LECTURES ON SUPERCONDUCTIVITY

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LECTURE 10

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DIRTY SUPERCONDUCTORS

Non-BCS Superconductivity

Experimental fact:

Quite strong nonmagnetic disorder (e.g. alloying) does little harm to superconductivity, while even tiny amounts (~ a few ppm) of magnetic impurities suppress it completely.

Why?

A. Nonmagnetic Disorder

$$\hat{H} = \hat{H}_0 + \hat{V}$$

single-electron

inter-electron interaction

potential due to atomic cores

$$\hat{H}_0 = \sum_i \left(\frac{\hat{p}_i^2}{2m} + \hat{U}(\boldsymbol{r}_i) \right)$$

spin-independent

Assume: $k_f l \gg 1$ (but possibly $l \lesssim \xi_0$)

Eigenstates of $\hat{H}_0$ are of form

$$\psi_n(\boldsymbol{r}, \sigma) = \phi_n(\boldsymbol{r})|\sigma\rangle \equiv |n, \sigma\rangle \,, |\sigma\rangle \equiv (|\uparrow\rangle, |\downarrow\rangle) \text{ with energy } \epsilon_n$$

where $\phi_n(r)$ is very complicated.

However, note that average density of states

$$\frac{dn}{d\epsilon} \equiv 2 \sum_n \delta(\epsilon - \epsilon_n)$$

is much the same (for $k_f l \gg 1$) as in original (crystalline) case.

Crucial point: since $\hat{H}_0$ is invariant under time-reversal

$$(|\uparrow\rangle \rightleftarrows |\downarrow\rangle \,, \phi_n(\boldsymbol{r}) \rightleftarrows \phi_n^*(\boldsymbol{r}) \equiv |\bar{n}\rangle,$$

then if state $|n, \uparrow\rangle$ is an eigenstate of $\hat{H}_0$ with energy ϵ_n,
then $|\bar{n}, \downarrow\rangle$ is also eigenstate of $\hat{H}_0$ with energy ϵ_n .

Note: $\phi_{\bar{n}}(\boldsymbol{r})$ may or may not be identical to $\phi_n(\boldsymbol{r})$, *i.e.* $\varphi_n(\boldsymbol{r})$ may or may not be real (doesn't matter!).

Recall that in free space, BCS ground state was

$$\Psi = \prod_k \Phi_k$$

$\Phi_k \equiv$ state vector in "occupation space" of $|k,\uparrow\rangle, |-k,\downarrow\rangle$

So, replace $|k\uparrow\rangle, |-k\downarrow\rangle$ by $|n\uparrow\rangle, |\bar{n}\downarrow\rangle$ and generalize BCS ansatz:

$$\Psi = \prod_n \Phi_n$$

$\Phi_k \equiv$ state vector in "occupation space" of $|n,\uparrow\rangle, |\bar{n},\downarrow\rangle$

Assume as in free-space case that at T=0 $|0,1\rangle, |1,0\rangle$ are irrelevant, then

$\Phi_n = u_n|0,0\rangle + v_n|1,1\rangle \qquad |u_n|^2 + |v_n|^2 = 1$

i.e. pair in time-reversed states

KE is identical to free-space case with $\boldsymbol{k} \to n$:

$$\langle T\rangle = 2\sum_n \epsilon_n |v_n|^2$$

For the PE, as in the free-space case, we need to calculate the matrix element

$\langle\psi_f|\hat{V}|\psi_{in}\rangle$ with $\psi_{in} \equiv (n\uparrow, \bar{n}\downarrow \text{ occupied};\ n'\uparrow, \bar{n}'\downarrow \text{ empty})$

$\psi_f \equiv (n\uparrow, \bar{n}\downarrow \text{ empty};\ n'\uparrow, \bar{n}'\downarrow \text{ occupied})$

