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Magnetic impurities in superconductors: A theory with different predictions

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The proclivity of paramagnetic solutes to degrade the transition temperature of a traditional singlet-pairing superconductor is studied anew. T_c degradation is proportional to the (conduction electron) spin-disorder scattering rate, $1/\tau_s$, caused by the solute spins. Accordingly the T_c loss increases with solute concentration. The initial slope (versus $1/\tau_s$) is found to depend on the superconductor and therefore is not the universal constant proposed by Abrikosov and Gor'kov. Instead the decrease is inversely proportional to λ, the electron-phonon coupling constant. Consequently a weak superconductor is doubly jeopardized by paramagnetic impurities: Its superconductivity is easily suppressed not only because T_c is small to begin with, but also because the initial slope is steeper. Another unexpected consequence of the theory involves potential scattering which, acting alone, does not significantly influence T_c (as surmised by Anderson). Nevertheless, the T_c reduction caused by exchange scattering will be partially suppressed when the overall mean free path becomes smaller than the coherence length. This compensation has been demonstrated experimentally by comparing the influence of magnetic impurities in a pure host superconductor with that in a similar host having (also) nonmagnetic solutes. Such observed recovery of T_c, expected from this study, contradicts prior theories for magnetic solutes.

I. INTRODUCTION

During an investigation[1] of the theory of impure superconductors we found that prior treatments needed modification. For nonmagnetic impurities T_c is insensitive to the solute fraction c. This conclusion, proposed by Anderson,[2] was apparently confirmed by the work of Abrikosov and Gor'kov[3] (AG), who studied both exchange scattering and potential scattering. A power series can be used to express the dependence of T_c on c:

$$T_c = T_{c0} + ac + bc^2 + \cdots , \tag{1}$$

where T_{c0} is the transition temperature of the pure host. Both previous theories alleged that, for *nonmagnetic* solutes, $a \approx 0$, $b \approx 0$, etc. However, we found that the only probable conclusion is $a \approx 0$. As long as c is not too large, Anderson's theorem remains intact. Furthermore, we noticed an unallowed mathematical approximation in AG's theory and found that their method (when corrected) actually leads to large negative values for the coefficient a. (Such values are contradicted by experiment as well as by Anderson's theorem.) So it appears that the AG method is *fundamentally* unsound.

The foregoing discernment indicates that the effect of exchange scattering by paramagnetic impurities needs to be reexamined. Although it is well known[4] that paramagnetic solutes cause the coefficient a of Eq. (1) to have a large negative value, quantitative comparison between theory and experiment is thwarted by unknown microscopic parameters, e.g., the exchange parameter J. In view of the foregoing uncertainties, the response of a superconductor to the presence of magnetic impurities is once again a theoretical frontier.

The present study, which is carried out within the original framework of BCS theory,[5] leads to conclusions which contradict the extensive theoretical literature spanning more than 30 years. Therefore, it is necessary to motivate strongly our approach and to call forth intuitions which may perhaps not be known to some workers.

The influence of impurities on T_c can be complex (for many reasons); so it is traditional to embrace a number of simplifications in order that a tractable theory ensues.

(i) The conduction band has a constant density of states, N_0 per spin, and has a width $2E_F$ (i.e., electron-hole symmetry).

(ii) The superconducting gap parameter Δ of the host superconductor is isotropic in **k** space.

(iii) The Fröhlich pairing interaction,[6] $V(\mathbf{k},\mathbf{k}')$, is a constant, $-V$, independent of $\mathbf{q}=\mathbf{k}'-\mathbf{k}$.

(iv) The weak-coupling version of BCS theory may be used; i.e., $\lambda \equiv N_0 V < 1$.

(v) Solute additions alter neither the band structure, the phonon spectrum, nor the electron-phonon interaction.

(vi) The Coulomb repulsion between electrons is neglected; i.e., μ and μ^* are set to zero.

(vii) The magnetic interaction between a conduction electron at $\mathbf{r}$ (having spin $\mathbf{s}$) and a magnetic solute (having spin $\mathbf{S}$), randomly located at $\mathbf{R}_i$, is

$$H_m = J\mathbf{s}\cdot\mathbf{S}_i v_o \delta(\mathbf{r}-\mathbf{R}_i) , \tag{2}$$

where $\mathbf{s}=\frac{1}{2}\boldsymbol{\sigma}$ and v_0 is the atomic volume. We will refer to scattering (real or virtual) caused by H_m as exchange scattering. (The exchange constant J has the dimension of energy. The three components of $\boldsymbol{\sigma}$ are the Pauli matrices.)

