

**Lecture-9**  
**Unconventional Superconductivity,**  
**Uemura plot, High-Tc**  
**Superconductivity**

So having discussed the conventional super conductivity, thus far with some details, let us resort to the, rather take a course of the discussion, towards the unconventional super conductivity and will explain what we mean by unconventional super conductivity.

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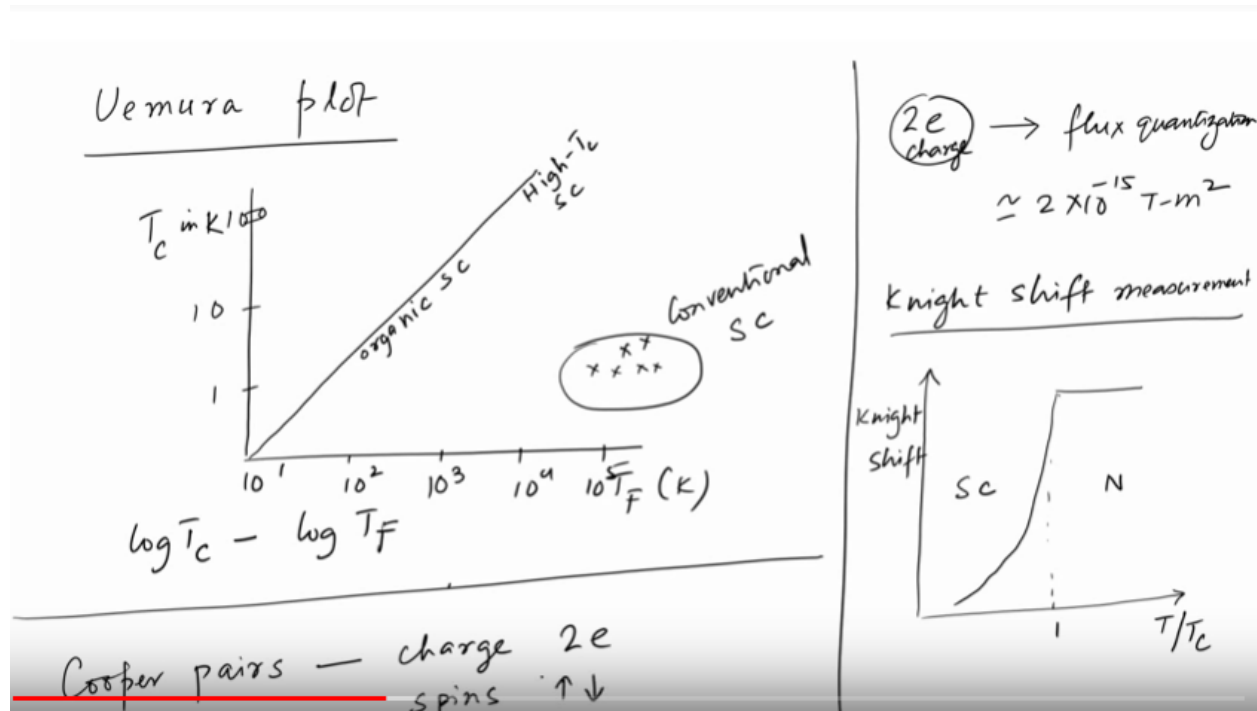
## Unconventional Superconductivity

### Features of Conventional Superconductors

- (i) Cooper pairs form with opposite spins and momentum formed via electron-electron interaction mediated by phonons
- (ii) Angular momentum of  $\bar{u}u$  pair as well as  $\bar{u}u$  superconducting condensate is zero.
- (iii)  $T_c$  is small &  $T_c \leq 25 \text{ K}$ .
- (iv) Magnitude of  $\bar{u}u$  gap  $\Delta \sim 1-2 \text{ meV}$ ,  $\frac{2\Delta(0)}{k_B T_c} \approx 3.52$