For a δ-function interaction $V(\boldsymbol{r}_i - \boldsymbol{r}_j) = V_0\delta(\boldsymbol{r}_i - \boldsymbol{r}_j)$, this is equal to

$$V_0 u_n v_{n'}^* u_{n'} v_n \int \phi_{n'}^*(\boldsymbol{r})\phi_{\bar{n}'}^*(\boldsymbol{r})\phi_n(\boldsymbol{r})\phi_{\bar{n}}(\boldsymbol{r})\mathrm{d}r$$

But since $\phi_{\bar{n}}^*(\boldsymbol{r}) = \phi_n(\boldsymbol{r})$ (etc.), this can be rewritten (regrouping the u's and v's)

$$V_0 u_n v_n u_{n'} v_{n'}^* \int |\phi_{n'}(\boldsymbol{r})|^2 \cdot |\phi_n(\boldsymbol{r})|^2 \mathrm{d}r$$

For normalization in unit volume the integral, though not exactly equal to 1, is very close to it, so

$$\langle V\rangle \cong V_0 \sum_{n,n'} (u_n v_n)(u_{n'} v_{n'}^*) \equiv V_0 \sum_n F_n F_{n'}^*$$

$\equiv u_n v_n$

The subsequent algebra goes through exactly as in the free-space case, and we end up with the gap equation

$$\Delta_n = -V_0 \sum_{n'} \frac{\Delta_{n'}}{2E_{n'}} \qquad E_n \equiv (\epsilon_n^2 + |\Delta_n|^2)^{\frac{1}{2}}$$

Assuming $\Delta_n = \Delta = \text{const}$ and turning the Σ_n into $\int \mathrm{d}\epsilon$:

$$1 = -V_0 \int_{-\epsilon_c}^{\epsilon_c} \frac{\rho(\epsilon)\mathrm{d}\epsilon}{2(\epsilon^2 + |\Delta|^2)^{1/2}}$$

Since $\rho(\epsilon)$ is (almost) the same as for the original free-space case, this is (almost) the original BCS gap equation and has the same solution

$$\Delta = 2\epsilon_c e^{-1/N(0)V} \qquad \left(N(0) \equiv \frac{1}{2}\left(\frac{\mathrm{d}n}{\mathrm{d}\epsilon}\right)_{\epsilon=\epsilon_f}\right)$$

Thus,

thermodynamics almost unaffected by alloying

(in zero magnetic field, for $k_F l \gg 1$)

(we have simply "shuffled the original plane-wave states around")

Similar results at non-zero T, e.g. $\frac{\chi(T)}{\chi_n} = Y(T)$ (Yosida function)

(since $n\uparrow, \bar{n}\downarrow$ still eigenstates of spin)

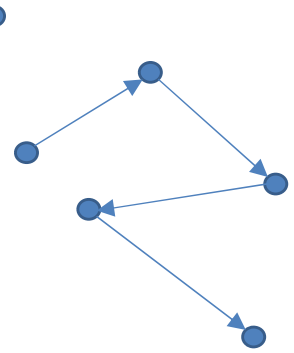
However, calculation of normal density does not go through

(∵single-particle energy eigenstates n, σ are not eigenstates of momentum)

Which quantities are qualitatively affected by (nonmagnetic) alloying?

As we have seen, thermodynamics (hence H_c, th) not qualitatively affected.

But: Single-particle motion is now diffusive rather than ballistic, so an electron which in free space would have travelled a distance *r* now travels only $\sim(r\ell)^{1/2}$ (ℓ =mean free path)



Thus, Cooper pair radius $\xi_0 \sim \hbar v_F/\Delta \rightarrow \sim(\xi_0 \ell)^{1/2}$,

i.e.

$$\xi'_{dirty} \sim (\ell/\xi_0)^{1/2} \xi'_{clean} \quad \text{(can be} \ll \xi'_{clean})$$

