Elements of superconductivity

1 Brief historical review

Superconductivity (SC) is one of the most fascinating properties that have emerged in condensed matter physics. It was discovered in 1911 by K. Onnes, who was trying to settle a dispute between theorists regarding what happens to the resistivity of metals at very low T. A few years prior he had succeeded in liquefying helium and cooling it down to $\sim 1.5K$, so he had access to such low temperatures. He found out that the resistence of mercury suddenly dropped to zero at 4.2K (needless to say, nobody had predicted that!). Since then, most elemental metals and simple alloys have been found to become superconducting at similarly low temperatures, so this is a rather generic property of metals and therefore it must have a simple and robust explanation. The temperature below which a metal becomes superconducting is called T_c = the critical temperature. In "conventional superconductors", which we understand and whose theory we will discuss here, this is usually from a few K up to 20-30K. More recently, classes of so-called **high-temperature superconductors** have been discovered, notably the cuprates in late 1980s and iron-based superconductors around 2008. Various other surprises appear on a fairly regular basis. These "unconventional superconductors" are not yet understood. They share many basic properties with the conventional ones, but the mechanism reponsible for superconductivity is (almost certainly) not the same. Depending on how much time we have I may comment on the unconventional ones, but the main focus will be the conventional SC, which we understand.

It is important to note that **zero resistivity**, which is one of the two defining characteristics of any superconductor, really means zero. This has been tested, for instance, by inducing currents (called supercurrents) to flow in a superconducting ring, then turning off the external field. In any normal metal, the current would decay to zero rather fast. As we know, this is because of scattering of the electrons on impurities, on phonons, and on each other (occurance of scattering processes is why the resistance is finite). Supercurrents have been found to run in superconducting rings for years without any measurable decay, showing that scattering is somehow prohibited.

The second defining characteristic is the **Meissner effect**: a magnetic field (if not too strong) cannot penetrate inside the superconductor. The way to think about this is that because supercurrents can run at no cost, when the superconductor is placed in a magnetic field supercurrents are generated on the surface in precisely the way required to cancel the magnetic field inside the material (so strictly speaking the magnetic field is not fully expelled, instead it penetrates over a narrow shell near the surface which supports these screening supercurrents). We will not have time to discuss the reason for this in detail, but basically what happens is that (for reasons which we will see soon) magnetic fields are detrimental to superconductivity. If the magnetic field is small enough, it is energetically favorable to screen it out so that the material stays superconducting. If the magnetic field is above a threshold, it becomes energetically too expensive to screen it so it penetrates the material and turns into a normal metal. For so-called "type II" SC, there is an intermediary stage in between the two, where the magnetic field passes through the material only in quantized bundles, called vortices; these way some regions are turned normal (where the vortices are and the magnetic field goes through) and the rest remains superconducting (outside the vortices).

There are many other characteristic properties like flux quantization, specific heat jump at T_C, certain effects on tunneling into such materials, the Josephson effect, etc. We will not discuss these in this introductory class. Hopefully you will take a dedicated superconductivity course, or learn more on your own. For conventional superconductivity, Tinkham's book is probably still the best

textbook. There are lots of books and articles about unconventional superconductivity, which is one of the most active areas in condensed matter research, but these (mine included) should be consumed with great skepticism: we simply do not know the answer yet.

The aim for us is to gain an understanding of why conventional superconductivity emerges and to study in some detail the Bardeen-Cooper-Schrieffer (BCS) model, which is the simplest generic model that explains it.

2 Cooper pairs

Conventional superconductivity is a direct consequence of the interactions between electrons and phonons. Remember that we found out that electron-phonon coupling leads to an effective attractive interaction between electrons within $\hbar\omega_D$ of the Fermi energy (note: we did that derivation for Einstein phonons, but a similar result appears for acoustic phonons and their maximum energy – the Debye energy – $\hbar\omega_D$ would play the role of $\hbar\Omega$. Of course, in reality all phonon modes will contribute to this, but if we consider elemental metals then acoustic phonons may be all there is).

At first sight, this attraction should not be expected to have any significant effect because it is very weak. In a 3D environment an attractive potential must be over a threshold (comparable to an "average" kinetic energy in the bound state) before it can bind two objects together. So if this phonon-mediated attraction is so weak it will only result in some additional scattering between electrons and therefore nothing dramatic, right?

