

PHYS 798C Spring 2024

Lecture 5 Summary

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I. THE COOPER PAIRING PROBLEM

A. Review of Free Electron Fermi Gas Model of a Metal

A graphical review of the free-electron [Fermi gas model](#) is posted on the class web site under Lecture 1.

Metals are made up of positively charged ions and the “free” electrons (meaning that they are not localized to the ions, but can go anywhere in the metal). The ions are stuck in equilibrium positions, but can execute small oscillations about those points.

The electrons are assumed to not interact with each other or with the ions, except through the Pauli exclusion principle.

One can solve the single-particle Schrodinger equation for a free particle in a box of size $L \times L \times L$ obeying periodic boundary conditions: $\psi(x + L, y, z) = \psi(x, y, z)$.

The solutions are plane (running) waves: $\psi(\vec{r}) \sim \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$, with $\vec{k} = \{k_x, k_y, k_z\}$, and $V = L^3$ is the volume of the metal box.

The eigen-energies are $E = \hbar^2 k^2 / 2m$.

The solutions are also eigenfunctions of the linear momentum operator, with eigenvalue $\hbar\vec{k}$.

The periodic boundary conditions force the momenta to be discrete and labeled by three integers which can be positive, negative, or zero. These discrete values of \vec{k} , plus the spin σ , label the available single particle states.

No two identical electrons with overlapping wavefunctions can occupy the same exact quantum state (i.e. the same exact list of quantum numbers).

All states are filled starting at $E = 0$, and then up to the last occupied state at the Fermi energy $E_F = \hbar^2 k_F^2 / 2m$. The collection of filled states is called the Fermi sea. In this simple free-electron model the surface of filled states is a sphere in momentum space (aka reciprocal space or k-space).

Typical Fermi energies for metals are on the scale of 1 to 10 eV.

The density of electronic states for free electrons in a 3D metal $D(E) \sim E^{1/2}$.

The density of electronic states can be determined from measurements of the electronic specific heat at low temperatures $C_{el} = \gamma T$, where $\gamma = \frac{\pi^2}{3} D(E_F) k_B^2$.

In Al the density of states at the Fermi energy is about 0.57 states/atom/eV. This quantity plays a role in the microscopic theory of superconductivity.

B. Cooper's Calculation

Here we follow the calculation made by Leon Cooper, posted on the [class web site](#).

Consider a metal at zero temperature with all of the electrons in the ground state occupying all states within the Fermi sphere, and no states occupied outside.

Now add two electrons to states outside the Fermi sphere. They do not interact with the electrons in the Fermi sea except through the Pauli exclusion principle - they cannot occupy any states inside the sphere in momentum space. The two electrons can, and do, interact with each other.

The objective now is to write down an ansatz for the two-electron wavefunction, put it in to the Schrodinger equation, and solve for the eigen-energy of this 2-particle system. If the ground state energy is less than $2E_F$ then a bound state of the two electrons is formed, and we are a step closer to a microscopic understanding of superconductivity.

We take the two-particle wavefunction to be of the form $\Psi(1, 2) \sim \psi(\vec{r}_1 - \vec{r}_2) e^{i\vec{Q}\cdot\vec{R}} \chi(\sigma_1, \sigma_2)$, where ψ is the relative coordinate ($\vec{r} = \vec{r}_1 - \vec{r}_2$) wavefunction, \vec{R} and $\hbar\vec{Q}$ are the center of mass position and momentum, respectively and χ is the two-electron spinor wavefunction.

In the ground state we expect the center of mass momentum to be zero $\vec{Q} = 0$. This means that the two electrons have equal and opposite momenta $\hbar\vec{k}$ and $-\hbar\vec{k}$. The two-particle wavefunction Ψ must be

anti-symmetric upon exchange of all the labels of the two particles. One way to accomplish this is to have a symmetric relative wavefunction $\psi \sim \cos(\vec{k} \cdot \vec{r})$ where $\vec{r} = \vec{r}_1 - \vec{r}_2$ is the relative coordinate, times an anti-symmetric spinor, namely the spin-singlet $|00\rangle$. The other option is to have an anti-symmetric relative wavefunction $\psi \sim \sin(\vec{k} \cdot \vec{r})$ times a symmetric spinor, namely the spin-triplet set of states $|11\rangle$, $|10\rangle$ and $|1-1\rangle$. Because we anticipate there will be an attractive interaction, we choose the symmetric space wavefunction since this brings the two particles closer together. Finally, the general ansatz is a sum over all possible states $(\vec{k}, -\vec{k})$ outside the filled Fermi sphere, weighted by a \vec{k} -dependent factor $g_{\vec{k}}$: $\Psi(1, 2) = \sum_{k > k_F} g_{\vec{k}} \cos(\vec{k} \cdot \vec{r}) |00\rangle$.