Perhaps less obviously, in GL regime $\alpha(T)$ and $\beta(T)$ little affected, but $\gamma(T)$ multiplied by factor $\sim \ell/\xi_o$. Hence

$$\Psi_{dirty}(T) \cong \Psi_{clean}(T)$$

but

$$\gamma_{dirty} \sim (\ell/\xi_0)^{1/2} \gamma_{clean} \ll \gamma_{clean}$$

Recall: $\xi(T) \sim (\gamma/\alpha(T - T_c))^{1/2}$, $\quad \lambda(T) \sim (\gamma/|\Psi(T)|)^2)^{1/2}$

Thus,

$$\xi_{dirty}(T) \sim (\ell/\xi_0)^{1/2} \xi_{clean}(T) \ll \xi_{clean}(T)$$

$$\lambda_{dirty}(T) \sim (\xi_0/\ell)^{1/2} \lambda_{clean}(T) \gg \lambda_{clean}(T)$$

$$\Rightarrow \quad \kappa_{dirty} \equiv (\lambda/\xi)_{dirty} \sim (\xi_0/\ell)\kappa_{clean} \gg \kappa_{clean}$$

$\Rightarrow$ alloying makes system much more type-II

in particular,

H_{c1} much decreased

H_{c2} much increased $\Rightarrow$ best (classic) high-field sups are very dirty!

B. Magnetic disorder

Now we have

$$\hat{H} = \hat{H}_0 + \hat{V}$$

single-electron

Inter-electron interaction

but now

$$\hat{H}_0 = \sum_i (\hat{p}_i/2m) + U(\boldsymbol{r}_i : \boldsymbol{\sigma}_i)$$

note all components of $\boldsymbol{\sigma}$!

so now TRI (Time Reversal Invariance) is broken, and state $|\overline{n}, -\sigma\rangle$ (when $\varphi_{\bar{n}}(\boldsymbol{r}) \equiv \varphi_n^*(\boldsymbol{r})$) is no longer degenerate with $|n, \sigma\rangle$. (Indeed, in general neither of these is even an energy eigenstate, since the latter are in general 2-component spinors.)

Two obvious proposals for GS:

(a) Pair in exact eigenfunctions of single-particle Hamiltonian, i.e. if exact spinor eigenstates of $\hat{H}_0$ are denoted $\varphi_m\ (r, \sigma)$, pair off n with some m ($\neq \bar{n}$).

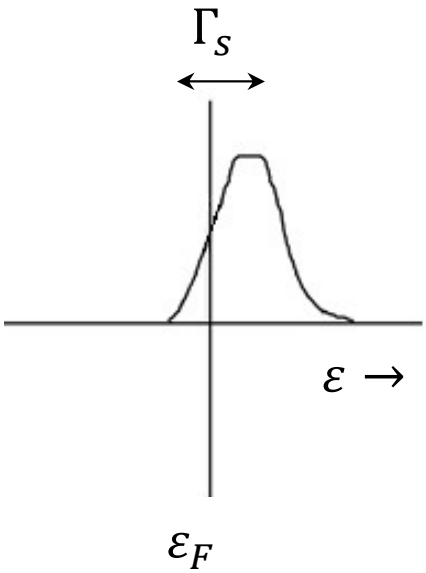
Then KE is much the same as in pure (BCS) case. However, even if we ignore the spin degree of freedom

$$\langle V \rangle \sim V_0 \sum_{mm'} \int dr \varphi_n^*(r) \varphi_m^*(r) \varphi_{m'}(r) \varphi_{n'}(r)$$

and since we no longer have $\varphi_{\bar{n}}(r) = \varphi_n^*(r)$, (etc.) the integral is oscillating and hence very small. This scheme is usually very energetically disadvantageous.

