Magnetic impurity and other 'pair-breaking' effects

References: de Gennes Chapter 8; AJL QL section 5.9

One of the most striking experimental facts about (classical) superconductivity is that while it is rather insensitive to nonmagnetic impurities, even a rather small concentration of magnetic impurities (i.e., those corresponding to a finite local moment) can lead to a drastic suppression of T_c or even the complete vanishing of superconductivity. The basic reason for this and related affects is that such impurities destroy the invariance of the (conduction-electron) Hamiltonian under time reversal. In the following, we suppose until further notice that the effect of magnetic impurities is to add to the conduction-electron Hamiltonian a term of the form

$$\hat{H}_{mag} = \sum_m J_m \mathbf{S}_m \cdot \boldsymbol{\sigma}(\mathbf{r}_m) \tag{1}$$

where $\boldsymbol{\sigma}(\mathbf{r}) \equiv \sigma_{\alpha\beta}\psi^\dagger_\alpha(\mathbf{r})\psi_\beta(\mathbf{r})$ is the conduction-electron spin density at the point $\mathbf{r}$. The spins $\mathbf{S}_m$ are taken to be classical and random both in orientation and in position (the orientation being fixed).

In lecture 9 we considered the case of nonmagnetic impurities, and showed that by pairing time-reversed eigenstates $(|n\uparrow\rangle, |\bar{n}\downarrow\rangle)$ of the single-particle Hamiltonian, we would obtain almost as large an (average) value of the quantity $F(\mathbf{r},\mathbf{r})$ as in the 'pure' case. To recapitulate the argument, we write in that case

$$\Psi_{\text{BCS}} = \prod_n (u_n + v_n a^+_{n\uparrow} a^+_{\bar{n}\downarrow})|\text{vac}\rangle \tag{2}$$

and the quantity $F(\mathbf{r},\mathbf{r})$ takes the value

$$F(\mathbf{r},\mathbf{r}) \equiv \langle \psi^\dagger_\uparrow(\mathbf{r})\psi^\dagger_\downarrow(\mathbf{r})\rangle = \sum_n u_n v_n \phi_n(\mathbf{r})\phi_{\bar{n}}(\mathbf{r}) \tag{3}$$

but since $\phi_{\bar{n}}(\mathbf{r}) \equiv \phi^*_n(\mathbf{r})$ this becomes simply

$$F(\mathbf{r},\mathbf{r}) = \sum_n u_n v_n |\phi_n(\mathbf{r})|^2 \tag{4}$$

and with an appropriate choice of the parameter $u_n v_n$ $(= \Delta_n/2E_n)$ this can be made approximately as large (or larger) as its value for the pure case. Thus, the pair term in the potential energy, which for the simple contact potential considered is simply

$$\langle V\rangle_{\text{pair}} = V_0 \int |F(\mathbf{r})|^2 d\mathbf{r} \tag{5}$$

is also just as large as in the pure case. Moreover, since $\epsilon_n = \epsilon_{\bar{n}}$, the kinetic energy required to form the pairs is much the same as in the pure case.

For a system lacking time reversal invariance we cannot repeat this argument, because in general the eigenstates of the single-particle Hamiltonian no longer occur in pairs related by time reversal. We therefore have two obvious choices: (a) pair in eigenstates of $\hat{H}_0$ (which are not in general time-reversed) (b) pair in time reversed states (which are not in general eigenstates of $\hat{H}_0$). Of course, intermediate choices are also possible. We say that magnetic impurities (and other time-reversal-noninvariant effects) are "pair-breaking"

Before embarking on a quantitative calculation, let's try to consider the pros and cons of choices (a) and (b) qualitatively. If we make choice (a), then from the kind of general arguments developed in lecture 5 we would expect that the best choice is to pair eigenstates of $\hat{H}_0$ with nearly degenerate energies ϵ_n. (These will not of course in general be eigenstates of spin). Such a choice will lead to a depression of the quantity $F(\mathbf{r},\mathbf{r})$, which is effectively equivalent to a suppression of the constant V_0; since T_c depends exponentially on V_0, we expect it to be strongly depressed (except in very special circumstances, cf. below). So let's consider alternative (b)(which is (something like) what the system actually does, cf. below). We then lose little or nothing on the pairing contribution to $\langle V\rangle$, but the price is that we increase the kinetic energy; crudely speaking, we have to start our pairing from a "pseudo-Fermi sea" that is the Fermi sea that would describe the normal system subject to a Hamiltonian without the magnetic terms. What does it cost us to create this "pseudo-Fermi sea" from the true normal-groundstate (i.e., the groundstate of $\hat{H}_0$ including the magnetic impurities)? A back of envelope argument goes as follows: consider a spin (or more generally time-reversal) eigenstate made up out of eigenstates of $\hat{H}_0$ close to the Fermi energy. Such a state will have a width Γ ($\equiv \hbar/\tau_K$, see below) which tends to a constant near ϵ_F, i.e., it is made up of a packet of eigenstates of $\hat{H}_0$ which have spread $\sim \Gamma/2$. Thus, to reconstitute a "pseudo-Fermi sea" out of such spin eigenstates we need to supply an extra energy $\sim \Gamma/2$ times the number of states involved in the rearrangement, which is $\sim (dn/d\epsilon)\Gamma/2$. The total energy required is thus $\sim \frac{1}{4}(dn/d\epsilon)\Gamma^2 \equiv \frac{1}{2}N(0)\Gamma^2$. On the other hand, the condensation energy of the superconducting state relative to this "pseudo-Fermi sea" is $\frac{1}{2}N(0))\Delta^2$ where Δ is the energy gap in the material without magnetic impurities. Thus, we expect superconductivity to become energetically unfavorable even at $T = 0$ (i.e. $T_c \to 0$) when $\Gamma \sim \Delta$. It is amusing that while the numerical factors in the above argument are clearly rather arbitrary, the exact criterion for the disappearance of superconductivity does in fact turn out to be $\Gamma = \Delta$ (see below). If for an "otherwise pure" material (i.e. in the absence of nonmagnetic impurities), we introduce the relaxation time τ_K against T-violating effects, so that $\Gamma \equiv \hbar/\tau_K$, and the corresponding mean free path $l_K \equiv v_F\tau_K$, and recall the definition of the Pippard coherence length ξ_0, this criterion can be rewritten $l_K = \pi\xi_0$.

