal ground state $|0\rangle$ is now unstable against forming pairs of bound quasiparticles. The basic idea that even a weak attraction can bind pairs of electrons into a bound state was presented by Cooper in 1956. He showed that the Fermi sea of electrons is unstable against the formation of at least one bound pair, regardless of how weak the interaction $|\lambda_l|$ is, so long as it is attractive.

Cooper introduced the following approximation: if the interaction is cut off at some energy ω_c,

$$w_k^l = \begin{cases} 1, & for \quad 0 < \eta_k < \omega_c \\ 0, & elsewhere \end{cases} \tag{13}$$

and the density of states for η_k is nearly constant in this interval, $N(\eta) = N(0)$, then with negative E_{lm}:

$$|E_{lm}| \sim \begin{cases} 2\omega_c exp\left[-\frac{2}{N(0)|\lambda_l|}\right], & for \quad N(0)|\lambda_l| \ll 1 \\ N(0)|\lambda_l|\omega_c, & for \quad N(0)|\lambda_l| \gg 1 \end{cases} \tag{14}$$

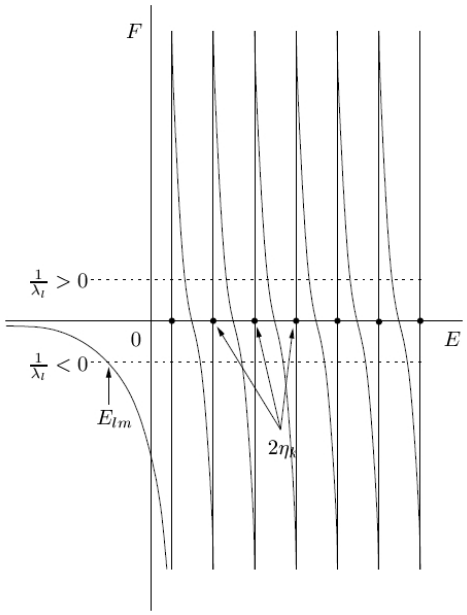

FIG. 1: The function $F(E_{lm})$ from equation (12).

in the weak and strong coupling limits.

As we discussed above, a negative λ_l-value is mandatory for an attractive interaction. Negative λ_l-values come in only when one takes the motion of the ion cores into account. The physical idea is that the first electron polarizes the medium by attracting positive ions; these excess positive ions in turn attract the second electron, giving an effective attractive interaction between the electrons. If this attraction is strong enough to override the repulsive screened Coulomb interaction, it gives rise to formation of bound pairs, and superconductivity results. This idea was first suggested by Fröhlich [8] in 1950, and it was confirmed experimentally by the discovery of the *isotope effect* [9]. For momentum conservation, we can see that if an electron is scattered from $\mathbf{k}$ to $\mathbf{k}'$, the relevant phonon must carry the momentum $\mathbf{q} = \mathbf{k} - \mathbf{k}'$, and the characteristic frequency must then be the phonon frequency ω_q. As a result, it is plausible that the phonon contribution to the scattering (screening) function w_k^l be proportional to $(\omega^2 - \omega_q^2)^{-1}$. Evidently, this resonance denominator gives a negative sign if $\omega < \omega_q$, corresponding to the physical argument above. Thus, the cutoff energy ω_c of Cooper's attractive matrix element is expected to be of the order of the Debye energy $\hbar\omega_D = k\Theta_D$, which characterizes the cutoff of the phonon spectrum.

Although the phonon-mediated attraction is the basis for superconductivity in the classic SCs, it is important to recognize that the BCS pairing model requires only an attractive interaction giving a matrix element that can be approximated as $-V$ over a range of energies near E_F. Different pairing interactions, involving the exchange of bosons other than phonons, may well be responsible for superconductivity in some of the more exotic organic, heavy fermion and high temperature SCs. In this case, the electron pairing may be p-wave or d-wave character, rather than the s-wave form assumed here.