(b) Continue to pair in time-reversed states, even though these are no longer eigenstates of $\hat{H}_0$. How much extra single-particle energy does this cost? Suppose "lifetime for different scattering of ↑ and ↓" is $\tau_s \equiv \hbar\Gamma_s^{-1}$ then by indeterminacy principle extra energy necessary to keep state of ↓ the time-reverse of that of ↑ is $\sim \Gamma_s$

⇒ extra energy required $\sim \Gamma_s \times$ no. of perturbed states $\sim \Gamma_s(\Gamma_s dn/d\varepsilon) \equiv \Gamma_s^2 dn/d\varepsilon$.



On the other hand, this scheme keeps (nearly) the whole of the pure-state condensation energy, which is

$E_{\text{cond}}^{(\text{pure})} \sim -\Delta_0^2(\frac{dn}{d\varepsilon})$ ($\Delta_0 \equiv$ gap of pure system)

Hence we expect that this scheme will give an energy lower than the $N-$state provided $|E_{\text{cond}}^{(\text{pure})}| > \Gamma_S^2 dn/d\varepsilon$, i.e. condition for magnetic impurities to suppress superconductivity completely is

$$\Gamma_s \gtrsim \Delta_0$$

which is equivalent to $l_s \lesssim \xi_0$. (i.e. mean free path against spin-dependent scattering $\lesssim$ (pure metal) pair radius). Actually, exact calculation (Abrikosov-Gor'kov) shows that while neither of the above schemes is exactly right, at $T = 0$ condition is in fact simply $\Gamma_s > \Delta_0$) .

(An extensive and beautiful discussion of superconductivity in the presence of time-reversal violation is given by P.-G. de Gennes in his classic book "Superconductivity of Metals and Alloys"

Non-BCS Superconductivity

"BCS" superconductors (i.e. those discovered (mostly) before 1975, and well explained by original BCS theory) seem to have the following properties in common:

A. Directly observed properties
   1. crystal structure simple (and 3-dimensional)
   2. T_c stoichiometry-insensitive (except for standard magnetic-impurity effects)
   3. No neighboring phase transition
   4. Normal state Fermi-liquid-like (e.g. R(T) fits Bloch-Gruneisen formula)
   5. Under ambient conditions, $T_c \lesssim 30K^*$

B. Inferred properties
   6. Mechanism is exchange of virtual phonons
   7. Order parameter s-wave

Some (classes of) non-BCS superconductors

Class	Example	A-list properties violated
–	BKBO, MgB_2	5
fullerenes	Rb_3C_{60}	1,2
heavy fermions	UPt_3	3,4
organics	BEDT-TTF	1,4
ruthenates	Sr_2RuO_4	1,4
ferropnictides	$LaFeAso_{1-x}O_{T-\delta}$	1,2,3,5
cuprates	$YBa_2Cu_3O_{7-\delta}$	all

Most of above are inferred to violate also 6 and/or 7. How do we tell?

*Some metallic hydrides are superconducting at close to RT, but only at pressures ~ 100 Gpa. In all other respects they are believed to be "BCS"

Phonon versus non-phonon mechanisms

Original BCS prediction: $T_c = 2\omega_D \exp -1/N(0)|V|$

Debye freq, $\propto M^{-1/2}$ — independent of isotopic mass

thus predict: if superconductors which are chemically identical but have different isotopic masses are compared

$$T_c \propto M^{-\alpha} \qquad \alpha = 1/2$$ ("isotope effect")

Prediction satisfied by most "classic" superconductors (Al, Sn, Pb, ...): a few exceptions, but understood by more sophisticated phonon-plus-Coulomb theory (McMillan) giving

$$\alpha = \frac{1}{2}(1 - A) \qquad A > 0 \text{ , may be } > 1$$

No examples of classic superconductor with $\alpha > 1/2$ known.

So $\alpha \cong 0$ (eg cuprates) suggests non-phonon mechanism

However, all evidence (flux quantization, Josephson effect...) suggests even exotic superconductivity still based on Cooper pairing.

If phonons don't play a role, must be "all-electronic", ie Coulomb mechanism!