The answer is no, and that is because the two electrons are not alone but in the presence of a Fermi sea of other electrons. To get a feeling for how this works, we will go first through a simple calculation due to Cooper: we will consider the ground-state of two electrons lying above a "passive" Fermi sea, if there is a weak attractive interaction between them when their energies are within $\hbar\omega_D$ of E_F. Of course, we cannot truly isolate these two electrons from the other ones, they are undistinguishable particles after all – but let's pretend we can do it, to see what we learn, and then we'll do things properly.

The Schrödinger equation for the two electrons is:

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

We can go to center-of-mass and relative coordinates. Because we're looking for the ground-state, we set the center-of-mass momentum to zero (that motion just describes overall translation of the pair), and consider the equation for the relative coordinate $\rho=\vec{r}_1-\vec{r}_2$:

$$\left[-\frac{\hbar^2}{m}\nabla^2+V(\vec{\rho})\right]\phi(\vec{\rho})=E\phi(\vec{\rho})$$

We Fourier transform $\phi(\vec{\rho})=\sum_{|\vec{k}|>k_F}\chi(\vec{k})e^{i\vec{k}\vec{\rho}}$. Remember that the states below the Fermi energy are occupied by the electrons in the passive Fermi sea, so the sum is only over momenta above the Fermi sea. This wavefunction means that if electron 1 has momentum $+\vec{k}$, then electron 2 has momentum $-\vec{k}$. This is not surprising if the total momentum = the center of mass momentum = zero, but it will be relevant later on so I wanted to emphasize it. This leads to:

$$[2\epsilon_k-E]\chi(\vec{k})=-\frac{1}{V}\sum_{|\vec{q}|>k_F}V(\vec{k}-\vec{q})\chi(\vec{q})$$

where $\epsilon_k = \frac{\hbar^2 k^2}{2m}$ and $V(\vec{k})$ is the Fourier transform of $V(\vec{\rho})$.

Now we remember that this potential is attractive when the electrons are within $\hbar\omega_D$ of the Fermi energy (and then it quickly goes to zero) so we simplify it to:

$$V(\vec{k}-\vec{q}) = \begin{cases} -V_0 = const. & \text{if } E_F \le \epsilon_k, \epsilon_q \le E_F + \hbar\omega_D \\ 0 & \text{otherwise} \end{cases}$$

and we immediately find:

$$\chi(\vec{k}) = \frac{V_0}{2\epsilon_k - E}\frac{1}{V}\sum_{E_F \le \epsilon_q \le E_F+\hbar\omega_D} \chi(\vec{q}) \to 1 = \frac{1}{V}\sum_{E_F \le \epsilon_k \le E_F+\hbar\omega_D} \frac{V_0}{2\epsilon_k - E}$$

from which we can find the gs energy as the lowest solution. As always in such cases, we transform the sum over momenta to an integral over energies $\frac{1}{V}\sum_{\vec{q}} F(\epsilon_q) \to 2\int d\epsilon N(\epsilon)F(\epsilon)$ where $N(\epsilon)$ is the density of states without spin; the 2 accounts for it. Furthermore, because we only integrate over a very narrow energy interval of width $\hbar\omega_d \ll E_F$, we can set the density of states at its E_F value and the integral is then trivial and results in, after some re-arranging:

$$\frac{2\hbar\omega_D}{2E_F - E} = e^{\frac{1}{N(E_F)V_0}} - 1 \approx e^{\frac{1}{N(E_F)V_0}}$$

The last equality is because the attraction V_0 is very small so the exponent is very large. Finally, we then find:

$$E \approx 2E_F - 2\hbar\omega_D e^{-\frac{1}{N(E_F)V_0}}$$

This result is quite amazing! Despite the peculiar assumptions we made to get it, it contains a wealth of information.

First: it tells us that the ground state corresponds to a bound state (two free electron energies are $2E_F$ and higher). This seems to contradict the statement I made above, that in 3D one needs a strong attraction to bind two particles. As already mentioned, the reason is the presence of the passive Fermi sea. Because the two electrons cannot have momenta below k_F but will not go much above k_F either (that would increase the kinetic energy without gaining any additional attraction), their motion is effectively 2D as they move in a thin shell just above the Fermi energy. Indeed, in 2D it is known that any attractive potential can bind (exponentially weakly) a pair of particles – and this is what happens here. Such a bound pair of electrons is called **a Cooper pair**.

