# General Derivation for Spin Paramagnetic Susceptibility of Electrons in a Superconductor*

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Using the Green's-function formulation, we obtain a general expression for the spin paramagnetic susceptibility of electrons in a superconductor, $\chi_s = (1-\rho_s'/\rho)\chi_n$, where $\chi_n$ is the spin paramagnetic susceptibility of electrons in the normal state and $\rho_s'$ is a pseudosuperelectron density. The result with $\rho_s'$ replaced by the superelectron density is sufficiently general to apply to cases of strong coupling, to superconductors with magnetic and nonmagnetic impurities, and to type-II superconductors. We find a finite spin paramagnetic susceptibility at zero temperature for a pure strong-coupling superconductor. For impure superconductors, the result agrees very well with the results found in the Knight shift experiments.

The main purpose of this paper is to derive a general expression for the spin paramagnetic susceptibility of electrons in a superconductor, using the Green's-function formulation.

Since the theory of Bardeen, Cooper, and Schrieffer[1] (BCS) for a superconductor is based on the pairing of electrons with opposite momentum and spin, the total spin of the system in the ground state ($T=0$) is zero and the spin paramagnetic susceptibility vanishes.[2] The latest experiment[3] on superconducting Al agrees with the BCS theory, but the experiments on superconducting Sn, Pb, and Hg have indicated that the spin paramagnetic susceptibility for these superconductors[4,5] is finite at zero temperature. Many explanations for this finite spin paramagnetic susceptibility have been proposed,[6] and for the case of weak coupling, Abrikosov and Gor'kov[7] were able to show that the spin-orbit interaction leads to a finite value of the spin paramagnetic susceptibility at zero temperature.

We have used the Green's-function formulation to derive a general expression for the spin paramagnetic susceptibility of electrons in a superconductor,

$$\chi_s = (1-\rho_s'/\rho)\chi_n \ , \qquad (1)$$

where $\chi_n$ is the spin paramagnetic susceptibility of electrons in the normal state and $\rho_s'$ is a pseudosuperelectron density. We show that $\rho_s'$ can be replaced by the superelectron density for a pure strong-coupling superconductor, and for a superconductor with magnetic and nonmagnetic impurities $\rho_s'$ is identical with the superelectron density in the special case where the spin-flip and ordinary scatterings are equal. For type-II superconductors, we argue that $\rho_s'$ may be replaced by the superelectron density.

To derive Eq. (1) we consider a small magnetic disturbance $\delta B(\vec{r})$ at the point $\vec{r}$; the interaction associated with this disturbance is given by

$$\int d\vec{r}\, \vec{\mu}(\vec{r}) \cdot \delta\vec{B}(\vec{r}) \ , \qquad (2)$$

where $\vec{\mu}(\vec{r})$ is the spin magnetic moment of the electrons at the point $\vec{r}$. We can write the spin magnetic moment in terms of the electron-wave field operators $\psi_\sigma^\dagger(\vec{r})$ and $\psi_\sigma(\vec{r})$:

$$\vec{\mu}(\vec{r}) = \mu_B[\psi_\uparrow^\dagger(\vec{r})\psi_\uparrow(\vec{r}) - \psi_\downarrow^\dagger(\vec{r})\psi_\downarrow(\vec{r})] \ , \qquad (3)$$

where $\mu_B$ is the Bohr magneton. It is convenient to write the above in the Nambu spinor notation[8]

$$\Psi = \begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow^\dagger \end{pmatrix} \text{ and } \Psi^\dagger = (\psi_\uparrow^\dagger, \psi_\downarrow) \ . \qquad (4)$$