In the following we are going to make extensive use of the time-reversal operator $\hat{K}$. This operator must by definition have the property of preserving the coordinate $\mathbf{r}$ but reversing both momentum $\mathbf{p}$ and spin $\boldsymbol{\sigma}$, i.e.

$$K\mathbf{r}K^{-1} = \mathbf{r}, \quad \hat{K}\hat{\mathbf{p}}\hat{K}^{-1} = -\hat{p}, \quad \hat{K}\boldsymbol{\sigma}\hat{K}^{-1} = -\hat{\boldsymbol{\sigma}}. \tag{6}$$

In the case of a simple scaler wave function $\varphi(\mathbf{r})$, it is clear that $\hat{K}$ may be chosen to be simply complex conjugation ($\hat{C}$)

$$\hat{K}\varphi(\mathbf{r}) \equiv \varphi^*(\mathbf{r}). \equiv \hat{C}\varphi(\mathbf{r}) \tag{7}$$

However, in general the eigenfunctions of the single-particle Hamiltonian, which are what we are going to apply the time-reversal operation to, are not eigenstates of spin, i.e. they are spinors $\left(\begin{smallmatrix} \varphi_\uparrow \ (\mathbf{r}) \\ \varphi_\downarrow \ (\mathbf{r}) \end{smallmatrix}\right)$, and in this case a little more care is needed. A choice which satisfies (6) is

$$\hat{K} = i\hat{\sigma}_y\hat{C} \qquad , i\hat{\sigma}_y \equiv \left(\begin{smallmatrix} 0 & 1 \\ -1 & 0 \end{smallmatrix}\right) \tag{8}$$

i.e. explicity,

$$\hat{K}\left(\begin{smallmatrix} \varphi_\uparrow \ (\mathbf{r}) \\ \varphi_\downarrow \ (\mathbf{r}) \end{smallmatrix}\right) \equiv \left(\begin{smallmatrix} \varphi_\downarrow^*(\mathbf{r}) \\ -\varphi_\uparrow^*(\mathbf{r}) \end{smallmatrix}\right) \tag{9}$$

It should be emphasized that $\hat{K}$ is <u>not</u> supposed to act on the localized spins $\boldsymbol{S}_m$, which are regarded as fixed throughout the discussion. Thus,

$$\hat{K}\hat{H}_{mag}\hat{K}^{-1} \ = \ -\hat{H}_{mag} \tag{10}$$

Note also that

$$\varphi_\uparrow(\mathbf{r})\left(\mathbf{K}\varphi(\mathbf{r})\right)_\uparrow \ + \ \varphi_\downarrow(\mathbf{r}) \ \left(\mathbf{K}\varphi(\mathbf{r})\right)_\downarrow \ = \ |\varphi_\uparrow(\mathbf{r})|^{\mathbf{2}} \ + \ |\varphi_\downarrow(\mathbf{r})|^{\mathbf{2}} \tag{11}$$

so that were we to pair in time-reversed states (i.e. construct the state $(\sum_n c_n a_n^+ a_{\bar{n}}^+)^{N/2}|vac\rangle$, where $\bar{n} \equiv Kn$) the value of $F(\mathbf{r},\mathbf{r})$ would be essentially the same as in the nonmagnetic problem, as already mentioned.

Let's start by generalizing the Cooper problem to the case of pair-breaking. We write the single-particle terms in the Hamiltonian in the form

$$\hat{H}_o = \sum_i \hat{H}_o\left(\hat{\mathbf{p}}_i, \hat{\mathbf{r}}_i, \hat{\boldsymbol{\sigma}}_i\right) \tag{12}$$

where

$$\hat{H}_o(\hat{\mathbf{p}}, \hat{\mathbf{r}}, \hat{\boldsymbol{\sigma}}) \equiv \hat{p}^2/2m + U(\hat{\mathbf{r}}) + \hat{H}_{PB} - \mu \tag{13}$$

where $\hat{H}_{PB}$ is a "pair-breaking" term; for example, in the case of magnetic impurities it is given by $\hat{H}_{mag}$ (eqn. (1)). We define the single-particle eigenfunctions φ_n (in general spinors) and eigenvalues ϵ_n by

$$\hat{H}_o(\hat{\mathbf{p}}, \hat{\mathbf{r}}, \hat{\boldsymbol{\sigma}})\varphi_n(\mathbf{r}, \sigma) = \epsilon_n\varphi_n(\mathbf{r}, \sigma) \tag{14}$$