Second: electrons bound in pairs!!! This never ever happens in vacuum because of the strong Coulomb repulsion. What happens in a metal is that most of this repulsion is screened out by the Fermi sea of electrons, and then the contribution of the ions turns it weakly attractive (we refer to this as overscreening) in a narrow energy range. So although this might sound simple, it is a complex behavior involving all the electrons and ions in the system.

Third: the binding energy is proportional to $\hbar\omega_D$. Since this is controlled by the masses of the ions (see acoustic phonons dispersions) it means that there should be a strong isotope effect: if different isotopes are used, the phonon frequencies scale accordingly and that will directly change the binding energy. This binding energy is related to T_C, as we'll see soon (roughly speaking, superconductivity has something to do with these Cooper pairs, and they are expected to survive as long as the thermal energy $k_B T < 2\hbar\omega_D e^{-\frac{1}{N(E_F)V_0}}$, from which we can estimate T_c). Indeed, it was the discovery of the isotope effect that was the needed breakthrough to help theorists explain conventional superconductivity, because it directly pointed out to the involvement of phonons into this phenomenology.

Fourth: Note that this binding energy is non-perturbative in V_0 – that exponential cannot be written as a well-behaved Taylor series in powers of V_0. It also shows that binding occurs no matter how weak V_0 is. This should give us confidence that it is there for more realistic potentials than the one we used, as well.

Fifth: because $\chi(\vec{k})$ depends only on $|\vec{k}|$ (through ϵ_k), it is straighforward to see that $\psi(\vec{\rho})$ depends only on $\rho = |\vec{r}_1 - \vec{r}_2|$. In other words, the amplitude of probability is the same no matter how the pair is oriented spatially. A bound-state with this symmetry is called a **s-wave** state. This symmetry can be detected experimentally and indeed is s-wave in conventional superconductors. Unconventional superconductors tend to different symmetries (cuprates are definitely d-wave).

Moreover, this means that the spatial component of the wavefunction is symmetric to electron interchange. In order to satisfy Pauli's principle, it then follows that the pair of electrons have their spins locked into a singlet.

Six: a singlet is a zero-spin object, so the Cooper pair is a boson! Now we finally start understanding what is happening here. Of course, not just these two electrons lock in a Cooper pair, but all the electrons do (as we'll see in a bit when we do things more properly). So below T_c, our liquid of fermions turns itself into a liquid of Cooper pairs, i.e. of bosons! As you know, bosons in 3D can undertake Bose-Einstein condensation (BEC) if the temperature is low enough. It turns out that T_c is so low that it is below the BEC temperature of these bosons, so as soon as the Cooper pairs form they all condense. Superfluidity (flow without friction) is a hallmark of a superfluid and that is what happens here, except we have charged bosons (charge of $2e$) so we have supercurrents.

Seven: from $\psi(\vec{\rho})$ we can estimate the typical size of the Cooper pair. In conventional superconductors it is $\sim 1000\mathring{A}$, i.e. extremely big. So you should not think of these electrons as being bound in the usual sense, i.e. like a molecule in real space, instead the pairing is in the momentum space between a singlet of two electrons with momenta $+\vec{k}$ and $-\vec{k}$. This will become a bit more clear when we study the BCS model.

In cuprates, the pair size is $\sim 10\mathring{A}$, so many physicists believe that these are more like "molecules" bound in real space. That, and the different symmetry, and the absence of a systemativ isotope effect (although there are claims that there is some) plus the very high T_C (well above the maximum one might expect getting out of phonons) are some of the reasons why we do not believe that exchange of phonons explains why Cooper pairs form there. Of course, there are other excitations in a material beside phonons, that could mediate electron-electron attractions, so the race is on to see which one of those (or maybe a combination of several) might explain the peculiarities of cuprates.

Finally, before going on to the BCS model, let me point again how amazing this phenomenon is, given that it is explained in terms of a (super)liquid of bosons instead of the expected soup of fermions. No wonder that it took several decades to figure this one out (well, quantum mechanics was also developed during that interval, which helped).

