LECTURE 4. Definition and diagnostics of "exotic" superconductivity

Principal characteristics of "classic" (BCS) superconductors:

1. $T_c \leq 25$K (except BKBO, MgB_2)
2. Normal state is well described by Fermi liquid theory
3. Mechanism of Cooper-pair formation is phonon-induced attraction
4. Symmetry of pairs is s-wave

and usually but not always:

5. Structure essentially 3-dimensional
6. Superconducting state not close to other broken symmetry phase (e.g. antiferromagnetic)
7. (For alloys) superconductivity not particularly sensitive to stoichiometry.

An "exotic" superconductors fail to satisfy at least one of $(1-7)$:

Property	Classic	Heavy fermions	Organics	Ruthcnatcs	Fullerenes	Ferropictides	Cuprates
$T_c < 25$K	$(\surd)$	$\surd$	$\surd$	$\surd$	$\times$	$\times$	$\times$
Fermi liquid normal state	$\surd$	$\times$	$\times$	$\times$	$\surd$	$(\surd)$	$\times$
No neighboring phase trans.	$\surd$	$\times$	$\surd$	$\surd$	$\surd$	$\times$	$\times$
Order parameter s-wave	$\surd$	?	?	$\times$	$\surd$	$(\times)$	$\times$
Phonon mechanism	$\surd$	$\times$	?	?	$\surd$	$\times$	$\times$
Crystal structure simple	$\surd$	$\surd$	$\times$	$\times$	$\times$	$\times$	$\times$
Stoichiometry-insensitive	$\surd$	$\surd$	$\surd$	$\surd$	$\times$	$\times$	$\times$
Maximum T_c/K	40	2	15	2	40	56	150

How do we know the above?
(1),(5),(6),(7) from direct inspection: (2) from experiment plus a little theory.
What about (3) and (4)?

DIAGNOSTICS OF NON-PHONON MECHANISM

A. (Absence of) isotope effect

Isotope effect in BCS theory:

In general, theory of T_c for realistic phonon-plus-Coulomb interaction is complicated and requires solution of Eliashberg eqns. (cf. below). However, McMillan argued that a good analytic approximation is

$$T_c = \left(\frac{\Theta_D}{1.45}\right) \exp\left(-\left\{\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}\right),$$

where

$$\lambda \equiv 2\int_0^{\omega_D} \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega = \text{(const.}\times\text{)}\ \underline{\text{static}}\ \text{local compressibility of lattice, so independent of isotopic mass } M$$

where $\alpha(\omega)$ is the phonon coupling and $F(\omega)$ is the phonon density of state, and

$$\mu^* \equiv \frac{N(0)\langle V_c\rangle}{1 + N(0)\langle V_c\rangle \ln(\varepsilon_F/\Theta_D)} = \text{renormalized Coulomb interaction},$$

where $\langle V_c\rangle$ is the averaged Coulomb interaction. In approximation of ignoring Θ_D-dependence of μ^*, $T_c \propto \Theta_D \propto M^{-1/2}$, i.e., in terms of "isotope exponent" $\alpha \equiv -\dfrac{\partial(\ln T_c)}{\partial(\ln M)}$,

$$\alpha = \frac{1}{2} \quad [\text{“textbook” BCS result}]$$

More exactly:

$$\alpha = \frac{1}{2}\left[1 - \frac{1.04{\mu^*}^2(1+\lambda)(1+0.62\lambda)}{[\lambda - \mu^*(1+0.62\lambda)]^2}\right] \left(< \frac{1}{2}\right)$$

Thus even if μ^* is small, α can deviate appreciably from 0.5 (and even be < 0) in BCS theory. But crudely speaking:

- $\alpha \simeq 0.5 \Rightarrow$ probably phonon-mediated
- $\alpha \ll 0.5 \Rightarrow$ probably but not certainly non-phonon-mediated
- $(\alpha > 0.5) \Rightarrow$ possibly phonon-mediated but BCS theory certainly inapplicable ($\leftarrow$ no cases known so far)

Above does not take into account other possible ways in which isotopic substitution could modify T_c, e.g., lattice distortion (especially for ^{1}H$\to$^{2}D).