(where σ is the spin projection on the z-axis). We construct the "normal groundstate" of the N-2-particle system in the form

$$\Psi_{N-2} = \prod_{n(\epsilon_n<0)} a_n^+|vac\rangle \tag{15}$$

Now, following Cooper, we consider the "last two" electrons to be excluded from the Fermi sea (i.e. the states occurring in the product (15)) and interacting by the BCS potential

$$V(\mathbf{r}) = -V_o \delta(\mathbf{r}) \tag{16}$$

with a cutoff ϵ_c on the allowed states which is much longer than Δ_o, the value of the binding energy which would have occurred for the original "pure" Cooper problem (i.e. in the absence of pair-breaking). As in the original problem, we seek the condition for the occurrence of a bound state of the last two electrons.

Quite generally, we can write any (allowed) state of the two-particle system in the form

$$\psi\left(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2\right) = \sum_{mn} c_{mn} \cdot 2^{-1/2} \left(\varphi_m(\mathbf{r}_1\sigma_1)\varphi_n(\mathbf{r}_2\sigma_2) - \varphi_m(\mathbf{r}_2\sigma_2)\varphi_n(\mathbf{r}_1\sigma_1)\right) \tag{17a}$$

or in a different and more compact notation (for the whole many-body system)

$$\Psi_N = \sum_{mn} c_{mn} a_m^+ a_n^+ \Psi_{N-2} \tag{17b}$$

with the constraints $0 < (\epsilon_m, \epsilon_n) < \epsilon_c, c_{mn} = -c_{nm}, \sum_{mn} |c_{mn}|^2 = 1$. The single-particle energy of the state (17a) (or (17b)) is evidently

$$\langle H_o \rangle = \sum_{mn} |c_{mn}|^2 \left(\epsilon_m + \epsilon_n\right). \tag{18}$$

What about the potential energy? With the choice (16) of potential its expectation value is given by the expression

$$\langle V \rangle = -V_o \int dr |F(r,r)|^2 \tag{19}$$

where the quantity $F(\mathbf{r},\mathbf{r})$ is given by

$$\begin{aligned} F(\mathbf{r},\mathbf{r}) &\equiv \sum_{\sigma_1\sigma_2} \psi(\mathbf{r}\sigma_1, \mathbf{r}\sigma_2) = \sum_{\sigma} \psi(\mathbf{r}, \sigma, -\mathbf{r}, -\sigma) \\ &= 2^{-1/2} \sum_{mn} \sum_{\sigma} c_{mn} \{\varphi_m(\mathbf{r}\sigma)\varphi_n(\mathbf{r}, -\sigma) - (m \rightleftarrows n)\} \end{aligned} \tag{20}$$

where we used the fact that $\psi(\mathbf{r}, \sigma, \mathbf{r}\sigma) \equiv 0$, by the Pauli principle.

Now, were our objective simply to maximize $|F(\mathbf{r}, \mathbf{r}|^2$ and hence $-\langle V \rangle$, we could simply choose the c_{mn} so that $\sum_n c_{mn}\varphi_n(r, -\sigma) = \hat{K}\varphi_m(r, -\sigma) \equiv \varphi_m^*(\mathbf{r}, \sigma)$; this is essentially tactic (b) above. However, by doing this we would risk paying too high a price in kinetic energy. On the other hand, were we to simply minimize $\langle H \rangle$ using the general form (20) of $F(rr)$, the resulting equation would involve the product of four single-particle wave functions and be very messy. To get around this difficulty we proceed as follows: for any given m in expression (20), write

$$\varphi_n(r,-\sigma) \equiv \langle m|\hat{K}|n\rangle \varphi_m^*(\mathbf{r},\sigma) + \varphi'_n(\mathbf{r},-\sigma) \tag{21}$$

with $\hat{K}$ the time reversal operator as above. Then in view of the randomly oscillating phase of $\varphi'_n(\mathbf{r}-\sigma)$ relative to $\varphi_m(\mathbf{r},\sigma)$ we do not expect any contribution "on average" to $F(r,r)$, which is therefore given (see eqn. (11)) by

$$F(\mathbf{r},\mathbf{r}) = \sum_{mn} c_{mn} K_{mn} \Big| \sum_\sigma \psi_m(\mathbf{r}\sigma)|^2 \quad \Big(K_{mn} \equiv \langle m|\hat{K}|n\rangle\Big) \tag{22}$$

In view of the fact that

$$\int dr \left(\sum_\sigma |\psi_i\,(r\sigma)|^2\right)\left(\sum_\sigma |\psi_j(r\sigma)|^2\right) \cong 1/\Omega \tag{23}$$

($\Omega =$ volume of system) we then find from (22) and (19)

$$\langle V\rangle = -\frac{V_o}{\Omega}\left(\sum_{mn} c_{mn}K_{mn}\right)^2 \tag{24}$$