3 The BCS Hamiltonian

We will now redo this calculation properly, considering all electrons in the system (not just two special ones). The general Hamiltonian describing the electrons is:

$$\mathcal{H} = \sum_{\vec{k}\sigma} \epsilon_k c^\dagger_{\vec{k},\sigma} c_{\vec{k}\sigma} + \frac{1}{2V} \sum_{\substack{\vec{k},\vec{k}',\vec{q} \\ \sigma\sigma'}} V_{k,k',q} c^\dagger_{\vec{k}+\vec{q},\sigma} c^\dagger_{\vec{k}'-\vec{q},\sigma'} c_{\vec{k}'\sigma'} c_{\vec{k}\sigma}$$

where the interaction is generated by phonon exchange between the electrons, so again the interaction will be assumed to be an attractive constant within $\hbar\omega_D$ of E_F and zero otherwise. Note that strictly speaking we should use quasiparticle energies $E(\vec{k})$ in the first term, but we assume that the direct electron-electron interactions are weak enough that these are very close to the free electron energies (or, we include their effect into a renormalized mass m).

Based on the knowledge acquired from Cooper's calculation, that the interesting pairing involves $(\vec{k}\uparrow, -\vec{k}\downarrow)$ electrons, BCS further simplified this Hamiltonian keeping only terms with interactions between such pairs of states:

$$\mathcal{H}_{BCS} = \sum_{\vec{k}\sigma} \epsilon_k c^\dagger_{\vec{k},\sigma} c_{\vec{k}\sigma} + \frac{1}{2V} \sum_{\vec{k}\neq\vec{k}'} V_{k,k'} c^\dagger_{\vec{k}\uparrow} c^\dagger_{-\vec{k}\downarrow} c_{-\vec{k}'\downarrow} c_{\vec{k}'\uparrow}$$

where $V_{k,k'} = -V_0$ within $\hbar\omega_D$ of the Fermi surface, and zero otherwise. This interaction shows that by exchanging a phonon, a singlet pair of total momentum zero and relative momentum $2\vec{k}'$ will be scattered into another singlet pair of relative momentum $2\vec{k}$. Throwing away the other terms may seem unjustified, but at the end of the day we expect to find only pairs of zero momentum in the ground state so what we kept should be the most important ppart. Of course, we could add back the ignored parts and treat them fairly, but that doesn't change anything qualitatively from what we'll find out next.

Because V_0 is small, we will to treat this Hamiltonian in the spirit in which we treated weak-interactions in the Hartree-Fock approximation. First, for later convenience, let's relax the number of particles in the system, in other words work in a grandcanonical ensemble. This implies adding a $-\mu\hat{N}$ term, where the chemical potential μ will be chosen such that the average number of electrons $\langle\hat{N}\rangle = nV$ leads to the desired concentration of electrons. We will discuss after that how we can go back to solutions with a fix number of electrons, if we so wish. In practice, this means that from now on we replace $\epsilon_k \to \xi_k = \epsilon_k - \mu$ in the first term of $\mathcal{H}_{BCS}$.

Just like we did for the HFA, let us try to find the "best" quadratic approximation for this Hamiltonian, in other words we're trying to rewrite it in terms of quasiparticles (and ignore small interactions that arise between them). This being a homogeneous system, we know that quasi-momentum must be a good quantum number, and so must be the z-axis spin projection (the Hamiltonian conserves this quantity). This basically exhaust all the possible degrees of freedom, so we are trying to rewrite:

$$\mathcal{H}_{BCS} \approx E_0 + \sum_{\vec{k},\sigma} E(k) \gamma^\dagger_{\vec{k}\sigma} \gamma_{\vec{k}\sigma}$$

where $\gamma, \gamma^\dagger$ are the (so far unknown) operators for the quasiparticles and $E(k) > 0$ are their corresponding energies. The latter condition comes about because we want these to represent the excitations possible for the system, starting from its ground-state $|\psi_0\rangle$ of energy E_0. We don't know $|\psi_0\rangle$ either, but we will define it such that any $\gamma_{\vec{k}\sigma}|\psi_o\rangle = 0$ – i.e., it is the state without any excitations, which therefore has the smallest possible energy E_0.

The next step is to express these operators in terms of the old operators $c, c^\dagger$. Because of conservation of momentum and spin, the only option available is to try:

$$\gamma_{\vec{k}\uparrow} = u_{\vec{k}} c_{\vec{k}\uparrow} - v_{\vec{k}} c^\dagger_{-\vec{k},\downarrow} \qquad\qquad \gamma^\dagger_{\vec{k}\uparrow} = u_{\vec{k}} c^\dagger_{\vec{k}\uparrow} - v_{\vec{k}} c_{-\vec{k},\downarrow}$$

because adding a particle with momentum $-\vec{k}$ changes the total momentum as much as removing a particle with momentum $+\vec{k}$; and same with the spin. The second equation assumes that the

coefficients u_k, v_k are real numbers. We certainly can chose one to be real; you should try to see what happens if we allow the second one to be complex.