THE BCS MODEL

From the Cooper's analysis, and with the assumption that the attraction is in the $l = 0$ spin singlet channel, Bardeen, Cooper and Schrieffer (BCS) formulated the simple model Hamiltonian

$$\hat{H}_{BCS} = \sum_{\mathbf{k}\sigma} \hat{c}^\dagger_{\mathbf{k}\sigma}(\epsilon_k - \mu)\hat{c}_{\mathbf{k}\sigma} - \\ -\frac{g}{V} \sum_{\mathbf{k}\mathbf{k}'}^{\mu-\omega_c<\epsilon_k,\epsilon_{k'}<\mu+\omega_c} \hat{c}^\dagger_{\mathbf{k}'\uparrow}\hat{c}^\dagger_{-\mathbf{k}'\downarrow}\hat{c}_{-\mathbf{k}\downarrow}\hat{c}_{\mathbf{k}\uparrow}. \qquad (15)$$

$g > 0$ is the BCS coupling constant, and V is the normalization volume. The state $|0\rangle$ cannot be anymore the ground state of this Hamiltonian since Cooper's theorem tells us that this state is unstable against spontaneous formation of bound pairs with the gain of their binding energy. BCS solved this problem finding the new ground state and the quasiparticle energy spectrum of the BCS-Hamiltonian.

In order to do this, a transformation of variables (operators) was proposed by Bogoliubov and Valatin [10]. The quasiparticle operators in the ground state are now

$$\hat{b}_{\mathbf{k}\uparrow} = u_k\hat{c}_{\mathbf{k}\uparrow} - v_k\hat{c}^\dagger_{-\mathbf{k}\downarrow}, \qquad \hat{b}_{\mathbf{k}\downarrow} = u_k\hat{c}_{\mathbf{k}\downarrow} + v_k\hat{c}^\dagger_{-\mathbf{k}\uparrow} \quad (16)$$

where u_k and v_k are variational parameters. We consider again the isotropic problem and hence their dependence on $k = |\mathbf{k}|$ only. $\hat{b}_{\mathbf{k}\sigma}$ and $\hat{b}^\dagger_{\mathbf{k}\sigma}$ are defined to be fermionic operators. Hence, $[\hat{b}_{\mathbf{k}\sigma}, \hat{b}_{\mathbf{k}'\sigma'}] = 0$, and it can be shown that $[\hat{b}_{\mathbf{k}\sigma}, \hat{b}^\dagger_{\mathbf{k}'\sigma'}] = (u_k^2 + v_k^2)\delta_{kk'}\delta_{\sigma\sigma'} = 1$ if $u_k^2 + v_k^2 = 1$, which ensures that the transformation is canonical. The inverse transformation is then

$$\hat{c}_{\mathbf{k}\sigma} = u_k\hat{b}_{\mathbf{k}\sigma} - \sigma v_k\hat{b}^\dagger_{-\mathbf{k}-\sigma}, \qquad \hat{c}^\dagger_{\mathbf{k}\sigma} = u_k\hat{b}^\dagger_{\mathbf{k}\sigma} + \sigma v_k\hat{b}_{-\mathbf{k}\sigma} \quad (17)$$

Rewriting the $\hat{H}_{BCS}$, and noting that $\hat{n}_{\mathbf{k}\sigma} = \hat{b}^\dagger_{\mathbf{k}\sigma}\hat{b}_{\mathbf{k}\sigma}$ is the new number operator of the $|\Psi_0\rangle$ BCS-ground state, we can find the new eigenenergies:

$$E = 2\sum_k (\epsilon_k - \mu)v_k^2 + \sum_k (\epsilon_k - \mu)(u_k^2 - v_k^2)(n_{k\uparrow} + n_{k\downarrow}) - \\ -\frac{g}{V}\left[\sum_k u_k v_k(1 - n_{k\uparrow} - n_{k\downarrow})\right]^2 \quad (18)$$

Minimizing this relation with respect to the variational

parameters u_k and v_k we get the self-consistent condition

$$1 = \frac{g}{2V}\sum_k \frac{1-n_{k\uparrow}-n_{k\downarrow}}{\sqrt{(\epsilon_k-\mu)^2+\Delta^2}}, \tag{19}$$

$$\Delta = \frac{g}{V}\sum_k u_k v_k (1-n_{k\uparrow}-n_{k\downarrow}) \tag{20}$$

which determines Δ as a function of the BCS coupling constant g, the dispersion relation ϵ_k of the normal $\hat{c}$-quasiparticles (the Fermi velocity), and the occupation numbers $n_{k\sigma}$ of the $\hat{b}$-quasiparticles of the superconducting state.