DIAGNOSTICS OF NON-PHONON MECHANISM (cont.)

B. (Absence of) phonon structure in tunneling I-V characteristics

Recall that in BCS theory

$$\Delta_{\boldsymbol{k}} = -\sum_{\boldsymbol{k}'} V_{\boldsymbol{k}\boldsymbol{k}'} \frac{\Delta_{\boldsymbol{k}'}}{2E_{\boldsymbol{k}'}}.$$

Problem: in realistic theory of phonon-mediated interaction, $V_{\boldsymbol{k}\boldsymbol{k}'}$, even in the normal state, is energy dependent:

$$V_{\boldsymbol{k}\boldsymbol{k}'} = |g_{\boldsymbol{k}\boldsymbol{k}'}|^2 \frac{\varepsilon_{\boldsymbol{k}'} + \omega_{\text{ph}}(\boldsymbol{k} - \boldsymbol{k}')}{(\varepsilon_{\boldsymbol{k}'} + \omega_{\text{ph}}(\boldsymbol{k} - \boldsymbol{k}'))^2 - \varepsilon_{\boldsymbol{k}}^2}$$

$\Rightarrow$ need for Eliashberg theory (non-intuitive). "Gap" (off-diagonal field) becomes frequency-(energy-)dependent $\Delta \to \Delta(\omega)$ (but nearly independent of momentum). At $T = 0$, gap eqn. becomes:

$$\begin{aligned}\Delta(\omega) &= \frac{1}{Z(\omega)} \int_0^\infty \mathrm{d}\omega' \mathrm{Re} \left\{ \frac{\Delta(\omega')}{(\omega'^2 - \Delta^2(\omega'))^{1/2}} \right\} \\ &\times \left\{ \int_0^\infty \mathrm{d}\Omega \alpha^2(\Omega) F(\Omega) \frac{2(\omega' + \Omega)}{(\omega' + \Omega)^2 - \omega^2} - \mu^* \right\}\end{aligned}$$

Here $Z(\omega)$ is the renormalization function, given by a 2nd Eliashberg eqn., $\alpha(\omega)$ is the phonon-coupling function, and $F(\omega)$ is the phonon density of state.

McMillan + Rowell: differential tunnel conductance measures $\Delta(\omega)$ via

$$\frac{(\partial I/\partial V)_S}{(\partial I/\partial V)_N} = \mathrm{Re} \left\{ \frac{\omega}{(\omega^2 - \Delta^2(\omega))^{1/2}} \right\}, \quad \hbar\omega = eV.$$

Can then reconstruct function $\alpha^2(\Omega)F(\Omega)$ + compare with e.g. neutron data. For BCS superconductors, fit usually very good.

Qualitative message: if origin of Cooper pairing is phonon-mediated attraction, then peaks in neutron scattering spectrum (i.e., in $F(\Omega)$) must be reflected in tunnelling I-V characteristic. Conversely, absence of such reflection $\Rightarrow$ non-phonon mechanism.

Of the existing "exotic" superconductors, the only ones when the mechanism seems to be phonon-mediated are the alkali fullerides and (probably) the organics.

DIAGNOSTICS OF ORDER PARAMETER SYMMETRY

Since many body wave-function unlikely to be of simple BCS type, to discuss this need more general definition of OP ← order parameter (pair wave function). (Yang, 1962)