Then the interaction energy becomes

$$\mu_B \int d\vec{r}\, \Psi^\dagger(\vec{r})\Psi(\vec{r})\delta B(\vec{r}) \ , \qquad (5)$$

where we neglect a constant term which does not affect the final result. The induced magnetization associated with $\delta B$ is given by

$$M_s(\vec{r},t) = \mu_B^2 \int dx' \langle [\Psi^\dagger(x)\Psi(x), \Psi^\dagger(x')\Psi(x')]\rangle \delta B(x') \ , \qquad (6)$$

where $x=(\vec{r},t)$. By taking the Fourier transform of Eq. (6), we may write the spin paramagnetic susceptibility of the electrons at temperature $T$ as

$$\chi_s(T) = \lim \mathrm{Tr} \textstyle\sum_k mG(k+q)MG(k) \quad \text{as} \quad q\to 0 \ , \qquad (7)$$

where $k=(\vec{k},k_0)$, $q=(\vec{q},q_0)$, and $G$ is the $2\times 2$ matrix Green's function[9]

$$G^{-1}(k) = Z(k)[k_0\tau_0 - \Delta(k)\tau_1] - \epsilon_k\tau_3 \ . \qquad (8)$$

Here we denote the Pauli matrices by $\tau_i$; the wave-function renormalization factor $Z(k)$, gap parameter $\Delta(k)$, and renormalized quasiparticle energy $\epsilon_k$ are solutions of the integral equations given in Ref. 9, $M$ is the usual dressed $2\times 2$ vertex matrix function, and $m$ is the bare vertex function, $m=\mu_B\tau_0$.

For a weak-coupling superconductor with magnetic and nonmagnetic impurities, after averaging over the impurities and performing the angular integration, we can write the integral equation for $M$ as[9,10]

$$M = m + (\Gamma - \Gamma_s) i \int \frac{d\epsilon_k}{\pi} \tau_3 G(k) M G(k) \tau_3 , \qquad (9)$$

where $2\Gamma$ and $2\Gamma_s$ are the inverse of the relaxation times due to the ordinary and spin-flip scatterings, respectively. We have used the fact that at low temperatures only the electrons near the Fermi surface play an important role in the calculation of the properties of the system, and the vertex function $M$ is assumed to depend only on $\omega$. Inserting the representation of the vertex function

$$M = \mu_B (M_0 \tau_0 + M_1 \tau_1 + M_2 \tau_2 + M_3 \tau_3) \qquad (10)$$

into Eq. (9), we find

$$M_0 = [1 - (\Gamma - \Gamma_s) B]/D ,$$
$$M_1 = (\Gamma - \Gamma_s) C/D , \qquad (11)$$

and

$$M_2 = M_2 = 0 ,$$

where

$$D = 1 - (\Gamma - \Gamma_s)(A + B) + (\Gamma - \Gamma_s)^2 (AB - C^2)$$
$$= [(\omega_n^2 + \Delta_n^2)^{1/2} + 2\Gamma_s]/Z_n ,$$
$$A = \int \frac{d\epsilon_k}{2\pi} \mathrm{Tr} \tau_0 G(k) \tau_0 G(k) = \frac{\Delta_n^2}{R_n} ,$$
$$B = \int \frac{d\epsilon_k}{2\pi} \mathrm{Tr} \tau_1 G(k) \tau_1 G(k) = \frac{\omega_n^2}{R_n} , \qquad (12)$$
$$C = \int \frac{d\epsilon_k}{2\pi} \mathrm{Tr} \tau_0 G(k) \tau_1 G(k) = \frac{\omega_n \Delta_n}{R_n} ,$$
$$R_n = (\omega_n^2 + \Delta_n^2)^{3/2} Z_n ,$$
$$Z_n = 1 + (\Gamma + \Gamma_s)/(\omega_n^2 + \Delta_n^2)^{1/2} ,$$

and

$$\Delta_n = \Delta - 2\Gamma_s/(\omega_n^2 + \Delta_n^2)^{1/2} .$$

The integrals were performed by using the Green's function (8) with $k_0 = \omega = i\omega_n = (2n+1)\pi T$, and $Z(k)$ and $\Delta(k)$ are assumed to be functions of only $\omega$, i.e., $Z_n = Z(i\omega_n)$ and $\Delta_n = \Delta(i\omega_n)$. The gap parameter $\Delta$ is the solution of the integral equation[9]