So, so the topic is unconventional super conductivity. But in order to do that, let us look at some of the features, of the conventional superconductors, which differ from, the unconventional superconductors and we'll see that, how they differ and how much they differ by. So, the features are that the Cooper pairs, form with opposite spins and momentum, just to remind you that the Cooper pairs have, momentum  $K$  and minus  $K$  and the spins are up and down and these are the constituents of the Cooper pair and they form, via wire electron-electron interaction, mediated by phonons, a very important point which, is not explicitly, stated is that the angular, momentum of the pair, that is a net angular momentum of the pair, of the pair as well as the condensate, superconducting condensate, is zero, the  $T_c$  the transition temperature that, we actually see for these superconductor, that is the temperature at which the system makes a transition from a normal metal to a superconductor, it's of the order of so,  $T_c$  is small and in most cases  $T_c$  is less than equal to, about 25 Kelvin. So, that's a maximum  $T_c$  that one can get for these conventional superconductors. The magnitude of the gap, gap is rather small, it's 1 to 2 mille, electron volt or it could be 3 or 4 mille electron volt. But, it's of the order of a few mille electron volts and so, this is called as the, "Delta" and this quantity - Delta zero, over  $k_B T_c$  it's a number which is like 3.52, usually it varies from 3 to 4 point 5 and these are the and Delta 0 is the, the magnitude of the gap at, zero temperature. So, how do we now, recognize that the uninvent, unconventional super conductors, how do they differ, from these conventional superconductors.

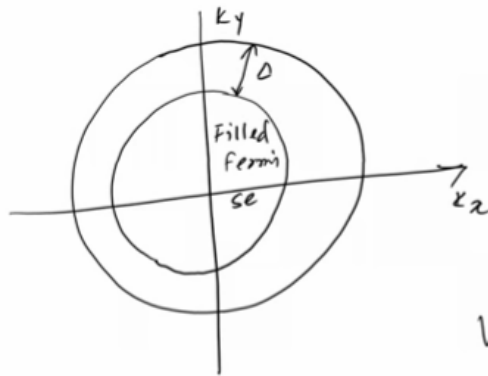
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So, in order to understand that, there are some empirical, data that were first plotted by Vemura and they are presented in, in the name Vemura plot. So, what happens is that the  $T_c$  versus  $T_F$ ? So, this is  $T_F$  in Kelvin and this is  $T_c$  in Kelvin again; they are plotted in the log, log scale. So, it's a, it's a log, log plot so it's actually a log  $T_c$ , log  $T_F$  plot and so this is like, 10 to the power 1, this is 10 to the power 2, 10 to the power 3 and 10 to the power 4, in 10 to the power 5 and these are again; so 1, 10 and hundred and so on. So, Vemura found that, for the unconventional superconductors, they fall in a reasonably a straight line in this log, log plot. So, this is where, the organic superconductors' line and here are the so-called, "High-Temperature Superconductors" and we'll include a discussion, on them and this is where, the you know? The conventional superconductors. So, these are, the conventional superconductors, in short writing SC and these are, the line the straight line that is drawn, is where the unconventional superconductors light. So, in the locked EC, versus log  $T_F$ ,  $T_F$  being the Fermi, temperature so, they lie on the straight line, where these initial portion is occupied, by some of the organic, superconductors and the later ones are occupied by the high  $T_c$  superconductor. So, this is called as a, "Vemura Plot" and the conventional superconductors stay far, away from this straight line. So, if you take this, I mean of course there are you know? Sort of it's not along a line it's, just in a region, which is far away from this straight line. So, if you take this as a, marker for the unconventional superconductors from those, from the conventional ones, then of course we know that so, this is an empirical plot and so, what happens in this unconventional superconductors do we, still have Cooper pairs, we have to have, Cooper pairs. Right? Because the Cooper pairs are the, the most important ingredients, for an energy gap in the, excitation spectrum and that makes the superconductivity stable, even if the gap is of the order of you mille electron volt, it still gives rise to a transition temperature, to the tune of ten to fifteen Kelvin. So, if it involves, formation of Cooper pairs, as the unconventional superconductors still, have cooper pairs have you know? The most important elements or constituents. So, there's a  $2e$  charge, that needs to be seen and this  $2e$  charge, as we have seen earlier, that the  $2e$  charge is confirmed, from the flux quantization,