But Coulomb interaction, even when screened, is intrinsically repulsive!

$$\langle \hat{H} \rangle = \langle \hat{H}_0 \rangle + \langle \hat{V} \rangle \qquad \hat{H}_0 \equiv \hat{T} + \hat{U} \qquad \hat{V} \equiv \hat{V}_{\text{coul}}$$

kinetic energy potential of static lattice

so prima facie only 2 possibilities:

1. Cooper pairing reduces $\langle \hat{H}_0 \rangle$
2. " " " $\langle \hat{V} \rangle$

Option 1 ⇒ $\langle \hat{H}_0 \rangle$ in N state already considerably > noninteracting-electron value, i.e. N state is not simple Fermi sea.

Option 2 ⇒ $\langle \hat{V}_{\text{coul}} \rangle$ already large in N state

So in either case

non-phonon superconductivity ⇒ "strongly correlated" normal state

Symmetry of OP

For an arbitrary geometry in the absence of spin-orbit coupling, the possible symmetries of the OP are characterized by orbital parity and total spin and the Pauli principle implies that the spin singlet state is associated with even parity and the spin triplet with add parity. Thus in free space (e.g. Superfluid ^3He) L+S = even.

In the real-life "exotic" superconductors symmetry considerations modified:

(1) many are quasi-2D -> symmetry of OP defined only within plane

(2) crystal lattice breaks symmetry, e.g. in square lattice $O(3) \rightarrow C_{4v}$. In the following I use this example (which has played an important role historically) to illustrate the general principles.

Note: asymmetry usually assumed to be pinned to lattice.

Symmetry of the order parameter (OP) in a crystal lattice

Any given crystal lattice will be invariant under a group of symmetry operations. These include crystal translations (not of much interest in the present context) plus the operations of the point group: e.g. a tetragonal lattice is invariant under the "group of the square", C_{4v}. This group contains

rotation through $\pi/2$ around the z-axis $\left(\hat{R}_{\pi/2}\right)$
inversion in a crystal axis $\hat{I}_{axis}$
inversion in a diagonal axis $\hat{I}_{diag}$

but these are actually not independent since $\hat{R}_{\pi/2}\hat{I}_{axis}\hat{I}_{diag} = \hat{1}$ (the identity). Consequently it will be necessary to deal with (say) only $\hat{R}_{\pi/2}$ and $\hat{I}_{axis}$: note that $\hat{I}_{axis}^2 = \hat{R}_{\pi/2}^4 = \hat{1}$. Moreover, it is unnecessary in the present context to distinguish between coordinate and momentum space: the considerations related to symmetry are the same in the two cases.

In BCS theory, the $\boldsymbol{k}$- space components of the OP, $F_{\boldsymbol{k}}$, are simply related to those of the (complex) energy gap function $\Delta_{\boldsymbol{k}}$:

$$F_k = \Delta_k / 2E_k$$

so that provided that the scalar quantity E_k is invariant under the operations of the point group, the quantities F_k and Δ_k transform identically under those operations. While it is perhaps not 100% obvious that this remains true in non-BCS theories, I shall follow the vast bulk of the literature in assuming that it does, and thus talk indifferently about the symmetry of the OP and that of the (complex) gap.