C. Two-particle Schrodinger Equation

The two-electron time-independent Schrodinger equation is

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 + V(\vec{r}_1 - \vec{r}_2) \right) \psi(\vec{r}_1, \vec{r}_2) = E \psi(\vec{r}_1 - \vec{r}_2),$$

where $V(\vec{r})$ is the interaction potential between the two electrons. Our objective is to solve for the eigen-energy E .

Substituting the ansatz wavefunction in to the 2-electron Schrodinger equation, multiplying through by $e^{-i\vec{k}' \cdot \vec{r}}$ and integrating over all space yields the following result:

$$(E - 2\varepsilon_k) g_{\vec{k}} = \sum_{\vec{k}'} g_{\vec{k}'} V_{\vec{k}, \vec{k}'}$$

where $\varepsilon_k \equiv \hbar^2 k^2 / 2m$ is the single particle kinetic energy, and we have defined the Fourier transform of the pairing interaction $V(\vec{r})$,

$$V_{\vec{k}, \vec{k}'} = \int_{\text{Volume}} d^3r V(\vec{r}) e^{i(\vec{k} - \vec{k}') \cdot \vec{r}}.$$

$V_{\vec{k}, \vec{k}'}$ characterizes the strength of the potential for scattering a pair of electrons with momentum $(\vec{k}, -\vec{k})$ to momentum $(\vec{k}', -\vec{k}')$. It turns out that momentum space is the best setting for understanding Cooper pairing. If we can find a set of g_k with $E < 2E_F$ then a bound pair exists.

Cooper introduced a simplified potential (based on the Frohlich potential that we will derive later),

$$V_{\vec{k}, \vec{k}'} = \begin{cases} -V & E < \hbar\omega_c \\ 0 & E > \hbar\omega_c \end{cases}$$

where energy is measured relative to the Fermi energy, energy $V > 0$ (NOTE that V is NOT the volume of the box anymore!), and $\hbar\omega_c$ is the energy scale of the pairing interaction. It is assumed that $\hbar\omega_c \ll E_F$. We shall see that for “conventional” superconductors the ion lattice vibrations will set this energy scale, and it is about 10 meV in a metal like Pb. This pairing interaction will be studied in detail in the next lecture. Using this potential, the Schrodinger equation now becomes,

$$g_{\vec{k}} = \frac{V \sum_{\vec{k}' < \vec{k}_c} g_{\vec{k}'}}{2\varepsilon_k - E}. \text{ Note the restricted sum on } k'.$$

Summing both sides on k (over the same restricted range), canceling the sums on k' of $g_{k'}$ (which are just numbers), one arrives at,

$$\frac{1}{V} = \sum_{\vec{k}' < \vec{k}_c} \frac{1}{2\varepsilon_k - E}$$

We can replace the sum on k by an integral on energy through use of the density of states, $D(\varepsilon)$ with $\varepsilon = \hbar^2 k^2 / 2m$,

$$\frac{1}{V} = \int_{E_F}^{E_F + \hbar\omega_c} \frac{D(\varepsilon) d\varepsilon}{2\varepsilon - E}.$$

Since $\hbar\omega_c \ll E_F$ we can take the density of states to be constant and equal to that at the Fermi energy, $D(E_F)$. (Recall that $D(E_F)$ can be obtained from the electronic specific heat and has the units of states/atom/eV) The integral is now straightforward and one finds (exercise for the reader!) that the energy eigenvalue is,

$$E = 2E_F + \frac{2\hbar\omega_c}{1 - e^{-2/D(E_F)V}}.$$

At first glance it appears that $E > 2E_F$, but examine the exponential with the dimensionless quantity $D(E_F)V$ more closely. If we take the “weak coupling approximation” and assume that $D(E_F)V \ll 1$, then the eigenenergy can be written to good approximation as,

$E \simeq 2E_F - 2\hbar\omega_c e^{-2/D(E_F)V}$, which is less than $2E_F$, showing that a bound state, a Cooper pair, is formed.

Note that the binding energy is non-analytic in the small parameter, meaning that this result cannot be derived by ordinary perturbation theory, accounting for the many failures to produce a theory of superconductivity before BCS. The other interesting thing to note (Ashcroft and Mermin, p. 740) is

that there is a Cooper pair bound state no matter how weak the attractive interaction strength V . This is in contrast to the fact that for two particles interacting in 3D a minimum strength is required to find a bound state in quantum mechanics.