measurement and the value that we, we get, is around,  $2 \times 10^{-15}$  Tesla meter square, is a small value. But it still confirms that one means, a  $2e$  charge in order to get the flux quantum, to be having this value, which are verified in experiments. Now, we need to understand that how the spin, our spins are opposite equal and I mean that is the, the formation of Cooper pairs, is facilitated by the pairing of an up and down spin electron, that can be done, or understood by the night shift measurement and so, what's a night shift measurement? Let me, describe this, in ordinary metals, the electrons the magnetic moment effective, magnetic moment of the electrons, they are really, the net magnetic moment is really small and it gives no, contribution to the precision of the atomic nuclei. But, however, if you put them, in an external magnetic field, the electron spins, will tend to align, in the direction of the field, due to Simon coupling and because of this, the atomic nuclei now, will be, in a much greater field and will start precessing, about that, that magnetic field with a frequency, which is known as Larmor frequency. Now, what happens is that? If in a superconducting specimen, this conduction electrons, or minimal or they are almost absent, then this, precessional frequency of the atomic nuclei or the nuclear, as the spins, these frequency will go down, drastically and this shift, in the frequency, as we go deeper, into the superconducting specimen, is called as a, "Night Shift". So, a night shift measurement is, usually like this. So, this is plotted as a function of  $T/T_C$  and it falls off like this very, quickly, up beyond. So, this is  $T/T_C$  equal to 1. So, this is the superconducting part, of the sample and this is a normal phase of the sample. So as the number of conduction electron go down drastically this night shift also go down drastically as we a deeper, in to the super conducting specimen. So, this again gives rise to the fact that the Cooper pairs are indeed, formed of charge to  $e$  that is there are two electrons involved, along with, the fact that they have, the total angular momentum, equal to zero. Now, we are going to talk, about angular momentum having different values and that could be one way, to give rise to unconventional super conductivity. So, let's just write this, thing that Cooper pairs, charge, to  $e$  spins, up and down, which is encoded into this discussion.

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gap is isotropic in a conventional SC.  $\Delta$  has no  $k$  dependence.

$$\Delta_k = \sum_{k'} \frac{V_{kk'}}{2E_{k'}} \tanh\left(\frac{\beta E_{k'}}{2}\right)$$

$$V_{kk'} = -V_0 \text{ for } |\xi_k|, |\xi_{k'}| \leq \hbar\omega_D$$

$\Delta_k$  is independent of  $k$ .