Combining (18) and (23), subtracting a Lagrange multiplier $-E\sum_{mn}|c_{mn}|^2$ to ensure renormalization and minimizing with respect to c_{mn}, we obtain a Schrödinger equation of the form

$$(\epsilon_m + \epsilon_n - E)c_{mn} = \frac{V_o}{\Omega}K_{mn}\sum_{m'n'} c_{m'n'}K_{m'n'} \tag{25}$$

Then multiplying by K_{mn} and summing both sides over m and n, we finally obtain an implicit eigenvalue equation of the form

$$V_o^{-1} = \Omega^{-1}\sum_{mn}\frac{|K_{mn}|^2}{\epsilon_m + \epsilon_n - E} \tag{26}$$

which in the limit of no pair-breaking (each m associated with $\bar{m}$ such that $K_{m\bar{m}} = \delta_{m\bar{m}}, \epsilon_{\bar{m}} = \epsilon_m$) reduces to the corresponding form in the original Cooper problem, $1 = \Omega^{-1}V_o\sum_k(2\epsilon_k - E_o)^{-1}$ (1.5, p.2), as it of course should.* We can use this fact to eliminate the potential V_o in favor of the eigenvalue E_o of the Cooper problem in the limit of no pair-breaking. In fact, writing

$$\sum_{mn}|K_{mn}|^2\delta(\epsilon_n - \epsilon)\delta(\epsilon_n - \epsilon') \equiv K(\epsilon,\epsilon') \tag{27}$$

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*Note moreover that "option B" would correspond to taking $c_{mn} \propto K_{mn}$ and hence to the replacement of $(\epsilon_m + \epsilon_n)$ in the denominator of (26) by a constant.

we have (with the usual assumption of a nearly constant density of single-particle states near the Fermi energy)

$$\int_o^{\epsilon_c}\int_o^{\epsilon_c} d\epsilon \frac{d\epsilon' K(\epsilon,\epsilon')}{\epsilon+\epsilon'-E} = \int_o^{\epsilon_c} \frac{d\epsilon}{2\epsilon - E_o} \tag{28}$$

which has the advantage that for "reasonable" choice of $K(\epsilon,\epsilon')$ the high-energy cutoff ϵ_c drops out of the problem (see below). It is clear that the effect of the pair-breaking is, qualitatively speaking, to smooth out the singularity which occurs in the integral on the RHS of eqn. (27) in the limit $E_o \to 0$; thus we may anticipate that for any given ϵ_o, strong enough pair-breaking will eliminate the Cooper brand state. To investigate this question quantitatively we of course need to know the explicit form of the function $K(\epsilon,\epsilon')$; if we anticipate the result, to be established below, that for a wide variety of problems this form is

$$K(\epsilon,\epsilon') = \frac{1}{\pi}\ \frac{\Gamma_k}{(\epsilon-\epsilon')^2+\Gamma_k^2} \tag{29}$$

where $\Gamma_K \equiv \hbar/\tau_K$ is the inverse of a "pair-breaking time" τ_K, then (28) can be written in the form (changing the COM variable $\epsilon+\epsilon' \equiv \epsilon$ to 2ϵ)

$$\int_o^{\epsilon_c} \frac{\left(\frac{2}{\pi}\tan^{-1}(2\epsilon/\Gamma_K)\right) d\epsilon}{2\epsilon - E} = \int_o^{\epsilon_c} \frac{d\epsilon}{2\epsilon - E_o} \tag{30}$$

and even without detailed evaluation of the LHS it is clear that $E \to 0$ when Γ_k is of the order of E_o, in agreement with the qualitative considerations explored above.

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Now let us turn to the real many-body problem. We first note that the obvious generalization of the particle-conserving version of the BCS ansatz (eqn. (9) of 1.5), namely (apart from renormalization)

$$\Psi_N = \left(\sum_{mn} c_{mn} a_m^+ a_n^+\right)^{N/2} |\text{vac}\rangle \tag{31}$$

involves some complications, since unlike in the simple BCS case a given single-particle state may occur in more than one term in the sum and we then need to take account of the Pauli principle. However, it turns out that provided we are interested only in the criterion for the instability of the normal state, these complications go away and we are left with what is essentially a straight forward extension of the Cooper problem, the difference with the latter residing mainly in the fact that we need to allow for excitation of pairs of holes as well as pairs of particles. It turns out that to explore this aspect it is advantageous to modify the formalism slightly,[*] and to explain this point I now digress briefly back to the original BCS problem.

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[*] An essentially equivalent approach using the BdG equations is given in deGennes ch.