For the ground state, it is easy to show that the condition (19) reduces to

$$1 = \frac{g}{2V}\sum_k \frac{1-n_{k\uparrow}-n_{k\downarrow}}{\sqrt{(\epsilon_k-\mu)^2+\Delta^2}} \sim \frac{gN(0)}{2} ln \frac{4\omega_c^2}{\Delta_0^2} \tag{21}$$

resulting in the value of Δ in the ground state

$$\Delta_0 = 2\omega_c exp\left\{-\frac{1}{gN(0)}\right\}. \tag{22}$$

It is also possible to show that the $\hat{H}_{BCS}$ can be simplified using mean-field approximation. In that case, the BCS-Hamiltonian is diagonalized by the Bogoliubov-Valatin transformation, resultin in

$$\hat{H}_{m-f} = const. + \sum_{k\sigma} \eta_{k\sigma} \hat{b}^\dagger_{\mathbf{k}\sigma} \hat{b}_{\mathbf{k}\sigma} \tag{23}$$

with the $\hat{b}$-quasiparticle energy dispersion relation

$$\eta_k = \sqrt{(\epsilon_k-\mu)^2+\Delta^2}. \tag{24}$$

Equations (23) and (24), and the fact that the second term in the energy relation (18) is positive defined, show that the absolute minimum of energy (ground state) is attained if all occupation numbers of the $\hat{b}$-orbitals are zero.

This dispersion relation η_k (24) together with the normal state dispersion relation $\epsilon_k - \mu$ and the normal state excitation energy dispersion $|\epsilon_k - \mu|$ is shown in Fig. 2. It is seen that the physical meaning of Δ is the gap in the $\hat{b}$-quasiparticle excitation spectrum of the superconducting state. The name *bogolons* is often used for these quasiparticles.

BCS also obtained the pair wavefunction for the ground state. They showed that the N-particle ground state is represented by

$$\Psi_0(x_1 \dots x_N) \sim \mathcal{A}\phi(\mathbf{r_1}-\mathbf{r_2})\chi_\mathbf{0} \dots \phi(\mathbf{r_{N-1}}-\mathbf{r_N})\chi_\mathbf{0}$$
$$\phi(\rho) \sim \sum_\mathbf{k} g_k e^{i\mathbf{k}\cdot\rho}, \quad g_k = \frac{v_k}{u_k} \tag{25}$$

ρ is the distance vector of the two electrons in the pair, and χ_0 represents the singlet spin state. u_k and v_k may also be written as functions of Δ_0 and $(\epsilon_k - \mu)/\Delta_0 \sim \hbar v_F k/\Delta_0$. Hence

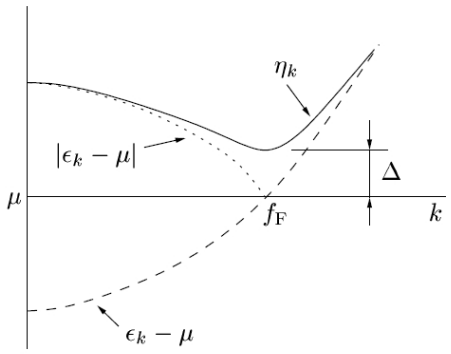

FIG. 2: Quasiparticle dispersion relation in the SC state.

$$\phi(\rho) \sim f(\rho/\xi_0), \qquad \xi_0 \approx \frac{1}{\pi\delta k} = \frac{\hbar v_F}{\pi\Delta_0} \tag{26}$$

ξ_0 has the meaning of the coherence length of the superconductor at zero temperature. For a real SC, the gap Δ_0 can be measured (*e.g. via* specific heat experiments). With the independently determined Fermi velocity v_F of the electrons in the normal state, this measurement yields directly the averaged distance of the electrons in a pair which can be compared to the average distance r_s of arbitrary conduction electrons in the solid given by the electronic density. For a weakly coupled Type-I SC the ratio is typically $\xi_0/r_s \approx 10^3 - 10^4$. In this case, there are $10^9 - 10^{12}$ electrons of other pairs in the volume between a given pair; there is a pair correlation resulting in a condensation of all electrons into one coherent state and at the same time delocalized pair orbital in the superconducting state, however, the picture of electrons grouped into individual pairs would be by far misleading.

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