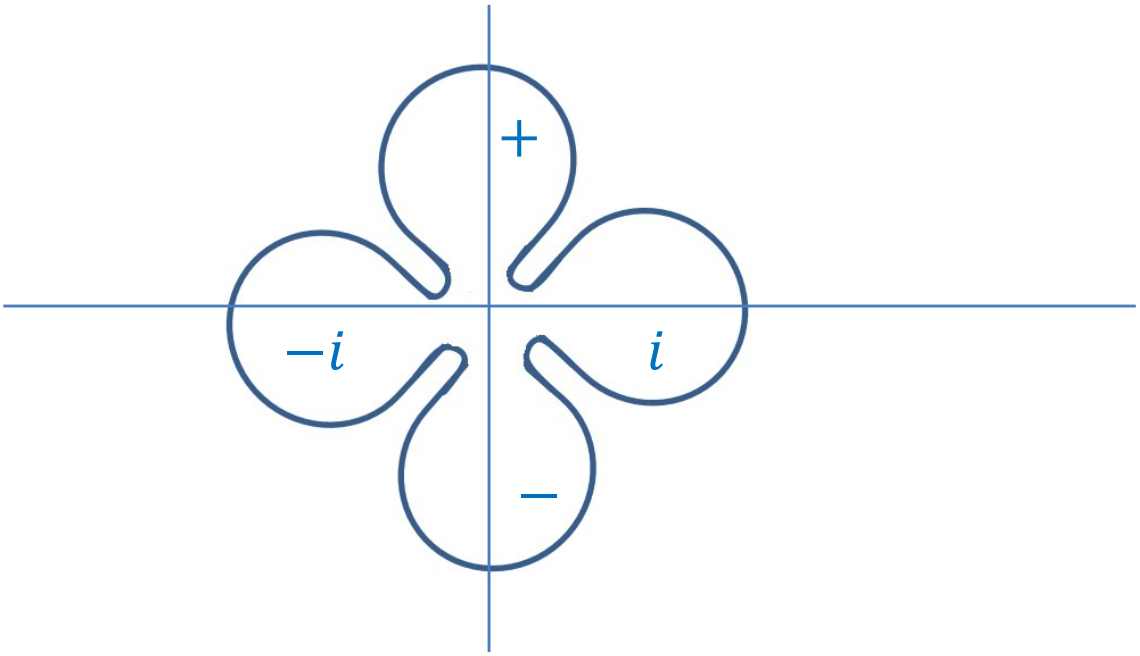
Since the Hamiltonian is invariant under the operations of the point group, it follows that if F_k (or $F(\boldsymbol{r})$) describes a possible superconducting state, then so does $\hat{Q}F_k$ where $\hat{Q}$ is any operation of the point group. A sufficient (though not obviously in general necessary*) condition for this to hold is that

$$\hat{Q}F_k = e^{i\varphi}F_k$$

where, since the quantity F_k must return to itself under operations which return the identity, φ must be equal to $n\pi$ when $\hat{Q} = \hat{I}_{axis}$ and equal to $n\pi/2$ when $\hat{Q} = \hat{R}_{\pi/2}$.

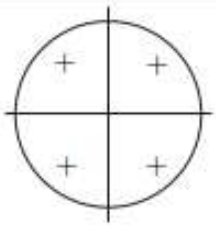
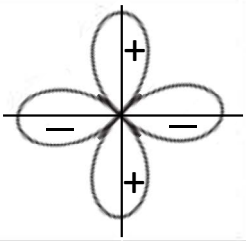
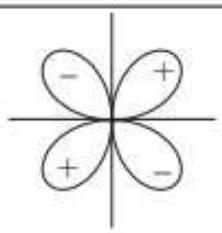
*In the general case, the usual statement is that any viable OP, at least in the limit $T \to T_c$, must correspond to an "irreducible representation" of the relevant point group. The results quoted here for C_{4v} are a special case of this prescription.

Let's consider first the odd-parity representations of C_{4v}, that is, those for which $\hat{I}_{axis}$ has eigenvalue -1. Since in 2D $\hat{I}_{axis} = \hat{R}^2_{\pi/2}$, this means that the only possibilities for the eigenvalue of $\hat{R}_{\pi/2}$ are $\pm i$. Thus the allowed form of the OP in $\boldsymbol{k}$-space is schematically of the form



conventionally known in the literature as the $(p + ip)$ (or $(k_x + ik_y)$) form, or its twin "$p - ip$" with $i \leftrightarrows -i$. This form of OP (not so far definitely established to occur in any metallic superconductor, but believed to be realized in the superfluid A phase of liquid ^3He) is of great interest in the context of topological quantum computing, see lecture 14. Note that there is no requirement that the gap vanishes on the diagonals.