In the BCS problem the normal groundstate (Fermi sea, $|FS\rangle$) may be written in the form

$$|FS\rangle = \prod_{k<k_F} a^+_{k\uparrow}\ a^+_{-k\downarrow}|\text{vac}\rangle \tag{32}$$

In view of this the particle-nonconserving BCS ansatz, which apart from normalization is

$$\Psi_{\text{BCS}} \ = \ \prod_k (1 + c_k a^+_{k\uparrow}\ a^+_{-k\downarrow})|\text{vac}\rangle \qquad (c_k \equiv v_k/u_k) \tag{33}$$

may be rewritten in the identically equivalent form (again up to normalization)

$$\Psi_{\text{BCS}} \ = \ \prod_{k>k_F} (1 + c_k\ a^+_{k\uparrow}\ a^+_{-k\downarrow}) \ \cdot \ \prod_{k<k_F} (1 + d_k\ a_{-k\downarrow}\ a_{k\uparrow}\ |FS\rangle \tag{34}$$

with $d_k \equiv c_k^{-1} \equiv u_k/v_k$. For pairs in an s-wave state* (34) is just a rewriting of (33) in different notation, and all physical properties predicted by the two forms are identical. Note that if we insert in (34) the standard forms of u_k and v_k for the BCS groundstate, the upper limit on both $|c_k|$ and $|d_k|$ is $2^{-1/2}$.

Now let's return to the case of real interest, that of pair-breaking. In that case the natural way to write the normal groundstate $|FS\rangle$ is

$$|FS\rangle \equiv \prod_{\epsilon_m<0} a^+_m|vac\rangle \tag{35}$$

(though of course it would be possible, by "pairing" the occupied states in an arbitrary way, to write it in a form analogous to (32)). Consider now the (particle-nonconserving) ansatz analogous to (34):

$$\Psi \ = \ \prod_{\epsilon_m,\epsilon_n>0} (1 + c_{mn}\ a^+_m\ a^+_n) \ \cdot \ \prod_{\epsilon_m,\epsilon_n<0} (1 + d_{mn}\ a_n\ a_m)|FS\rangle \tag{36}$$

where we note that there are no terms for which the signs of ϵ_n and ϵ_m are different.† Since we are interested only in the criterion for instability of the normal state, and thus in the limit $|c_{mn}|$, $|d_{mn}| \ll 1$, we may legitimately expand (36) to give

$$\Psi \cong (1 + \sum_{\epsilon_m,\epsilon-n>0} c_{mn}\ a^+_m\ a^+_n) \ \cdot \ (1 + \prod_{\epsilon_m,\epsilon_n<0} d_{mn} a_n a_m) \ \cdot \ |FS\rangle \tag{37}$$

We see that up to bilinear order in the c's and d's the "Pauli-principle" difficulty mentioned above does not affect the results. In fact, let us define the quantity (analogous to F_k in the BCS case)

$$F_{mn} \equiv \langle a_n a_m \rangle \tag{38}$$

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*In the case of $l \neq 0$ pairing the situation is more complicated, see AJL QL, appendix 6A.

†Any such terms would have to be of the form $e_{mn} a^+_m a_n$, and would thus possibly enter the Hartree and Fock terms in the potential energy (already accounted for in the N state) but not the pairing terms.

Then we see that for $\epsilon_m, \epsilon_n > 0$ F_{mn} evaluated for the state (37) is equal to c_{mn} and for $\epsilon_m, \epsilon_n < 0$ to d^*_{mn} (for sgn $\epsilon_m \neq$ sgn ϵ_n F_{mn} is zero). Thus for the (normalized) state (37) the single-particle energy has the form (cf. eqn. (18))

$$\langle H_o \rangle \; = \; \sum_{mn} (|\epsilon_m| + |\epsilon_n|) \; |F_{mn}|^2 \tag{39}$$

As regards the potential energy (or more precisely the pairing contributions thereto) the situation is closely analogous to that which we already met in the Cooper problem; as there, the expression for $\langle V \rangle$ for arbitrary F_{mn} is

$$\langle V \rangle = -V_o \int |F(r, r)|^2 d\mathbf{r} \tag{40}$$

where now $F(\mathbf{r}, \mathbf{r})$ is given by the slightly more general expression

$$F(\mathbf{r}, \mathbf{r}) \equiv \sum_{mn} F_{mn} \varphi_m(\mathbf{r}) \varphi_n(\mathbf{r}) \tag{41}$$

The considerations concerning the optimum choice of the F_{mn} are exactly analogous to those in the Cooper problem, so that we end up with the expression (cf. (24))

$$\langle V \rangle = -V_o |\Psi|^2 \tag{42}$$

$$\Psi \equiv \sum_{mn} \; K_{mn} \; F_{mn} \tag{43}$$

with as above K_{mn} the matrix element of the time-reversal operator $\hat{K}$. Thus, combining (34) and (42), the expectation value of the complete Hamiltonian $\hat{H}$ is

$$\langle \hat{H} \rangle \; = \; \sum_{mn} (|\epsilon_m| + |\epsilon_n|) \; |F_{mn}|^2 \; - \; V_o |\sum_{mn} \; K_{mn} \; F_{mn}|^2 \tag{44}$$

and to find the groundstate we must minimize this with respect to the F_{mn}. However, in doing so we must bear in mind the constraint that $F_{mn} \equiv 0$ when the signs of ϵ_m and ϵ_n are different; to implement this constraint it is convenient to define a quantity

$$\Theta_{mn} \equiv \frac{1}{4} (\text{sgn } \epsilon_m \; + \; \text{sgn } \epsilon_n)^2 \tag{45}$$

and require that $F_{mn} \propto \Theta_{mn}$. If now we define a quantity

$$\Delta \equiv -V_o \Psi \equiv -V_o \sum_{mn} \; K_{mn} \; F_{mn} \tag{46}$$

we find from the minimization that

$$F_{mn} \; = \; \frac{\Delta \cdot K_{mn} \Theta_{mn}}{|\epsilon_m| + |\epsilon_n|} \tag{47}$$