Lets talk about  
finite momentum pairing  
pair can be (i) even

Angular momentum of the pair multiple of  $\hbar$ , (ii) odd multiple

So, in the conventional superconductors, this is the free Fermi sea, and this is what the so-called Fermi surface is. So, if we write it in a  $k_x, k_y$  in a two-dimensional momentum space, this is basically the Fermi surface. So, this is the gap that we call as, "Delta", which is of course a function of temperature, but we are just denoting it at a given temperature. So, this gap is isotropic, in a conventional superconductor. Okay? Which means, that the Delta, has no  $k$  dependence. Okay? And this was also clear, when we actually derived, the BCS equations, in which the gap equation took a form, that there is a sum over  $k'$  and  $V_{kk'}$ , with a  $\Delta_{k'}$  and  $2E_{k'}$  and then of course we can have a tanh hyperbolic,  $\beta E_{k'}/2$ . Now this, if we take an approximation that  $V_{kk'}$  equal to a minus  $v_0$ , for  $Z_i k$  and  $Z_i k'$ , to be both within, an energy range, which is  $\hbar\omega_D$ , then of course, then this equation tells you that, if you put  $V_{kk'}$  equal to minus  $v_0$ , it tells that  $\Delta_k$  is independent of  $k$  and we have an isotropic gap that doesn't matter which way you try to or which part of the Fermi surface you try to excite an electron, to overcome the gap you have to supply, the same amount of energy. So, this is the story with the conventional superconductor. Now, the question is that, if that does not happen for the unconventional superconductor, then let's see or less SS, evaluate the scenario. Now, it could happen, the unconventional features could actually, get generated from a variety of factors, but at this point, we are considering that this is one of the reasons that, unconventional superconductivity can arise. So, let's talk about, finite momentum pairing, in other words, the two electrons come and they collide to form a pair and which is mediated by this pairing is, mediated by phonons, in this particular case, the vertex actually, contributes to the momentum either it carries, momentum away from this collision or it imparts momentum to the collision. So, a finite momentum pairing, we can think of, that the angular, momentum of the pair, can be a 1, even multiple of  $\hbar$  and 2 odd, multiple of  $\hbar$ . This odd multiple of  $\hbar$ , involves what are called as triplet pairings or p-wave pairings and so on, which will shell for the time, and only talk about, even multiple of  $2\hbar$  or even

multiple of  $\hbar$  cross. So, which is the lowest value is to  $\hbar$ , cross and that is called as a, so this even multiple of  $\hbar$  cross is called as the, 'Singlet Pairing' and the odd multiple is called as a, 'Triplet Pairing'.

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Singlet pairing ( $l=2(\hbar)$ , d wave pairing).

$l=2$ ,  $m_l = -2, -1, 0, 1, 2$ .

$(2, -2)$   $(2, -1)$ ,  $(2, 0)$ ,  $(2, 1)$   $(2, 2)$ .

(i)  $d_{xy}$ , (ii)  $d_{yz}$ , (iii)  $d_{zx}$ , (iv)  $d_{x^2-y^2}$ , (v)  $d_{3z^2-r^2}$ .

$d_{x^2-y^2}$  for illustration, take  $d_{x^2-y^2}$  in the  $x-y$  plane.

$f(x, y) = x^2 - y^2$  on a unit circle  $x^2 + y^2 = r^2 = 1$

or,  $y^2 = 1 - x^2$

$f(x, y) = 2x^2 - 1$

(i) minimum when  $x = 0$  (y-axis) assumes a value  $-1$

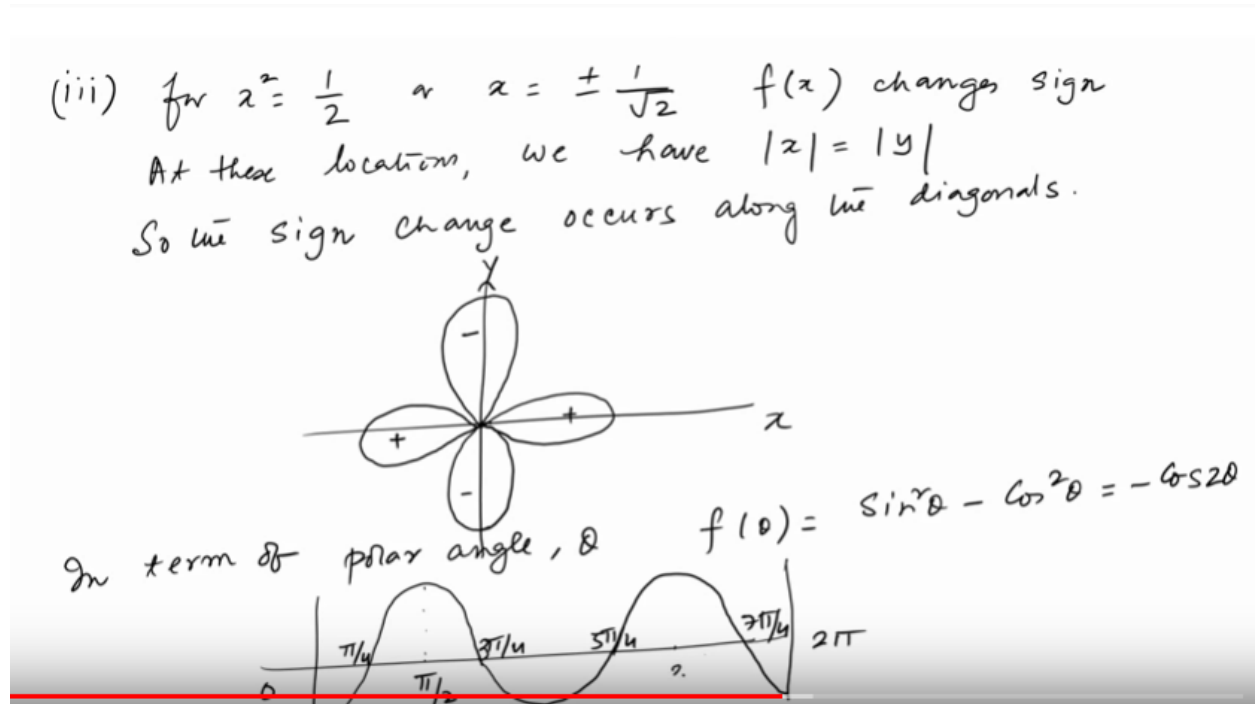
(ii) Maximum when  $x = 1$  (x-axis) assumes a value  $+1$