Note that we must have $\{\gamma_{\vec{k}\uparrow}, \gamma^\dagger_{\vec{k}\uparrow}\} = 1$, because these are fermionic quasiparticles (they carry spin 1/2). As a result, $u_k^2 + v_k^2 = 1$, meaning we could chose $u_k = \cos(\theta_k), v_k = \sin(\theta_k)$, so this is simply a rotation between operators.

We also need the operators for spin-down quasiparticles. Those have to anticommute with the ones we defined above for spin-up. It is easier to impose this if we work with the same momentum,spin combination that appears there, so let me define:

$$\gamma_{-\vec{k}\downarrow} = u_{\vec{k}} c_{-\vec{k}\downarrow} + v_{\vec{k}} c^\dagger_{\vec{k},\uparrow} \qquad\qquad \gamma^\dagger_{-\vec{k}\downarrow} = u_{\vec{k}} c^\dagger_{-\vec{k}\downarrow} + v_{\vec{k}} c_{\vec{k},\uparrow}$$

The $+v$ term appears because we need $\{\gamma_{\vec{k}\uparrow}, \gamma_{-\vec{k}\downarrow}\} = 0$, etc. Again, there are other possible choices but they won't make a difference in the end. The + sign also makes sense for a rotation by angle θ_k, see comment above.

So, with these general choices, all anticommutation operators are fine. This type of transformation between an old basis of operators and the new one is known as a **Bogoliubov-Valatin** transformation.

We now know how to proceed. If the Hamiltonian could be fully diagonalized, then $[\gamma_{\vec{k}\uparrow}, \mathcal{H}_{BCS}] = E(k)\gamma_{\vec{k}\sigma} = E(k)\left(u_{\vec{k}} c_{\vec{k}\uparrow} - v_{\vec{k}} c^\dagger_{-\vec{k},\downarrow}\right)$ so that:

$$E(k)u_k = \{[\gamma_{\vec{k}\uparrow}, \mathcal{H}_{BCS}], c^\dagger_{\vec{k}\uparrow}\} = u_{\vec{k}}\{[c_{\vec{k}\uparrow}, \mathcal{H}_{BCS}], c^\dagger_{\vec{k}\uparrow}\} - v_{\vec{k}}\{[c^\dagger_{-\vec{k},\downarrow}, \mathcal{H}_{BCS}], c^\dagger_{\vec{k}\uparrow}\}$$

and similarly for $E(k)v_k$.

However, because the true BCS Hamiltonian is quartic, some of those commutators will still be operators, not numbers. For instance, $\{[c^\dagger_{-\vec{k},\downarrow}, \mathcal{H}_{BCS}], c^\dagger_{\vec{k}\uparrow}\} = \frac{1}{2V}\sum_{\vec{k}'} V_{k,k'} c_{-\vec{k}'\downarrow} c_{\vec{k}'\uparrow}$, so the two sides of the equation cannot possibly be equal. So, just like we did in HFA, we replace them by their ground-state expectation values. Defining:

$$\Delta_k = \frac{1}{2V}\sum_{\vec{k}'} V_{k,k'} \langle\psi_0| c_{-\vec{k}'\downarrow} c_{\vec{k}'\uparrow} |\psi_0\rangle \tag{1}$$

the resulting equations are:

$$E(k)u_k = \xi_k u_k - \Delta_k v_k$$
$$E(k)v_k = -\Delta_k u_k - \xi_k v_k$$

(because $\xi_{-k} = \xi_k$, the free electron energy depends only on the magnitude of the momentum). It follows right away that we must have (remember that $E(k) > 0$):

$$E(k) = \sqrt{\xi_k^2 + \Delta_k^2}$$

and:

$$u_k = \sqrt{\frac{1}{2}\left[1 + \frac{\xi_k}{E_k}\right]} \qquad\qquad v_k = -\mathrm{sgn}(\Delta_k)\sqrt{\frac{1}{2}\left[1 - \frac{\xi_k}{E_k}\right]}$$

Quick "reasonability check": if there is no $V_{k,k'}$, i.e. if $\Delta_k = 0$, then $E_k = |\xi_k|$. So we get $u_k = 1, v_k = 0$ if $\xi_k > 0$, i.e. excitations with $|k| > k_F$ are created by adding electrons above the Fermi sea, since here $\gamma^\dagger = c^\dagger$. However, if $\xi_k < 0$, then $u_k = 0, v_k = 1$, so excitations with $|k| < k_F$

correspond to creating holes in the Fermi sea, since now $\gamma^\dagger = c$. So this is indeed reasonable. We can now also see what the role of a finite $|\Delta_k|$ is, namely to make u_k, v_k transition smoothly from 0 to 1 and 1 to 0, respectively, instead of being step-like functions.