Finally, substituting (47) back into (44), we find that the expectation value $\langle\hat{H}\rangle_\Delta$ of $\hat{H}$ as a function of Δ is given by the expression

$$\langle\hat{H}\rangle_\Delta \;=\; \Delta^2\left(\sum_{mn}\frac{|K_{mn}|^2\Theta_{mn}}{|\epsilon_n|+|\epsilon_m|} \;-\; V_o^{-1}\right) \tag{48}$$

Hence, the criterion for the normal state ($\Delta = 0$) to be unstable against the formation of Cooper pairs is

$$\sum_{mn}\frac{|K_{mn}|^2\Theta_{mn}}{|\epsilon_m|+|\epsilon_n|} \;<\; V_o^{-1} \tag{49}$$

or in terms of the function $K(\epsilon,\epsilon')$ defined by eqn. (27), and assuming as usual that the single-particle density of states near the Fermi energy can be approximated by a constant $N(0)$.

$$\boxed{Q \equiv 2N(0)\int_o^{\epsilon_c} d\epsilon\int_o^{\epsilon_c} d\epsilon'\;\frac{K(\epsilon,\epsilon')}{\epsilon+\epsilon'}\;<V_o^{-1}} \tag{50}$$

We must now discuss the form of the function $K(\epsilon,\epsilon')$, which we recall is defined by (eqn. (27))

$$K(\epsilon,\epsilon') \;\equiv\; \sum_{mn}|K_{mn}|^2\;\delta(\epsilon-\epsilon_n)\;\delta(\epsilon'-\epsilon_m) \tag{51}$$

We first note a general point: since (51) simply describes properties of the single-particle states and the Fermi energy ϵ_F enters only as a reference energy for ϵ, there is no reason for K to depend on the "COM" variable $\epsilon+\epsilon'$; thus we can write it in the form $K(\epsilon,\epsilon') \;=\; K(\omega)$, where $\omega\equiv\epsilon-\epsilon'$ and

$$K(\omega) \;=\; \sum_n |K_{mn}|^2\;\delta(\omega-(\epsilon_n-\epsilon_m) \tag{52}$$

Moreover, since K is antiunitary we must have $\sum_n|K_{mn}|^2 \;=1$, i.e.

$$\int_{-\infty}^{\infty} K(\omega)d\omega \;=\; 1 \tag{53}$$

A convenient way of evaluating the function K(ω) is to relate it to properties of the normal phase which, while they may not be calculable a priori, are known experimentally, and it is often possible to do this. Consider for example the case of magnetic impurities as described by eqn. (1). As regards its effect on single spins (only!)* The time reversal operator $\hat{K}$ can be written in the form

$$\hat{K} = \hat{C}\left(n_c^{-1}\sum_i(i\sigma_{yi})\right) \;=\; 2n_c^{-1}\hat{C}(i\hat{S}_y) \tag{54}$$

where $\hat{C}$ is the operator of complex conjugation and the factor n_c^{-1}, the total number of conduction electrons, is introduced so as to satisfy the antiunitarity condition, and $\hat{S}_y$ is

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*In the general case the sum over i should be replaced by a product.

simply the y-component of the total conduction electron spin. Since for the magnetic-impurity problem $\hat{C}$ commutes with the complete Hamiltonian (including $\hat{H}_{mag}$) and the eigenfunctions can always be chosen real (hence satisfying $\hat{C} = +1$), the matrix elements of $\hat{K}$ are up to an overall constant exactly those of $\hat{S}_y$, as that the quantity $K(\omega)$ is, up to normalization exactly that of the corresponding quantity with $\hat{K}$ replaced by $\hat{S}_y$. But the letter is just the imaginary part of the response function $\chi_{ss}(\omega)$ (autocorrelation function) of $\hat{S}_y$; and since the behavior of $\langle S_y(t)\rangle$ in the magnetic-impurity case is usually very well described by a simple relaxation equation of the form

$$\frac{d\langle S_y(t)\rangle}{dt} = -\frac{\langle S_y\rangle}{\tau_\kappa} \tag{55}$$

with τ_κ a phenomenological relaxation time which can be read off from experiment, it is easy to show that $Im\chi_{ss}(\omega)$ has a simple Lorentzian (Breit-Wigner) form. Thus, taking into account the normalization condition (53), we find that the function $K(\omega)$ is given for the magnetic-impurity case by the simple expression

$$K(\omega) = \frac{1}{\pi}\,\frac{\Gamma_K}{\omega^2+\Gamma_K^2} \quad \text{with } \Gamma_K \equiv \hbar/\tau_s \tag{56}$$

The form (56) is likely to apply more generally in cases when the relaxation of $\hat{K}$ is due to random pair-breaking terms in the Hamiltonian analogous to $\hat{H}_{mag}$, but of course in general Γ_κ is then not inverse to τ_κ and must be found by other methods.