Consider 2-particle reduced density matrix

$$\begin{aligned} &\rho_2(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2 : \boldsymbol{r'_1}\sigma'_1, \boldsymbol{r'_2}\sigma'_2 : t) \\ \equiv\ & N(N-1)\sum_s p_s \sum_{\sigma_3\cdots\sigma_N} \int \mathrm{d}^3\boldsymbol{r_3}\cdots \mathrm{d}^3\boldsymbol{r_N} \quad (p_s : \text{probability of occupation of Many-body states }) \\ & \quad \Psi^*_S(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2, \boldsymbol{r_3}\sigma_3\cdots \boldsymbol{r_N}\sigma_N : t)\Psi_S(\boldsymbol{r'_1}\sigma'_1, \boldsymbol{r'_2}\sigma'_2, \boldsymbol{r_3}\sigma_3\cdots \boldsymbol{r_N}\sigma_N : t) \\ \equiv\ & \langle \hat{\psi}^\dagger_{\sigma_1}(\boldsymbol{r_1}t)\hat{\psi}^\dagger_{\sigma_2}(\boldsymbol{r_2}t)\hat{\psi}_{\sigma'_2}(\boldsymbol{r'_2}t)\hat{\psi}_{\sigma'_1}(\boldsymbol{r'_1}t)\rangle \\ \simeq\ & \text{best possible representation of ``behavior of 2 electrons averaged over behavior of remaining } N-2\text{''} \end{aligned}$$

Note all 2-particle expectation values can be expressed in terms of ρ_2: e.g. if

$$\hat{V} \equiv \frac{1}{2}\sum_{ij} V(\hat{\boldsymbol{r}}_i - \hat{\boldsymbol{r}}_j),$$

then

$$\langle \hat{V}\rangle(t) = \sum_{\sigma_1\sigma_2}\int\int \mathrm{d}^3\boldsymbol{r_1}\mathrm{d}^3\boldsymbol{r_2} V(\boldsymbol{r_1}-\boldsymbol{r_2})\rho_2(\boldsymbol{r_1}\sigma_1\boldsymbol{r_2}\sigma_2 : \boldsymbol{r_1}\sigma_1\boldsymbol{r_2}\sigma_2 : t).$$

Also, 1-particle reduced density matrix given by

$$\rho_1(\boldsymbol{r}\sigma, \boldsymbol{r'}\sigma' : t) = \frac{1}{N}\sum_{\sigma_2}\int \mathrm{d}^3\boldsymbol{r_2}\rho_2(\boldsymbol{r}\sigma, \boldsymbol{r_2}\sigma_2 : \boldsymbol{r'}\sigma', \boldsymbol{r_2}\sigma_2 : t)(+O(N^{-2})).$$

As $f(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2)$ ρ_2 is Hermitian $\Rightarrow$ can be diagonalized, i.e., written

$$\rho_2(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2 : \boldsymbol{r_1'}\sigma_1', \boldsymbol{r_2'}\sigma_2' : t) = \sum_i n_i(t)\chi_i^*(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2 : t)\chi_i(\boldsymbol{r_1'}\sigma_1', \boldsymbol{r_2'}\sigma_2' : t),$$

where $\{\chi_i\}$ is an orthonormal set $(\chi_i, \chi_j) = \delta_{ij}$ and

$$\sum_i n_i(t) = N(N-1).$$

However (Yang) maximum value of any one n_i is $O(N)$.

Note: ρ_2 must be antisymmetric under $(\boldsymbol{r_1}\sigma_1 \rightleftharpoons \boldsymbol{r_2}\sigma_2)$ (etc.) (due to Fermi statistics), hence so must be eigenfunctions χ_i.

More general definition of order parameter, cont. (assume from now on state time-independent)

Recap: $\rho_2 = \sum_i n_i \chi_i^*(\boldsymbol{r_1}\sigma_1\boldsymbol{r_2}\sigma_2)\chi_i(\boldsymbol{r'_1}\sigma'_1\boldsymbol{r'_2}\sigma'_2)$.