Now we turn to the even-parity representations of C_{4v}; which have been of great interest in the context of the cuprates, which are known to be spin singlet and thus even parity. The results are most easily displayed in the form of a table:

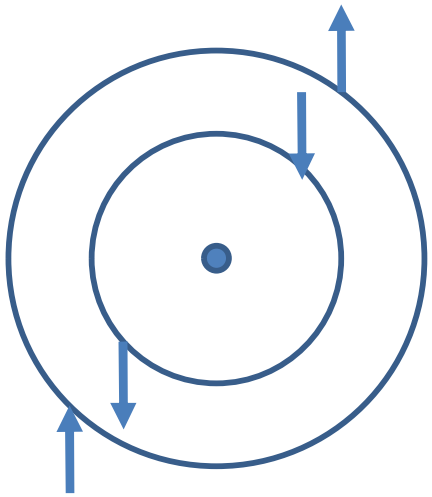
	Informal name	Group-theoretic notation	$\hat{R}_{\pi/2}$	$\hat{I}_{\text{axis}}$	Representative state
	s^+	A_{1g}	$+1$	$+1$	const
	s^- ('g')	A_{2g}	$+1$	-1	$xy(x^2-y^2)$
	$d_{x^2-y^2}$	B_{1g}	-1	$+1$	x^2-y^2
	d_{xy}	B_{2g}	-1	-1	xy

Possible even-parity forms of the OP in tetragonal symmetry

Symmetry of OP: how do we tell?

(1) spin susceptibility χ : if $S = 0$ $(l = \text{even})$, χ is reduced in S state because to polarize system must break up Cooper pairs (c.f. lecture 7). For $S = 1$ pairing effect is either absent or reduced, e.g. if $S_z = \pm 1$ (as in ^{3}He-A), since pairing scheme below is possible,

$$\chi_S = \chi_N$$



(2)s-wave state usually has non-zero minimum value of excitation energy ("gap") ⇒ as $T \to 0$ number of excitations $\propto \exp(-\Delta/T)$ ⇒ specific heat, etc., exponentially small.
By contrast most (but not all) exotic pairing states have "nodes" in gap ($\Delta \to 0$ for some $\vec{k}$) -> substantial number of excitations as $T \to 0$ → specific heat, etc. proportional to some power of T.

(3) Effect of nonmagnetic impurities: for a simple s-wave state in free space (BCS case) T_c is virtually unaffected. For the case of an s-wave state in a lattice, expect some depression but not to 0. However, for an "exotic" state (p-wave, d-wave, ...) nonmagnetic impurities have a qualitatively similar effect to magnetic impurities in BCS, i.e.

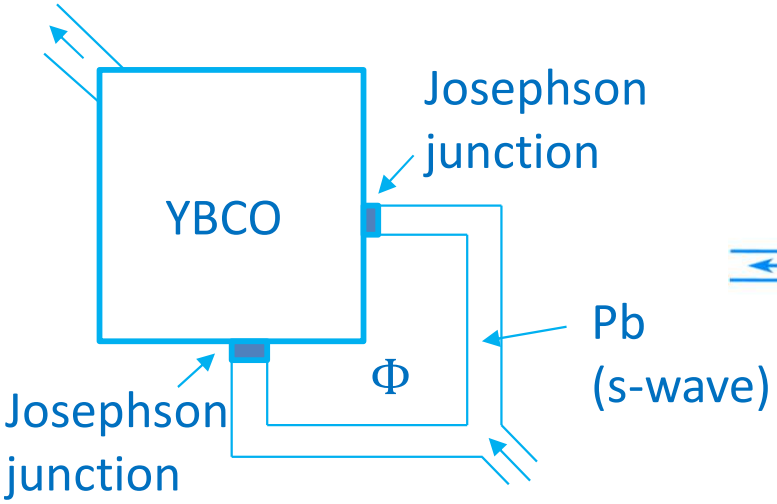
$$T_c \to 0 \text{ for } \Gamma \gtrsim \Delta_0$$