So, we are just going to talk about, the singlet pairing and we'll, talk about an angular momentum equal to 2  $\hbar$  cross and so, this is called as a, 'Di Wave Pairing'. This is true, in the context of atlasses believed to be true in the context of the high TC superconductors, that many of the high TC superconductors, they have a d-wave paring, now in order to understand what d-wave paring is, let us see that, you're so, this is in units of  $\hbar$  cross so, we'll just take that unit out. So, L equal to 2, that's angular momentum quantum number.

So, basically the capital L has got to  $\hbar$  cross, so L equal to 2 means,  $m_l$  equal to, minus 2, minus 1, 0, 1, 2. So, these are magnetic quantum number values. So, these so they'll be, a terms such as 2, minus 2, 2 minus 1, 2, 0 and 2 1 and 2, 2 so, these are the possible, d-wave pairing and they have names, we are not writing them particularly in order, but they are written as, d XY pairing and d YZ pairing, and d ZX pairing and then or it's also called, "XZ Paring" and the DX square minus, y square and B, 3 Z square minus R square. So, let us only discuss, one candidate and see that how this, this particular symmetry each of these, symmetries they look like and we'll, just take a look at, this DX square minus y square paring and for illustration, let us take a function, take DX square, Y square, in the XY plane. Okay? And we'll write this, f of, X Y, as X square minus y square, on a unit, circle X square plus y square equal to R square, equal to one. So, which means that, Y square is equal to one minus X square, if we substitute in F X Y this will be like two X square minus one and so, this two X square minus one is the function. So, you see that, this function, is maximum or rather it is minimum and has a value which is, when X equal to zero, that is on Y axis and it has a, assumes a value, assumes a value minus 1. Right? When X is equal to

0, it is equal to minus 1. So, this is 1 & 2, it is maximum for X equal to 1. So, maximum when X equal to 1, that's of course on the x-axis and assumes a value plus 1. So, that's the, nature of this and so, basically it changes sign somewhere, of going from y-axis to the x-axis.