$$\Delta = N(0) V_{\mathrm{BCS}} \int d\omega \, (\tanh \omega/2T) \, \mathrm{Re}\{\Delta / [\Omega^2(\omega) - \Delta^2]^{1/2}\} , \qquad (13)$$

where $N(0)$ is the density of states of one spin at the Fermi surface, $V_{\mathrm{BCS}}$ is the BCS coupling constant, and $\Omega$ is the solution of

$$\Omega(\omega) = \omega + i 2\Gamma_s \Omega(\omega) / [\Omega^2(\omega) - \Delta^2]^{1/2} , \qquad (14)$$

so $\Delta$ depends on the depairing parameter $\Gamma_s$ and the temperature.

Inserting the $M$ into Eq. (7), we obtain the spin paramagnetic susceptibility as

$$\chi_s = \chi_n (1 - \rho_s'/\rho) , \qquad (15)$$

where[11]

$$\rho_s'/\rho = \sum_n 2\pi T \Delta_n^2 / [(\omega_n^2 + \Delta_n^2)^{3/2} + (\omega_n^2 + \Delta_n^2) 2\Gamma_s] . \qquad (16)$$

In Eq. (5.36) of Ref. 9 we calculated the superelectron density $\rho_s(\Gamma_s, \Gamma)/\rho$ for an impure superconductor, and comparing that result with Eq. (16), we see that Eq. (16) is just the expression for the superelectron density when $\Gamma_s = \Gamma$, i.e., $\rho_s(\Gamma_s, \Gamma_s) = \rho_s'(\Gamma_s)$. We note that it has not been necessary to make any assumption about the relative size of $\Gamma$ and $\Gamma_s$ in order to obtain Eq. (15). At zero temperature we can evaluate the sum in Eq. (16) [see Eq. (5.41) in Ref. 9] and the spin paramagnetic susceptibility becomes

$$\chi_s = \chi_n [\tfrac{3}{8} x (\tfrac{1}{2}\pi - \tan^{-1} x_0) + x_0 (\tfrac{5}{8} - \tfrac{1}{4} x^{-2})/x] , \qquad (17)$$

where $x_0 = \theta(x-1)(x^2-1)^{1/2}$ and $x$ is the solution of

$$x = \frac{2\Gamma_s}{\Delta(\Gamma_s, 0)} = \frac{\pi \xi_0}{l_s} [x_0 + (1 + x_0^2)^{1/2}] \exp\left[\frac{x}{2}\left(\frac{\pi}{2} - \tan^{-1} x_0\right) - \frac{x_0}{2x}\right] . \qquad (18)$$

Here $\theta(x-1)$ is the usual step function, 1 for $x > 1$ and zero otherwise, $\xi_0$ and $l_s$ are the BCS coherence length and the mean free path due to the spin-flip scattering.

We note that from Eqs. (13) and (18) in the limit of $2\Gamma_s \to \frac{1}{2}\Delta(0,0) = \frac{1}{2}\Delta_{\mathrm{BCS}}$, the gap parameter $\Delta(\Gamma_s, 0)$ vanishes; i.e., the system becomes the normal state. For $0.456 < 2\Gamma_s/\Delta(0,0) < 0.5$ or $1 \leq x \leq \infty$, the effective energy gap vanishes and we have gapless superconductivity where excitations of arbitrarily low energy are allowed.[9,10] In fact, from Eq. (17) for $x = 1$ we obtain $\chi_s = 0.59 \chi_n$, and for $x = 2$, $\chi_s = 0.88 \chi_n$, and this is the range of the experimental results.[4,5,12]

If we approximate $\Delta_n = \Delta$ and set $2\Gamma_s = 2/3\tau_{so}$, where $\tau_{so}$ is the relaxation time due to the spin-orbit interaction, Eq. (16) reduces to the result found by Abrikosov and Gor'kov,[7] who needed to assume $\Gamma \gg \Gamma_s$ in contrast to our derivation. Setting $2\Gamma_s = 0$ in Eq. (16), we obtain the result found by Yosida[2] for a pure weak-coupling superconductor.