In principle, 3 possibilities:

1. All eigenvalues $n_i \sim o(1)$ (normal state) (ex: free Fermi gas)
2. 2 or more eigenvalues $O(N)$, rest $o(1)$ ("fragmented" pseudo-BEC, usually disregarded [1])
3. One eigenvalue (only) $O(N)$, rest $o(1)$ ("simple" pseudo-BEC, i.e. Cooper pairing)

In case 3, label the "special" ($n_i \sim N$) state o, then define ($n_o \to N_o$)

$$F(\boldsymbol{r_1}\sigma_1\boldsymbol{r_2}\sigma_2) \equiv \sqrt{N_o}\chi_o(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2) \leftarrow \text{order parameter (pair wave function)}$$

For the BCS case this definition reduces to the one given in ℓ.2. Note that from the orthonormality condition on the χ_i,

$$\sum_{\sigma_1\sigma_2} \int \mathrm{d}^3\boldsymbol{r_1}\mathrm{d}^3\boldsymbol{r_2} |F(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2)|^2 = N_o,$$

so N_o is "number of Cooper pairs".

Note: alternative definition of F is

$$F(\boldsymbol{r_1}\sigma_1, \boldsymbol{r_2}\sigma_2) \equiv \langle N+2|\hat{\psi}^\dagger_{\sigma_1}(\boldsymbol{r_1})\hat{\psi}^\dagger_{\sigma_2}(\boldsymbol{r_2})|N\rangle \; (|N\rangle, |N+2\rangle : \text{ ground states})$$

(often "abbreviated" $\langle\hat{\psi}^\dagger_{\sigma_1}(\boldsymbol{r_1})\hat{\psi}^\dagger_{\sigma_2}(\boldsymbol{r_2})$ with implicit assumption of N-non-conservation)

If we define

$$\boldsymbol{R} = \frac{(\boldsymbol{r_1}+\boldsymbol{r_2})}{2} \text{ (COM)}, \; \boldsymbol{r} = \boldsymbol{r_1} - \boldsymbol{r_2} \text{ (relative)},$$

then

$$F \equiv F(\boldsymbol{R}, \boldsymbol{r}, \sigma_1, \sigma_2),$$

and (for this course) we will usually be interested in the case F is independent of $\boldsymbol{R}$, i.e.,

$$F = F(\boldsymbol{r}, \sigma_1, \sigma_2) \text{ (not quite accurate in crystal, cf. below)}.$$

"Symmetry of order parameter" $\equiv$ dependence of F on $\boldsymbol{r}, \sigma_1, \sigma_2$.

[1] but cf. discussion (ℓ.3) of spin triplet pairing in limit $g_D \to 0$

SYMMETRY OF ORDER PARAMETER IN CRYSTAL[2]

In a crystal, because of effect of lattice potential, cannot strictly assume F independent of $\boldsymbol{R}$ ($\leftarrow$ COM coordinate). So more convenient to restrict ourselves for the moment to the case where a single band intersects Fermi surface[3]... and take Fourier transform of F in Bloch basis, i.e.

$$F_{\alpha\beta}(\boldsymbol{k}) \equiv \langle a^\dagger_{\boldsymbol{k}\alpha} a^\dagger_{-\boldsymbol{k}\beta} \rangle \equiv -F_{\beta\alpha}(-\boldsymbol{k}) \quad \leftarrow \text{ Fermi statistics}$$

(where $\boldsymbol{k}$ is Bloch waves)

Can classify possible forms of $F_{\alpha\beta}$ according to their parity, i.e. by

$$F_{\alpha\beta}(-\boldsymbol{k}) = \pm F_{\alpha\beta}(\boldsymbol{k})$$

From Fermi statistics

$$\text{even parity} \rightleftharpoons \text{spin singlet}$$
$$\text{odd parity} \rightleftharpoons \text{spin triplet}$$

In singlet case,

$$F_{\alpha\beta}(\boldsymbol{k}) = F_{\alpha\beta}(-\boldsymbol{k}) = -(i\sigma_y)_{\alpha\beta} F(\boldsymbol{k}) \quad \text{i.e. } \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) F(\boldsymbol{k})$$

In triplet case, define as for ^{3}He

$$\boldsymbol{d}(\boldsymbol{k}) \equiv (i\sigma_y \boldsymbol{\sigma})_{\alpha\beta} F_{\beta\alpha}(\boldsymbol{k})$$

if $\boldsymbol{d}(\boldsymbol{k})$ is real, it is direction along which pair $(\boldsymbol{k}, -\boldsymbol{k})$ has $S_z = 0$.