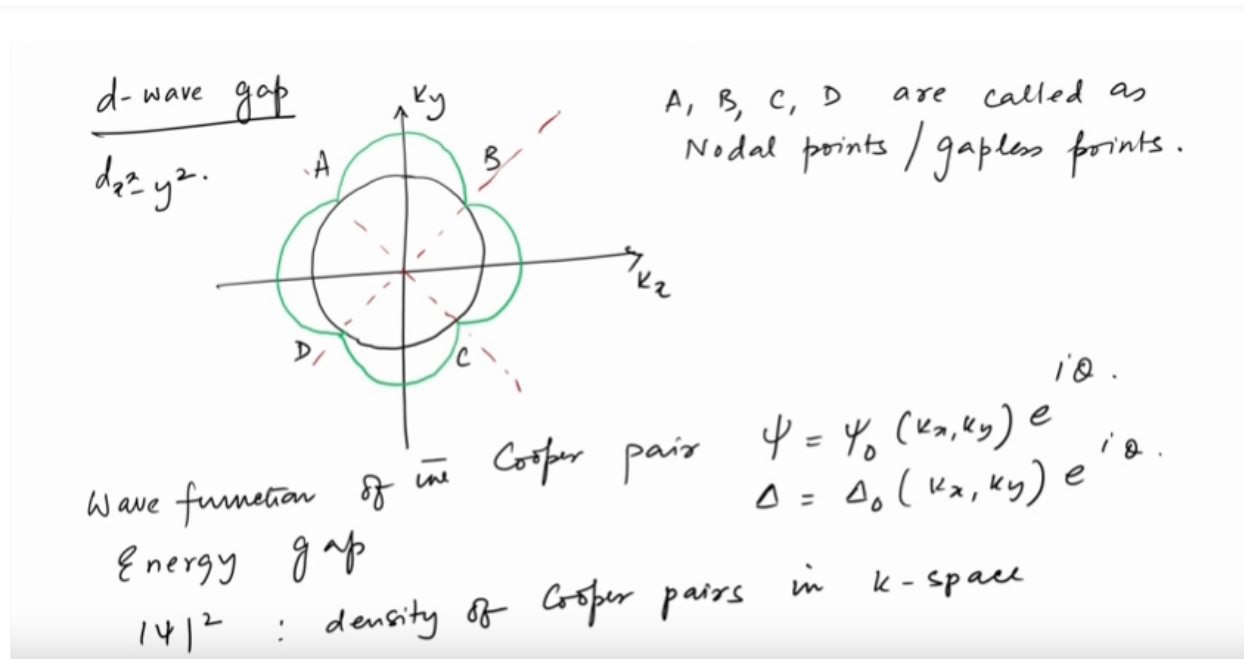
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Let's see, what more we can learn from this, third is simple, that for x squared equal to 1/2 or X equal to plus minus 1 by root 2, basically FX changes sign, you saw that on the y-axis its minus 1, on the x-axis its equal to +1 and so, it must be changing sign, somewhere and we want to say and see where it changes sign, it changes sign, along the diagonal. So, at this locations, we have, mod of X equal to mod of Y, ok. So, so the sign change, along the diagonal, diagonals there are of course, two diagonals there so, so how what does the function look like? The function looks like this, it's called as a, "Clover Leaf" and it has a form which is. Okay? So, this is equal to minus or this is y axis, this is x axis, this is plus and this is minus, again and this is plus and this looks like a cloverleaf. So, this is the form, of this DX square minus y square symmetry and we can also, you know? Characterize this, F X Y in terms of, in terms of polar angle, theta I mean, F of theta can be written as sin squared theta minus a, cosine square theta, which is minus cosine of two theta and if you plot it, it looks like, minus one and then it goes, down and then it goes up and then it goes down and so on. So, this is, where it goes down once more, so this is zero and this is two pi, this is PI by 4, where it is zero, this is three PI by 4, this is 5 PI by 4 and this is 7 PI by 4 and these are the positions which are PI by 2 and 3, PI by 2 and 5, PI by 2 and so on. So, this is I'm sorry, so this is PI by 2

and so, this is actually  $3, \pi$  by 2 and so on anyway. So, that is the, form for this d-wave water parameter, now what is it good at and how are we going to connect it to the superconducting order parameter.