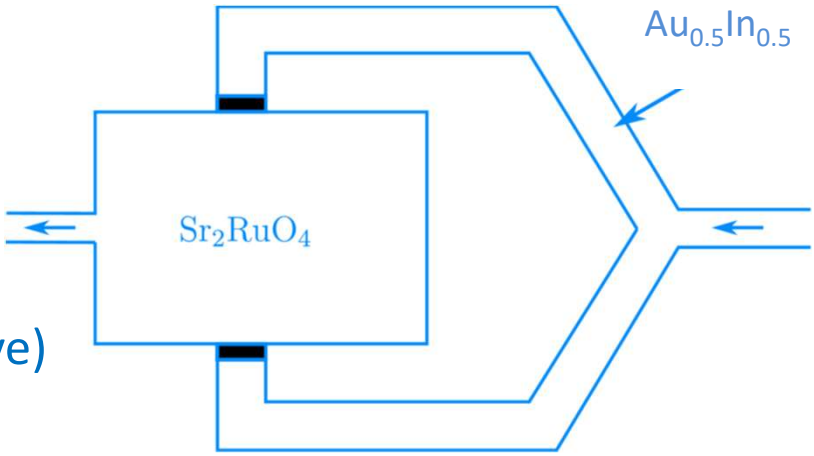
relevant scattering rate (rms) gap for pure case

Thus, e.g., the fact that very small concentrations of impurities in Sr_2RuO_4 drive T_c to 0 was (until 2019) usually taken as evidence for exotic pairing.

(4). Phase-sensitive (Josephson) experiments (UIUC,PSU,…)

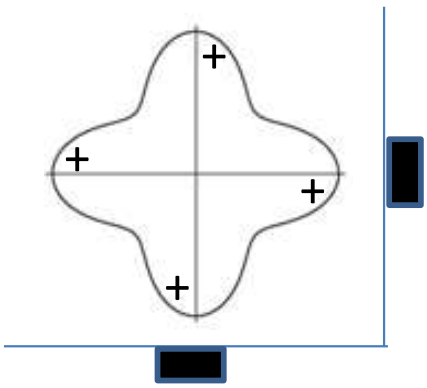
refinement of SQUID geometry



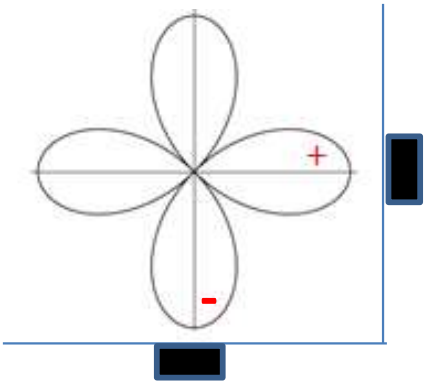


General principle: For maximum critical current of device as whole, $\Phi = \sum_i \Delta\varphi_i$ where $\Delta\varphi_i$ includes "internal" phase differences due to "rotation" of pair wave function

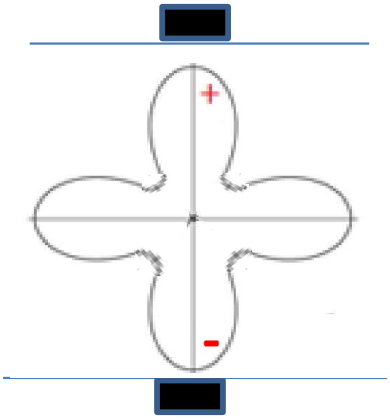
e.g. in YBCO



s-wave



$d_{x^2-y^2}$



similarly for Sr_2RuO_4 if p-wave