In the case of a pure strong-coupling superconductor, the vertex correction resulting from the electron-phonon interaction is of the order of the square root of the electron and ion mass ratio, $(m_e/M_i)^{1/2}$, and can be neglected.[13] Then we may write Eq. (7) as

$$\chi_s(T) = \mu_B^2 \lim \sum_k \mathrm{Tr}\, G(k+q)G(k) \quad \text{as} \quad q \to 0 \ . \tag{19}$$

There are some difficulties in the limiting processes $q_0 \to 0$ and $\vec{q} \to 0$. To avoid these difficulties it is convenient to write the difference between the susceptibilities in the superconducting and normal states:

$$\frac{\chi_s - \chi_n}{\chi_n} = \tfrac{1}{2} N(0)^{-1} \lim_{q\to 0} \mathrm{Tr} \sum_k [G(k+q)G(k) - (GG)_n] \ , \tag{20}$$

where $(GG)_n$ is the value of $GG$ in the normal state. The right-hand side of Eq. (20) is just the expression for the superelectron density in a superconductor. To see this, we consider the induced current density $\vec{J}$ associated with the vector potential $\vec{A}$ and find[9]

$$\begin{aligned} J_\mu(q=0) &= e^2 \lim_{q\to 0} \mathrm{Tr} \sum_k [\gamma_\mu G(k+q)\Gamma_\nu G(k) - (\gamma_\mu G \Gamma_\nu G)_n] A_\nu(q) \\ &= \tfrac{1}{2}[N(0)\Lambda]^{-1} \lim_{q\to 0} \mathrm{Tr} \sum_k [G(k+q)G(k) - (GG)_n] A_\mu(q) = -(\rho_s/\rho)\Lambda^{-1} A_\mu(q=0) \ , \end{aligned} \tag{21}$$

where $\Lambda$ is the London parameter. Combining Eqs. (20) and (21), we obtain Eq. (1) with $\rho_s' = \rho_s$. For a pure strong-coupling superconductor such as Pb, the depletion of the superelectron density[14] is about 22 to 25%, and we expect a finite spin paramagnetic susceptibility at zero temperature.

For a type-II superconductor, we may write[15] the superelectron density in terms of the pair wave function $\Psi$:

$$\frac{\rho_s}{\rho} = \langle |\Psi|^2 \rangle = \frac{2\kappa^2}{(2\kappa^2 - 1)\beta}\left(1 - \frac{H}{H_{c2}}\right) \ , \tag{22}$$

where $\kappa$ is the Ginzburg-Landau parameter[16] ($\kappa > 2^{1/2}$) and

$$\beta = \langle |\Psi|^4 \rangle / \langle |\Psi|^2 \rangle^2 \ .$$

The numerical value of $\beta$ is 1.16 for a triangular lattice[17] structure of flux lines and 1.18 for a square lattice structure of flux lines in a superconductor. $H$ and $H_{c2}$ are the effective and the second critical magnetic fields, respectively. If we set $\rho_s' = \rho_s$ in Eq. (15), then the spin paramagnetic susceptibility in a type-II superconductor at the magnetic field near $H_{c2}$ would be[18]

$$\chi_s/\chi_n = H/H_{c2} \ . \tag{23}$$

The right-hand side of Eq. (23) is proportional to the number of flux lines in a superconductor, which is a result that one obtains by consideration of the bound states in a superconductor.[19] It is desirable to check Eq. (23) experimentally. We note that this is the same form as the resistivity due to flux lines in a type-II superconductor.[20]

In conclusion, the depletion of the superelectron density yields a finite value of the spin paramagnetic susceptibility of electrons in a superconductor at zero temperature. The depairing scattering may give the major contribution to the depletion of the superelectron density, but it is not required in order to obtain a finite value of the spin paramagnetic susceptibility at zero temperature. The depletion of the superelectron density can be caused by strong-coupling effects as well.