But what is Δ_k? This is defined by Eq. (1), so let's find its value for self-consistency to hold. It requires us to compute that expectation value. At first site this seems impossible since we don't know (yet) what is $|\psi_0\rangle$, but remember that we know that it is such that any $\gamma^\dagger|\psi_0\rangle = 0$. So we rewrite the old c operators in terms of the new γ operators and use this:

$$\langle\psi_0|c_{-\vec{k}'\downarrow}c_{\vec{k}'\uparrow}|\psi_0\rangle = \langle\psi_0|\left(u_{\vec{k}'}\gamma_{-\vec{k}',\downarrow} - v_{\vec{k}'}\gamma^\dagger_{\vec{k}',\uparrow}\right)\left(u_{\vec{k}'}\gamma_{\vec{k}',\uparrow} + v_{\vec{k}'}\gamma^\dagger_{-\vec{k}',\downarrow}\right)|\psi_0\rangle = u_{\vec{k}'}v_{\vec{k}'} = -\frac{\Delta_{\vec{k}'}}{E(\vec{k}')}$$

if we use the expressions for u, v from above. So we get a self-consistency equation:

$$\Delta_{\vec{k}} = -\frac{1}{2V}\sum_{\vec{k}'} V_{k,k'}\frac{\Delta_{\vec{k}'}}{E(\vec{k}')} = -\frac{1}{2V}\sum_{\vec{k}'} V_{k,k'}\frac{\Delta_{\vec{k}'}}{\sqrt{\xi^2_{\vec{k}'} + \Delta^2_{\vec{k}'}}} \tag{2}$$

similar to those familiar from HFA. Let's solve it.

Remember that for us, $V_{k,k'} = -V_0$ within $\hbar\omega_D$ of E_F, and 0 otherwise. From Eq. (1) it now follows that Δ is independent of k. We can then switch the integral to one over energies, and simplify a bit to get:

$$1 = \frac{V_0}{2V}\sum_{|\xi_{\vec{k}'}|<\hbar\omega_D}\frac{1}{\sqrt{\xi^2_{\vec{k}'} + \Delta^2}} = \frac{V_0}{2}\int_{-\hbar\omega_D}^{\hbar\omega_D} d\xi N(\xi+\mu)\frac{1}{\sqrt{\xi^2+\Delta^2}} = V_0 N(\mu)\int_0^{\hbar\omega_D}\frac{d\xi}{\sqrt{\xi^2+\Delta^2}} = V_0 N(\mu)\sinh^{-1}\frac{\hbar\omega_D}{\Delta}$$

so that

$$\Delta = \frac{\hbar\omega_D}{\sinh\frac{1}{V_0 N(\mu)}} \approx 2\hbar\omega_D e^{-\frac{1}{V_0 N(\mu)}}$$

if we consider that in normal metals, $V_0 N(\mu) \ll 1$ because V_0 is a very weak attraction. Note that this is precisely the binding energy we got for the Cooper pair, and indeed Δ is interpreted as being precisely that. It is usually called **the gap energy** because from the expression of E_k, you can see there is a gap of magnitude $|\Delta_k|$ in the excitation energies. For the example we had here this gap has s-wave symmetry, being the same for all k values. You can see that for more complicated interactions, the gap may acquire k-dependence and even change its sign in different regions of the momentum space, so other symmetries are also possible, at least in principle.