Thus, in any such case the expression for the quantity Q on the LHS of the inequality (50) is

$$Q = 2N(0)\,\frac{1}{\pi}\int_o^{\epsilon_c} d\epsilon \int_o^{\epsilon_c} d\epsilon' \;\frac{\Gamma_K}{(\epsilon-\epsilon')^2 + \Gamma_K^2}\cdot\frac{1}{\epsilon+\epsilon'} \tag{57}$$

Before examining the implications of the zero-temperature result (57), let us generalize it to nonzero temperatures. The simplest way to do this is probably to represent each pair of states m, n or by an Anderson pseudospin subject to a "z-component" of field $\epsilon_m + \epsilon_n$ and a transverse field Δ, which as we are interested only in the instability of the normal phase we shall allow to tend to zero. The quantity Δ must be determined self-consistently by the appropriate generalization of eqns. (46) and (47), with F_{mn} now representing the quantum-mechanical and thermal expectation value of the quantity $a_n a_m$. Thus, eqn. (46) is unchanged. However, in considering (47) we need to bear in mind that the quantum-mechanical expectation value of $a_n a_m$ is zero in the broken-pair states and the negative of its groundstate value in the excited-pair state.; hence the RHS of eqn. (47) should be multiplied by a factor

$$p_{GP} - p_{EP} = (1-n_m)(1-n_n) - n_m n_n = \frac{1}{2}(\tanh\beta|\epsilon_m|/2+\tanh\beta|\epsilon_n|/2) \equiv f(\epsilon_m,\epsilon_n)$$

and the combination of (46) and (47) yields the self-consistent equation for $\Delta \to 0$ of the form

$$\sum_{mn}\frac{|K_{mn}|^2\Theta_{mn}f(\epsilon_m,\epsilon_n)}{|\epsilon_m|+|\epsilon_n|} = V_o^{-1} \tag{58}$$

Proceeding as in the zero-temperature case and eliminating V_0^{-1} in favor of the non-pairbreaking transition temperature $T_{co} \equiv k_B \beta_{c0}^{-1}$, we finally arrive at the fundamental result

$$\frac{1}{\pi}\int_0^{\epsilon_c} d\epsilon \int_0^{\epsilon_c} d\epsilon' \frac{(\tanh(\beta_c\epsilon/2) + \tanh\beta_c\epsilon'/2)}{\epsilon+\epsilon'} \frac{\Gamma_K}{(\epsilon-\epsilon')^2+\Gamma_K^2}$$
$$= \int_0^{\epsilon_c} \frac{(tanh(\beta_{c0}\epsilon/2))d\epsilon}{\epsilon} \qquad (59)$$

In the limit $\Gamma_\kappa \to 0$ the Lorentzian factor reduces to $\pi\delta(\epsilon-\epsilon')$, so the LHS reduces to the RHS if we put $\beta_c = \beta_{c0}$. Also, in the limit $\beta_c \to \infty$ eqn. (59) reduces to the combination of (54) and (57), which using the zero-T nonpairbreaking gap equation can be written

$$\frac{2}{\pi}\int_0^{\epsilon_c} d\epsilon \int_0^{\epsilon_c} d\epsilon' \frac{\Gamma_K^{(c)}}{(\epsilon-\epsilon')^2+\Gamma_K^{2(c)}} \frac{1}{\epsilon+\epsilon'} = ln 2\epsilon_c/\Delta_0 \qquad (60)$$

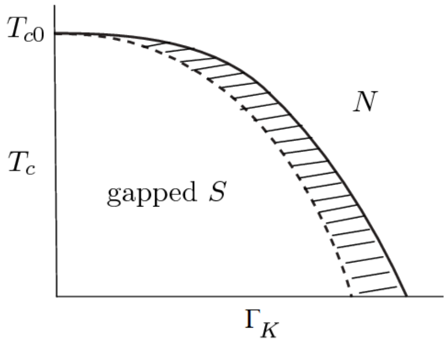
It is evident without detailed evaluation of the RHS of (60) the critical value $\Gamma_K^{(c)}$of Γ_k defined by (60) is some numerical constant times Δ_0, in agreement with our original intuitive argument. More generally, by rescaling the integration variables by a factor of β_{c0} we see that β_{c0}/β_c can be a function only of the ratio Γ_K/Δ_o (or Γ_K/k_BT_{c0})

In the literature it is conventional to write the result (59) in the less intuitive form

$$ln(T_{c0}/T_c) = \psi\left(\frac{1}{2} + \frac{\Gamma_K}{2\pi k_B T_c}\right) - \psi\left(\frac{1}{2}\right) \qquad (61)$$

where $\psi^{(}z)$ is the so-called digamma function $\Gamma'(z)/\Gamma(z)$ (here ($\Gamma(z)$ (no relation to Γ_K!) is the Euler Γ-function). Detailed study of this equation shows that the critical depairing note $\Gamma_K^{(c)}$ for superconductivity to disappear altogether (i.e. $T_c \to 0$) is in fact numerically equal[*] to the nonpairbreaking gap Δ_0.