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Now if you, have if you consider the same, picture as we have considered earlier, that is that there is a, Fermi sphere or the field Par C, which is like this and we break it into quadrants and so on and then, we draw diagonals, let's draw the diagonals with a different color. So, these are the diagonals and we could draw it with another color. So, these are the gap functions. Now, the gap has a K dependence it's not isotropic, along all directions and we have. So, this is called as the, 'd-wave gap'. Okay?? And so, what it means is, that there are points which are along the diagonals, these along the diagonals there are points which are zero gap or the gap less superconductors. So, along this, direction there is no gap, in the single particle excitation spectrum and the electrons can actually be excited, without imparting any extra energy and if this is truly the, the structure or the geometry, of a gap function, which has of course a K dependence. Now, we are drawing it as a function of KX and KY, then these should be, able one some experiments should be able to see, these gaps and let's call these, "Points", as A B C D which are these, points where the which are called the, "Gapless Points" and this ABCD are also called as, "Nodal Points" or they are also called as a, "Gapless Points". So, if this is the structure, of the order parameter, in an unconventional superconductor, in the conventional superconductor of course we have seen, that the gap is isotropic, in any direction. But suppose the gap has such, a symmetry, then what's what are the things that we, expect and of course as you can see that and the other d XZ, divisor and the XY etc,  $3 Z^2$  square minus R square, is more complicated, well these other things have gaps, around different directions and but, by and large this explains, that how's the DX square minus y square, that gap looks like. So, it has a K dependence so, the gap has a K dependence, which means, that the wave function, that the Cooper pair wave function, pear has a form, which is Si equal to size zero. K X K Y and exponential I theta where theta is a, phase factor and the energy gap has also a structure, this is Delta equal to Delta zero, K X K Y



and exponential  $I \theta$  and of course what we understand by these this picture is that so, this phase factor of course indicates the motion, of the center of mass of the Cooper pairs, along a specific direction, along a particular direction and the mod size squared, gives the density of Cooper pairs, in k-space. So, since along this diagonal, the density vanishes, which means at the nodal points, ABCD the density of Cooper pairs is equal to zero and additionally, one can say, that there could be gapless excitations at those nodal points and of course one understands that size zero is proportional, to  $\Delta_0$ . So, one actually gives a measure of, of another. So, if even if we talk about, just one quantity, that is going to be enough and let's now see that, a possible experiment that can determine, a gap structure of this kind.

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Angular resolved photoemission Spectroscopy (ARPES)

Signal is Fourier transformed to k-space to obtain a  $\vec{k}$  vs E plot.

Photoemission intensity is given by.

$$W_{fi} = \frac{2\pi}{\hbar} |\langle \psi_f | H' | \psi_i \rangle|^2 \delta(E_f - E_i - h\nu)$$

$$H' = -\frac{e}{2m} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) = -\frac{e}{m} \vec{A} \cdot \vec{p} \quad (\text{for } \vec{v} \cdot \vec{A} = 0)$$

$h\nu$  &  $\vec{A}$  are fixed during experiments. The kinetic energy of  $\vec{m}$  electron,  $E_k$ , work function,  $W$  and polar angles  $\theta, \phi$  are measured.

And that is called as the, “Angular Resolved Photo Emission Spectroscopy” and in short it's called, ARPES, let's draw this, 110. So, this is the surface of a superconductor and there is a, photon that comes, there is let's draw the coordinate axis here. So, there's an electron, that is emitted in this direction. So, this is a  $h\nu$ , which is characterized by a vector potential  $\vec{a}$  and this is, in a detector. So, this is a detector and the electron is actually, captured by the detector. So, this angle is called, “Phi” and this angle is called, ‘Theta’ and so, this is the y axis this right handed coordinate system and this is the z axis. So, the photon falls on a, certain material which is a superconductor and then electrons are emitted and they are collected by the detector. So, it's very clear, that if you have electrons available, in certain directions, then only the detector will be able to detect electrons and this detector, can be actually placed at any, angle in a 360 degree or rather full you know? Covering the full angle, it can be placed at any angle. So, this detector, only detects electrons at say for, locate on or the four points, in the  $k_x k_y$  direction, in which, the system has or the, the superconductor has gapless points and if we can do that, then only we see that the,