Orbital Symmetry

Will usually assume that the dependence of $F_{\boldsymbol{k}}$ on magnitude of $\boldsymbol{k}$ is not quantitatively different from BCS form $\Delta_{\boldsymbol{k}}/2E_{\boldsymbol{k}}$. $\Delta_{\boldsymbol{k}} \approx$ independent of $|\boldsymbol{k}|$. So interest is in dependence of $F_{\boldsymbol{k}}$ on direction of $\boldsymbol{k}$ on Fermi surface.

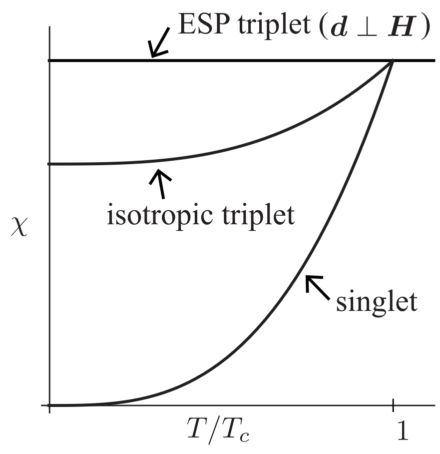
Possible forms of $F_{\boldsymbol{k}}$ classified by transformation properties under crystal symmetry operations (reflection, rotation...); usually, transforms according to a single irreducible representation of the crystal point group. If this is the identity representation, "conventional" ("s-wave"), otherwise "exotic".

[2] Exhaustive discussion: Gor'kov+Volovik, JETP **61**, 843 (1985)

[3] not true for Sr_2RuO_4, ferropnictides

Diagnostics of spin state

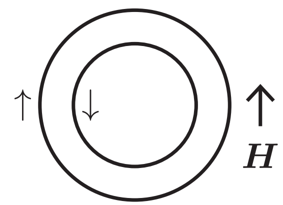
1. Spin susceptibility (via Knight shift)



For singlet, χ/χ_n falls to 0 as $T \to 0$. For an ESP state with ESP axes along field, ($\boldsymbol{d}(\boldsymbol{n}) \perp H$) $\chi/\chi_n \approx 1$. For a non-ESP triplet, (eg. BW-type state), $0 < \chi/\chi_n < 1$. Thus:

$$\chi(T=0) \neq 0 \quad \Rightarrow \quad \text{triplet}$$
$$\chi(T=0) = 0 \quad \Rightarrow \quad \text{either singlet, or ESP triplet with } \boldsymbol{d} \parallel \boldsymbol{H}.$$

2. CC (Chandrasekhar-Clogston) limit on upper critical field



Almost all exotic superconductors are extreme type-II $\Rightarrow$ "Meissner" H_{c2} very large $\Rightarrow$ actual H_{c2} may be limited by spin effects (depairing): $H_{c2} \sim \Delta(0)/\mu_B$. If pairing singlet or ESP with $\boldsymbol{d} \parallel \boldsymbol{H}$, expect effect. Thus,

$$\text{absence of CC limit on } H_{c2} \quad \Rightarrow \quad \text{triplet}$$
$$\text{CC limit} \quad \Rightarrow \quad \text{singlet or triplet with } \boldsymbol{d} \parallel \boldsymbol{H}.$$

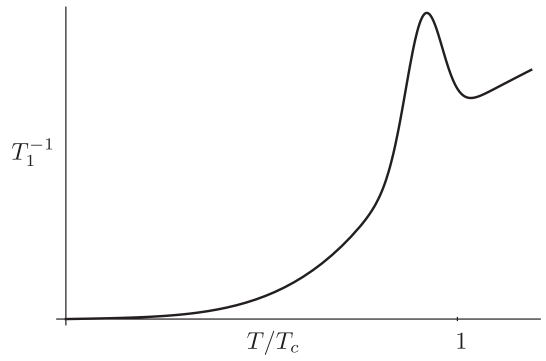
3. Coherence ("Hebel-Slichter") peak in NMR