The general behavior of T_c as a function of Γ_K is as shown. For small impurity concentration the slope is given approximately by $k_{\rm B}(T_{c0} - T_c) \cong R\pi\Gamma/_K$. The region just below the N-S transition temperature which is shaded in the figure is very interesting. As shown by Abrikosov and Gor'kov in their original paper, in this regime that superconductor is gapless, that is, there exist Bogoliubov quasiparticles of arbitrarily low energy. I follow the discussion of de Gennes (Section 8.2):



Consider for definiteness the case $T = 0$, but with a concentration of impurities close to critical; then we may reasonably assume that the "gap" Δ is small, and work as above to lowest order in it. To order $|\Delta|^2$ we have for the energy eigenvalues

$$E_n = |\epsilon_n| + |\Delta|^2 \sum_m \frac{|\langle n|K|m\rangle|^2}{|\epsilon_n| + |\epsilon_m|}, \qquad (62)$$

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[*] This result may be obtained directly from eqn. (60) by integrating over $(\epsilon+\epsilon')$, integrating by parts and noting the easily found result $\int_o^\infty \frac{lnz}{1+z^2}dz = 0$

If the one-electron part of the Hamiltonian is invariant under time reversal, then the only state m occuring in the sum is degenerate with ϵ_n, so that

$$E_n = |\epsilon_n| + |\Delta|^2/(2|\epsilon_n|) \tag{63}$$

This is the beginning of an expansion in $\Delta/|\epsilon_n|$: it clearly works for $|\epsilon_n| \to \infty$ but fails for $|\epsilon_n| \to 0$. If the system is not invariant under K, then the second term is not singular as $|\epsilon_n| \to 0$ and the perturbation theory may work. We can write

$$E_n = |\epsilon_n| + |\Delta|^2 \int d\epsilon' \operatorname{Im} \chi_K(\epsilon_n - \epsilon')/(\epsilon_n + \epsilon') \tag{64}$$

Suppose in particular K is proportional to χ_{ss} and thus relaxes exponentially to zero with time constant $\tau_K = \Gamma_K^{-1}$, then

$$E_n = |\epsilon_n| + |\Delta|^2 \int d\epsilon' \frac{\Gamma_K}{(\epsilon_n - \epsilon'|)^2 + \Gamma_K^2} \tag{65}$$

$$= |\epsilon_n| + \frac{|\Delta|^2\,|\epsilon_n|}{\epsilon_n^2 + (\Gamma_K^2)}$$

If now we take $|\epsilon_n| \ll \Gamma_K$, this tends to

$$E_n = |\epsilon_n|(1 + \frac{1}{2}(\Delta/\Gamma_K)^2) \tag{66}$$

which can be arbitrarily small. The density of states is

$$N_s(\epsilon) = N(0)d\epsilon/dE \cong \left\{1 + \frac{1}{2}\Delta^2 \frac{\epsilon^2 - (\Gamma_K^2)}{\epsilon^2 + (\Gamma_K^2)^2}\right\} \tag{67}$$

so for $\epsilon < \Gamma_K$ is less than the N-state value but for $\epsilon > \hbar/\Gamma_K$ greater. [cf. de Gennes Fig. 8.5.]

The above considerations work for most kinds of pair-breaking effects. However, we should always bear in mind that solutions we have obtained are at most variational ansätze, and we cannot exclude that there may exist other solutions which as it were differ by a finite amount from the simple perturbation-theoretic ones. As an example, consider the case of a constant finite Zeeman field (assumed to act only on the spins and not on the orbital degrees of freedom). We could follow through the above calculation, but now the spectrum of $\hat{S}_y$ and thus of $\hat{K}$ is a δ-function at $\epsilon - \epsilon' = 2\mu_B\mathcal{H}$, the energy necessary to flip a spin. Correspondingly, the zero-T linearized gap equation becomes

$$(N(0)V_0)^{-1} = \int_0^{\epsilon_c} \frac{d\epsilon}{\epsilon + \mu_B\mathcal{H}} \cong \ln(\epsilon_c/\mu_B\mathcal{H}) \tag{68}$$

(where in the last equality we assume ϵ_c is large). The zero-field $T = 0$ gap Δ satisfies the relation

$$(N(0)V_0)^{-1} = \int_0^{\epsilon_c} \frac{d\epsilon}{\sqrt{\epsilon^2 + \Delta^2}} \cong \ln(2\epsilon_c/\Delta) \tag{69}$$

and thus the critical field at $T = 0$ should apparently be given by $\mu_{\mathrm{B}}\mathcal{H} = \Delta/2$.

However, this conclusion is not correct. To see this, let us compare the energies of the normal state in field $\mathcal{H}$, and the paired state obtained by refusing to let the particles polarize in the field and then proceeding as if in field 0. Relative to the normal state in zero field, the first has energy $-(1/2)\mu_B^2\mathcal{H}^2(dn/d\epsilon) = -\mu_B^2\mathcal{H}^2 N(0)$, while the second has energy (cf. Lecture 6) $-(1/2)\Delta^2 N(0)$. Thus the second is stable for $\mu_{\mathrm{B}}\mathcal{H} < \Delta/\sqrt{2}$, i.e. beyond the limit $\Delta/2$ given by the perturbation calculation. The latter is actually the limit of metastability of the N phase, i.e. the "supercooling" field; cf. Maki and Tsuneto, Prog. Theor. Phys. 21, **945** (1964). It is an interesting question whether a similar situation could ever occur in the magnetic-impurity case.

(A further complication: FFLO state).