D. Binding Energy Systematics

The Cooper pair binding energy depends on the energy scale of the ion vibrations $\hbar\omega_c$ as well as the strength of the pairing interaction V and the density of states (DOS) at the Fermi energy $D(E_F)$. Let's examine these dependencies, assuming that the superconducting transition temperature scales with the binding energy of the Cooper pair, i.e. $k_B T_c \sim 2\hbar\omega_c e^{-2/D(E_F)V}$.

It is found in the transition metals that T_c scales very closely with the DOS at the Fermi energy, $D(E_F)$. The [Supplementary Material](#) on the class web site shows this dependence. The oscillatory $D(E_F)$ variation (and T_c variation) upon going across the 4d transition metal alloys arises from the Fermi energy moving through peaks and values of the DOS in the fairly rigid band structure. We will study the dependence of T_c on $\hbar\omega_c$ after the discussion of the pairing interaction in the next lecture.

E. Cooper Pair Wavefunction

Go back to calculate the expansion coefficients for the ansatz wavefunction:

$$g_{\vec{k}} = \frac{V \sum_{\vec{k}' < \vec{k}' < \vec{k}_c} g_{\vec{k}'}}{2\varepsilon_k - E}, \text{ now substituting the eigen-energy gives,}$$

$$g_{\vec{k}} = \frac{V \sum_{\vec{k}' < \vec{k}' < \vec{k}_c} g_{\vec{k}'}}{2\xi_k + 2\hbar\omega_c e^{-2/D(E_F)V}}, \text{ where we define } \xi_k \equiv \varepsilon_k - E_F, \text{ which is the energy difference from the Fermi surface.}$$

Treating the sum in the numerator as just a number, which can be subsumed into the normalization factor, we get for the full wavefunction,

$$\Psi(1, 2) \propto \sum_{k > k_F} \frac{\cos(\vec{k} \cdot \vec{r})}{2\xi_k + 2\hbar\omega_c e^{-2/D(E_F)V}} |00\rangle.$$

Note two things about this expression. First there is no preferred direction in k-space, that is the solution wavefunction is isotropic in \vec{k} . This isotropy of the wavefunction is noted as “s-wave pairing” in the literature. Other orbital symmetries are possible and observed, including “p-wave” and “d-wave” pairing states. Second, the expansion coefficients decrease quickly with increasing distance from the Fermi surface, falling off like $1/k^2$. This justifies to some extent the simplified treatment of the pairing potential $V_{\vec{k}, \vec{k}'}$.

F. Estimating the Coherence Length

If we imagine that the Cooper pair is a minimum uncertainty wave packet, we can make an order of magnitude estimate of its spatial extent. Using the position momentum uncertainty relation $\Delta x \Delta p \sim \hbar$, and estimating $\Delta p \sim \frac{\hbar\omega_c e^{-2/D(E_F)V}}{v_F} \sim \frac{k_B T_c}{v_F}$, we find the typical size of a Cooper pair is,

$\Delta x \sim \frac{\hbar v_F}{k_B T_c}$. More correctly, BCS theory predicts this length scale is $\xi_0 = a \frac{\hbar v_F}{k_B T_c}$, where $a = 0.18$. Plugging in numbers for Al we find $\xi_0 = 0.18 \times 13.1 \mu m = 2.4 \mu m$. The accepted experimental value is about $1.6 \mu m$. Al has a relatively high Fermi velocity and low T_c , so it's coherence length is rather large, putting it at the extreme end of type-I superconductors in fact. Most materials have coherence lengths ranging from about 1 to 100 nm. In Ginzburg-Landau theory we will interpret the coherence length as the characteristic length scale on which the superconducting order parameter can vary.

Going back to the Cooper pair size discussion, we see now that in a typical metal the pairs are highly overlapping. A Cooper pair of size 10^2 to 10^3 nm, with atoms of size 10^{-1} nm, will cover $(10^3)^3$ to $(10^4)^3$ or 10^9 to 10^{12} electrons! Hence each Cooper pair overlaps with “billions and billions” of others, making this very different from a Bosonic gas, such as ${}^4\text{He}$. The strongly overlapping nature of the pairs means that superconductivity is not simply a Bose-Einstein condensation of weakly interacting (spin-singlet) Bosons, but a phase transition of very different character.

Thinking ahead to the full BCS theory, we need to write down an ansatz wavefunction for ALL of the electrons in the metal. At this point it is clear that we are NOT able to write the full N -particle superconducting state wavefunction as $\Psi(1, 2, \dots, N) = \psi(1, 2)\psi(3, 4) \dots \psi(\frac{N}{2} - 1, \frac{N}{2})$. Something much more general that respects the Fermionic nature of the electrons is required. When viewed from a distance, a superconductor is basically a filled Fermi sea with a subtle re-arrangement of electron state occupations to enable Cooper pairing of all the electrons.