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[12]The results of Refs. 4 and 5 can be explained without recourse to the parameter $y$ introduced in Ref. 5. Additionally, it appears to the present author that the large depairing parameter $\rho_0 = 2\Gamma_s/\Delta(0,0)$ used in Ref. 5 is inconsistent with the fact that the depairing parameter $2\Gamma_s/\Delta(0,0)$ should be less than 0.5 for a superconductor. However, the parameter $x = 2\Gamma_s/\Delta(\Gamma_s, 0)$

can take any value from zero to infinity, and an independent experimental determination of this parameter $x$, i.e., the gap parameter $\Delta(\Gamma_s, 0)$, is desirable to verify the present theory.

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# Phonon Generation and Detection in Superconducting Lead Diodes

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We present a detailed experimental study of the behavior of Pb-Pb superconducting diodes in phonon generation and detection. It is shown that the detection process occurs via pair breaking as well as phonon-assisted tunneling. The present experimental results do not resolve the distribution in energy of the phonons emitted by the generator. However, the derivative of the detected signal with respect to the generator current contains well-defined structure coincident with the phonon density of states of Pb calculated by McMillan and Rowell.

## I. INTRODUCTION

Superconducting tunnel diodes have been successfully used[1] as phonon generators and detectors. Since then we set as our goal the experimental determination of at least the coarse features of the generated phonon spectrum for various levels of excitation and an understanding of the mechanisms responsible for the detection process. This information is essential if such a device is to be used for studying propagation and absorption of phonons in solids or in liquid helium in a frequency range not attainable by conventional ultrasonic devices.

We use superconductor-barrier-superconductor tunnel diodes evaporated on two parallel faces of a sapphire single crystal ~1 cm long and 1 cm diameter. The diode area is $0.1\times0.1$ cm and the film thickness is $\sim 1.5\times10^{-5}$ cm. To the diode used as phonon generator, we apply pulses of amplitude $V > 2\Delta$, where $2\Delta$ is the energy gap of the superconductor and $V$ is in electron volts. The excited quasiparticles produced by tunneling relax and recombine emitting phonons.[2,3] The relaxation produces phonons of energy $\omega$ in the range $0<\omega<V-2\Delta$ while the recombination into Cooper pairs produces phonons of $\omega \gtrsim 2\Delta$. Some of the generated phonons propagate in the sapphire crystal in rectilinear trajectories to the detecting diode. Coincident with the time of arrival of the phonons, a voltage pulse $S$ is measured across the detector which is biased at a voltage $V_B < 2\Delta$ from a dc constant-current source. The major contribution to the signal $S$ comes from those incident phonons of $\omega \geq 2\Delta$.[1] Such phonons break Cooper pairs in the detector resulting in an increase in the quasiparticle population above the gap edge, and hence an enhancement in the tunneling current at $V_B < 2\Delta$. Using this simple model for phonon generation and detection, an adequate interpretation was obtained for previously published results.[1] In the following paragraphs we discuss some details of the electron-phonon and electron-electron interactions relevant to phonon generation in superconducting tunnel diodes.

First we discuss the decay thresholds and their effects on the generated phonon spectrum. Excited particles of energy $E\sim\Delta$ will either directly recombine in pairs emitting phonons of energy $\omega \geq 2\Delta$ or first individually decay to the top of the gap emitting relaxation phonons with $\omega = E-\Delta$ and then recombine in pairs emitting phonons with $\omega = 2\Delta$. Since at $E = \Delta$ the group velocity of an excited quasiparticle is zero, the threshold[2,3] $E_d$ for the relaxation process is given by $(E_d-\Delta) \geq 8 v_s^2 v_F^{-2}\Delta$ where $v_s$ is the sound velocity and $v_F$ is the electron velocity at the Fermi level. This threshold is of the order of $2\times10^{-5}\Delta$ for the longitudinal and $0.26\times10^{-5}\Delta$ for the transverse phonons in Pb. Ignoring gap anisotropy, the recombination phonons are emitted in an extremely