Presence of HS peak requires

(a) singularity ($\propto (E^2 - \Delta^2)^{-1/2}$) in DOS at gap edge

(b) absence of canceling factor ($\propto (E^2 - \Delta^2)$) in matrix element, due to coherence.

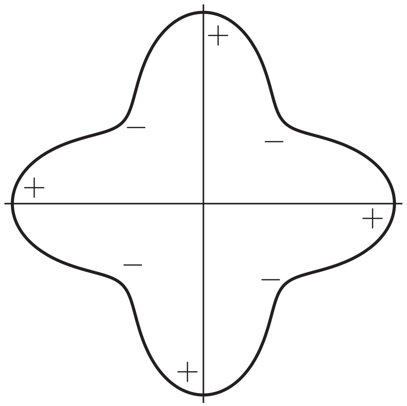
Unfortunately, (b) should still hold for spin triplet, so presence/absence of HS peak not informative about spin state. (peak predicted to be half "canonical" size, but difficult to check this.)



Diagnostics of orbital state

Two cautions:

(1) Even if order parameter transforms according to identity representation of crystal group, may have nodes ("extended s-wave")



(2) (important!) Order parameter $F_{\boldsymbol{k}}$ is 2-particle ("bosonic") quantity: energy gap $\Delta_{\boldsymbol{k}}$ is 1-particle ("fermionic"). Within BCS theory, the two are closely proportional since

$$F_{\boldsymbol{k}} = \Delta_{\boldsymbol{k}}/2E_{\boldsymbol{k}}$$

However, this need not necessarily be true in a more general theory.

Measurement of $|\Delta_{\boldsymbol{k}}|$ (note in triplet case this is "total" gap, $\propto |\boldsymbol{d}(\boldsymbol{n})|$)

(a) direct, e.g. ARPES, STM...

(b) thermodynamic, via DOS $N_s(E)$:

$$N_s(E) = \sum_{\boldsymbol{k}} \delta(E - E_{\boldsymbol{k}}) = N(0) \int_{|\Delta(\hat{\boldsymbol{n}})| \le E} \frac{\mathrm{d}\Omega}{4\pi} \frac{E}{\sqrt{E^2 - |\Delta(\hat{\boldsymbol{n}})|^2}}$$

$$\propto \text{ area of Fermi Surface for which } |\Delta(\hat{\boldsymbol{n}})| \le E.$$

Hence,

3D, point node: $N_s(E) \propto E^2$

3D, line node: $N_s(E) \propto E$

2D, point node: $N_s(E) \propto E$

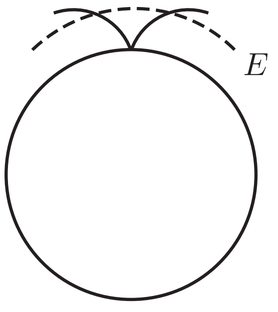
If DOS $\propto E^n$, then for $T \to 0$,

specific heat $C_v \propto T^{n+1}$

Landau penetration depth $\lambda(T) - \lambda(0) \propto T^n$

nuclear spin relaxation rate $T_1^{-1} \propto T^{2n+1}$

Knight shift $K_s \propto T^n$ (spin singlet)



Note: in 3D, for $\ell \geq 2$ must always have nodes.
in 2D, need not have node for any ℓ ($F_{\boldsymbol{k}} \sim \exp(i\ell\varphi)$)

General diagnostics of exotic order parameter symmetry: effect of impurities

Digression: Impurity scattering in BCS (s-wave) superconductor

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad \hat{H}_0 = \hat{K} + U(\boldsymbol{r}, \sigma)$$

where $\hat{H}_0$ ($\hat{V}$) is single(two)-particle Hamiltonian, and $\hat{K}$ is kinetic term and $U(\boldsymbol{r}, \sigma)$ is impurity potential.