Now let's consider what is the ground-state. Given that it is defined by $\gamma|\psi_0\rangle = 0$ for any γ, and given that γ are fermionic operators so that $\gamma\gamma = 0$ (Pauli's principle), we must have $|\psi_0\rangle = C\prod_{\vec{k}}\gamma_{\vec{k}\uparrow}\gamma_{-\vec{k}\downarrow}|0\rangle$, where $|0\rangle$ is the vacuum for electrons and C is some normalization constant. Going from γ to c operators, we find:

$$|\psi_0\rangle = C\prod_{\vec{k}}\left[u_{\vec{k}}c_{\vec{k}\uparrow} - v_{\vec{k}}c^\dagger_{-\vec{k},\downarrow}\right]\left[u_{\vec{k}}c_{-\vec{k}\downarrow} + v_{\vec{k}}c^\dagger_{\vec{k},\uparrow}\right]|0\rangle = C\prod_{\vec{k}}\left[u_{\vec{k}}v_{\vec{k}} + v^2_{\vec{k}}c^\dagger_{\vec{k},\uparrow}c^\dagger_{-\vec{k},\downarrow}\right]|0\rangle$$

and since $u_k^2 + v_k^2 = 1$, clearly the proper normalization is:

$$|\psi_0\rangle = \prod_{\vec{k}}\left[u_{\vec{k}} + v_{\vec{k}}c^\dagger_{\vec{k},\uparrow}c^\dagger_{-\vec{k},\downarrow}\right]|0\rangle$$

Now remember that well below k_F, $v_k \approx 1, u_k \approx 0$ and viceversa well above k_F. So this shows that small momentum states are fully occupied by pairs of electrons with $(\vec{k}\uparrow, -\vec{k}\downarrow)$ while high momentum states are mostly empty. This is precisely what we would expect if all the electrons were paired into Cooper pairs (and we remember that electrons are fermions, so we can't have more than 1 per state). If you'd prefer a ground-state with a fixed number of electrons, that can be obtained by projecting out of this state all components except the one that has precisely (even) N electrons. The trick to do that is to add a phase $e^{i2\phi}$ to each pair and then keep from the BCS wavefunction only the part that has precisely $e^{iN\phi}$ total phase, i.e. $\frac{1}{2\pi}\int_0^{2\pi} e^{-iN\phi}\prod_{\vec{k}}\left[u_{\vec{k}} + v_{\vec{k}}e^{2i\phi}c^\dagger_{\vec{k},\uparrow}c^\dagger_{-\vec{k},\downarrow}\right]|0\rangle$. However, we know that in the thermodynamic limit fluctuations about average decrease like $1/\sqrt{N}$, so we can use the grandcanonical results for all bulk calculations, the issue of fixed N is only an issue in small closed systems.

This wavefunction is called the **BCS wavefunction**. Just like we could also formulate HFA by finding the best Slater determinant (i.e., the one that leads to the minimum energy), one could also study this problem variationally, by finding the best u_k, v_k for the BCS wavefunction so as to minimize the ground-state energy. The answers are precisely the same as the ones we got from the equation-of-motion method (you should check this. Most books approach the problem that way, so it should be easy to verify your calculations).

We can now also calculate the ground-state energy $E_0 = \langle\psi_0|\mathcal{H}_{BCS}|\psi_0\rangle$. This is straightforward and you should check it, it's good practice. Using all the usual tricks, and in the limit $V_0 N(\mu) \ll 1$, we find the difference between the SC and the normal ground-state energies to be:

$$E_0 - E_0^{(n)} = -\frac{VN(\mu)}{2}\Delta^2$$

Of course this has to be negative, else SC would not happen. This expression is also quite easy to understand. As we discussed, the difference between normal and SC states is only visible within Δ of the Fermi energy, where u_k, v_k evolve smoothly as opposed to being step-like in the normal state. This interval Δ contains roughly $VN(\mu)\Delta$ electrons which, in the superconducting state, form half as many pairs, each of which lowers its energy by Δ when binding in a Cooper pair.

So far we have discussed $T = 0$ (ground-state) properties. Now let us also consider what happens at finite T, and especially calculate the critical temperature T_c. The extension to finite temperatures is quite straigthforward: now the system is no longer in the ground-state, instead with a finite probability it has excited quasiparticles. Because these are fermions, their average numbers when in equilibrium at temperature $T = 1/(k_B\beta)$ is:

$$\langle\gamma^\dagger_{\vec{k}\sigma}\gamma_{\vec{k}\sigma}\rangle = \frac{1}{e^{\beta E(k)}+1}$$

(the chemical potential for excitations is zero because we can have arbitrarily large numbers of them, their number is not conserved). Because $E(k) \geq \Delta$, this goes to zero as $\beta \to \infty$ and we recover the ground-state.