the electronic density of states and which is obtained, from peak, in the single particle density of states. So, it basically scans or rather detects the electronics, electron single particle electronic states. So, this signal, is a Fourier transform to k-space, to obtain,  $k$  Vs  $E$  plot, which is nothing, but the density of states, where the photo, emission intensity is given by, I'm going to write some, equations which are really required. But, just understanding the physical context, of doing this experiment is good enough. So, what I mean to say is that, this detector, only detects electrons in certain directions, when it's Fourier transformed into the  $k$  space and those, directions are the gapless points, or the nodal point from which electrons can be emitted, with, with absolutely without any difficulty, because the other, places there is a superconducting gap and the electrons cannot come out, because that is the, the energy barrier, that has been created by the formation of the Cooper pairs. So, the photo emission intensity is given by,  $W_{fi}$ , which is equal to  $2\pi$  over  $\hbar$  cross and  $\text{Si} \cdot \text{F} \cdot \text{H}'$ ,  $\text{Si} \cdot \text{mod}^2$ ,  $\Delta$  of  $E_F$  minus,  $e \cdot I$  minus  $H \nu$ , that's the energy conservation and what is the so one has to do a second order perturbation theory, in  $H'$  Prime, in order to get the intensity this called as a, "Fermi's Golden Rule", this you might be knowing from your, pores of quantum mechanics on perturbation theory of scattering theory and this  $H'$  Prime, is nothing but, the  $e$  buy  $2m$  and the  $\mathbf{a} \cdot \mathbf{P}$ , plus  $\mathbf{P} \cdot \mathbf{a}$ , that is the coupling between the, the vector potential and the momentum of the electron and by a suitable choice of gauge, one can show that these two, with the gauges that  $\Delta$ , there's divergence of  $\mathbf{a}$  equal to 0, in this gauge, this  $e$  over  $M$ , it becomes  $e$  over  $M$ ,  $\mathbf{a} \cdot \mathbf{P}$ , that is both the terms become equal and they add up, in order to give a factor of two which cancels, with this two, for a given gauge, I simply write it as this and this can be shown. Now  $H \nu$ , which is the energy of the photons and  $\mathbf{a}$ , are basically for a given radiation, are fixed during experiments, the kinetic energy of the electron,  $E_k$ , then the work function, which you must be knowing from Einstein's photoelectric effect, that there is a certain amount of wave, work function which is associated with a particular material, which is a property of the material, which is called, "Work Function", that has to be overcome in order for the electron to, to emit and the polar angles  $\theta$  and  $\phi$ , are measured. Okay?

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Conservation law:

$$E_k = h\nu - W - E_B$$

$$k_{||}^{\text{vacuum}} = k_{||}^{\text{solid}}.$$

$$\hbar k_{||}^{\text{vacuum}} = \sqrt{2m E_k} \sin\theta.$$

The ejected electron should be fast enough to be able to neglect its interaction with hole left behind.

ARPES gives direct information about the electronic states.

So, what are the conservation laws? The conservation laws for this, photoelectric or rather this angular resolve photoemission spectroscopy, are simple, that is the kinetic energy of the electrons, which is equal to  $h\nu$ , which is energy of the photon, minus the work function, minus the binding energy, of the electrons in a material and the parallel component, that is, conserved and this is equal to,  $2m e K$  and the sine theta. So, now the only constraint is that the ejected electron, of the emitted electron, rather this assumption, should be fast enough, to be able to, neglect the interaction, with the whole left behind. So, our ARPES, finally gives direct information, the electronic states. So, that is the way, that one can actually understand that the gap, function of this Cooper pairs, that has a structure and it's not uniform in  $k$ -space, it has some nodal points, from which electrons can be excited and that can be detected via an angular result, spectroscopy photo emission, spectroscopy and this has indeed confirmed, the presence of a D wave gap, in certain unconventional superconductors.