Let exact eigenfunctions of $\hat{H}_0$ be $\chi_{n\sigma}(\boldsymbol{r}, \sigma)$ with energies ε_n.

(A) If impurity potential $U(\boldsymbol{r})$ independent of σ (nonmagnetic impurities), T-invariant

$\Rightarrow$ $\chi_n^*(\boldsymbol{r}, -\sigma)$ also eigenfunction, with same energy ε_n.

$\Rightarrow$ can pair in time-reversal states. (Anderson's theorem)

so (a) expenditure of $\hat{H}_0$ minimal (b) $F(\boldsymbol{rr}) \sim \sum_n |\chi_n(\boldsymbol{r})|^2$ ~large, hence $-\langle \hat{V} \rangle$ also large.

(B) For magnetic impurities, ($U = U(\boldsymbol{r}, \sigma)$) T-invariance is broken. Then we have choice:

(a) pair in exact eigenstates ε_n: Then minimum expenditure of $\hat{H}_0$, but $F(\boldsymbol{rr})$ much reduced $\Rightarrow$ usually disadvantageous

(b) reconstitute "impurity-free" Fermi sea and pair in eigenstates of $\hat{K}$. This sacrifices energy due to U:

$$\Delta E_U = +\frac{1}{2} N(0) \Gamma_U^2 \quad \leftarrow \text{relaxation rate of T-reversal operator}$$

So becomes disadvantageous if $\Delta E_U > E_{\text{condansation}} = \dfrac{1}{2} N(0) \Delta_0^2$ $\leftarrow$ gap for pure system

Hence, expect superconductivity to disappear (at $T = 0$) for

$$\Gamma_U = \Delta_0 \quad \text{[confirmed by exact (Abrikosov-Gor'kov) theory]}$$

Generalization to exotic order parameter symmetry[4]

Even if impurities are nonmagnetic, exact eigenstates χ_n of $\hat{H}_0$ will now be complicated superposition of $\boldsymbol{k}$'s from all over Fermi surface, so if we pair in χ_n's, if dominant ℓ in $V_{\boldsymbol{kk'}} \neq 0$, $\langle \hat{V} \rangle$ will be very small. So must again "reconstitute" impurity-free eigenfunctions: cost some energy $\Delta E_U = \frac{1}{2} N(0) \Gamma_\ell^2$ $\leftarrow$ relaxation rate of ℓ-symmetry distortion.

By analogy with above argument, superconductivity disappear when $\Gamma_\ell = \Delta_0$.

[4] for details cf. eg. AJL Quantum Liquids, appendix 7B

Addendum: Effect of spin-orbit coupling

The discussion of spin triplet pairing in lecture 2 and above implicitly assumes that the eigenstates of the single-particle Hamiltonian $\hat{H}_0$ are (mostly[5]) invariant under spin rotation and the (orbital) crystal group separately. Under these conditions, the pairing state can usually be classified as

either $s = 0$, $\ell =$ even (or even-parity orbital state)
or $s = 1$, $\ell =$ odd (or odd-parity orbital state)

mixing of these two possibilities requires rather pathological values of the parameters.

However, if $\hat{H}_0$ is not invariant under spin and orbital operations separately, there may be strong mixing of the two. The most obvious origin of this is spin-orbit coupling. (scales as Z^3, so rapidly becomes important in heavy metals, e.g. U compounds)

Under these conditions the only symmetries left are P (parity) and T (time-reversal) (both preserved by spin-orbit coupling $\propto \boldsymbol{\ell} \cdot \boldsymbol{s}$), and we must use these (only) to classify the irreducible representations. See Gor'kov+Volovik, JEJP 61, 843 (1985).

[5]except for dilute magnetic impurities etc.