Now we can repeat the same calculations but we have to replace everywhere $\langle\psi_0|...|\psi_0\rangle$ by $\frac{1}{Z}\mathrm{Tr}\{e^{-\beta\mathcal{H}}...\} \equiv \langle...\rangle$. The first place this occurs is in the equations of motion, where now the definition for the gap changes from Eq. (1) to:

$$\Delta_k = \frac{1}{2V}\sum_{\vec{k}'} V_{k,k'}\langle c_{-\vec{k}'\downarrow}c_{\vec{k}'\uparrow}\rangle \tag{3}$$

The thermal average now becomes

$$\langle c_{-\vec{k}'\downarrow} c_{\vec{k}'\uparrow} \rangle = -u_{\vec{k}'} v_{\vec{k}'} \left[\langle \gamma_{-\vec{k}'\downarrow} \gamma^\dagger_{-\vec{k}'\downarrow} \rangle - \langle \gamma^\dagger_{\vec{k}'\uparrow} \gamma_{\vec{k}'\uparrow} \rangle \right] = -\frac{\Delta_{\vec{k}'}}{E(k')} \tanh \left[\frac{\beta}{2} E(k') \right]$$

So the gap now becomes a function of temperature:

$$\Delta_{\vec{k}} = -\frac{1}{2V} \sum_{\vec{k}'} V_{k,k'} \frac{\Delta_{\vec{k}'}}{\sqrt{\xi^2_{\vec{k}'} + \Delta^2_{\vec{k}'}}} \tanh \left[\frac{\beta}{2} E(k') \right]$$

The critical temperature is simply the temperature when the gap closes and we regain normal metal behavior. To find T_c, we go through precisely the same steps as we did at $T = 0$, again assuming $V_{k,k'} = -V_0$ within $\hbar\omega_D$ of E_F, etc, to find:

$$1 = V_0 N(\mu) \int_0^{\hbar\omega_D} \frac{d\xi}{\sqrt{\xi^2 + \Delta^2}} \tanh \left[\frac{\beta}{2} \sqrt{\xi^2 + \Delta^2} \right]$$

At $T_c = 1/(k_B \beta_c)$ the gap vanishes, so here:

$$1 = V_0 N(\mu) \int_0^{\hbar\omega_D} \frac{d\xi}{\xi} \tanh \left[\frac{\beta_c}{2} \xi \right] = V_0 N(\mu) \int_0^{\frac{\beta_c \hbar\omega_D}{2}} \frac{d\xi}{\xi} \tanh [\xi]$$

Integrating by parts, we find:

$$\frac{1}{V_0 N(\mu)} = \ln \frac{\beta_c \hbar\omega_D}{2} \tanh \left[\frac{\beta_c \hbar\omega_D}{2} \right] - \int_0^{\frac{\beta_c \hbar\omega_D}{2}} d\xi \ln \xi \frac{d}{d\xi} \tanh \xi$$

Now we will assume that $k_B T_C \ll \hbar\omega_D$, meaning that $\frac{\beta_c \hbar\omega_D}{2} \gg 1$. The reason for this is that we expect, roughly, the gap to close for $k_B T_C \sim \Delta(T = 0) = 2\hbar\omega_D e^{-\frac{1}{V_0 N(\mu)}} \ll 2\hbar\omega_D$, since $\Delta(T = 0)$ is the binding energy of Cooper pairs and they should start breaking at comparable temperatures. This allows us to set the tanh in the first term as equal to 1, and also to take the upper limit of the integral in the second term as being $+\infty$. That makes that integral equal to a number related to Euler's constant. We can now solve for T_c to find:

$$k_B T_c = 1.13 \hbar\omega_D e^{-\frac{1}{V_0 N(\mu)}} \ll 2\hbar\omega_D$$

validating our assumption. Interestingly, this means that there is a simple universal relation between the $T = 0$ gap and T_c for all (weakly coupled) BCS superconductors:

$$2\Delta = 3.52 k_B T_C \tag{4}$$

This is indeed in good agreement with experiments for many materials. It fails if the coupling starts to become stronger, in which case one needs to treat the problem more carefully. This strong(er) coupling approach is known as **the Eliashberg theory**.

Many other properties can be calculated, such as the specific heat and the jump in its value at $T = T_C$ (which also turns out to be universal in the weak coupling limit); sound attenuation; properties in magnetic field to understand the Meissner effect etc – the latter is usually done using the so-called Ginzburg-Landau formalism. To treat all these things properly requires basically a course of its own, so we'll have to stop here. I hope that this discussion gave you a basic understanding of what is happening in conventional, low-T_c superconductors. Here's a minitest: can you now explain why magnetic fields are detrimental to superconductivity?