(viii) The paramagnetic spins $\{\mathbf{S}_i\}$ have *fixed* orientations, which are *randomly* directed in 4π solid angle. Accordingly, when a conduction-electron spin is rotated during scattering events, the directions of $\{\mathbf{S}_i\}$ remain unchanged. ($\mathbf{S}_i\cdot\mathbf{S}_j$ interactions are consequently irrelevant.)

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Almost all workers have used this classical, fixed-$\mathbf{S}_i$ model, having imitated AG in this regard, as was noted by Jensen and Suhl.[7] A more correct model is, of course, to treat $\mathbf{S}_i$ dynamically, each spin having $2S+1$ magnetic sublevels; so that when a conduction electron suffers a spin flip, $\mathbf{S}_i$ undergoes an appropriate transition between its magnetic sublevels. We have carried out the theory for *both* models and, although the results are different, the relation between them is not complex and will be reported in Sec. VIII. Of course, when $|\mathbf{S}|^2$ appears in the fixed-spin theory, it will be replaced by $S(S+1)$. (The difference between the two models is deeper and more significant than this standard, trivial substitution.)

For simplicity we choose to present here the theory having fixed spins, a motivation apparently persuasive for most authors. Consider the alternative: A Cooper pair, as well as a BCS condensate, arises from the *coherent* coupling between eigenstate pairs. For a sample having N magnetic solutes, there are $Z=(2S+1)^N$ magnetic eigenstates $\{\chi_j\}$. Coherent coupling occurs between one eigenstate pair, $\phi_m(\mathbf{r}_1,\mathbf{r}_2)\chi_i$, and another, $\phi_n(\mathbf{r}_1,\mathbf{r}_2)\chi_j$, only if $i=j$. The appropriate formalism involves a $Z\times Z$ density matrix, since H_m causes off-diagonal matrix elements to arise. Had AG employed the dynamical-spin model, their Eq. (2) would have had to involve $2Z^2$ coupled equations instead of only 2. (ϕ_m and ϕ_n are four-component electron functions on account of the spin degrees of freedom for the electrons at $\mathbf{r}_1$, and $\mathbf{r}_2$.) Obviously the fixed spin model is *much* simpler. Exchange scattering does not then destroy quantum coherence.

In the normal (electronic) state, the effect of the magnetic Hamiltonian, Eq. (2), is to cause spin-disorder scattering. From golden-rule scattering theory, the spin-disorder scattering rate of a conduction electron (including spin-flip and nonflip events) is

$$\frac{1}{\tau_s}=\frac{\pi J^2 S(S+1)N_0 c_m}{2n\hbar}\ , \tag{3}$$

where n is the number of atoms per cm^3, i.e., $nv_0=1$, and c_m is the magnetic solute fraction. This relation is useful because it allows final results to be expressed in terms of the one (unknown) parameter τ_s, instead of the two (or three) unknowns on the right-hand side of Eq. (3). Finally, we stipulate our intention to develop a theory involving effects only to order $c_m J^2$. Suggestions that alternative theories are valid to higher powers of c_m are without merit because, as we shall show, the alternatives fail even in first order.

II. INSIGHTS FOR SPIN-DEPENDENT SCATTERING

Spin-flip virtual scattering of conduction electrons can be expected to influence superconductivity because a BCS condensation, based on the simplified, phonon-mediated Fröhlich interaction, (iii) above, requires singlet pairing. The coherent matrix elements which would arise if triplet basis pairs $(\mathbf{k}\uparrow,-\mathbf{k}\uparrow)$ were chosen would be zero: Each direct element, e.g., to $(\mathbf{k}'\uparrow,-\mathbf{k}'\uparrow)$, is canceled by an exchange term. For conventional $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ basis pairs, the exchange terms vanish. One should remember that the Slater determinant of a $(\mathbf{k}\uparrow,-\mathbf{k}\downarrow)$ basis pair is 50% singlet and 50% triplet. Pure singlet character ensues only after a properly phased, equal-amplitude superposition with the $(-\mathbf{k}\uparrow,\mathbf{k}\downarrow)$ basis determinant is incorporated.

Spin-flip *virtual* scattering by magnetic solutes will cause the pure-singlet superposition, just mentioned, to be contaminated with a triplet component; and this admixture weakens the coherent pairing matrix elements: Not only is the direct matrix element smaller, but the (newly acquired) exchange term cancels part of the remaining reduced value. These features will be shown in detail below.

It is of interest to consider also spin-flip virtual scattering that arises from spin-orbit coupling with *nonmagnetic* impurities. It is already known[8] that this effect does not reduce T_c, even though the direct matrix elements are also reduced. Remarkably, the exchange terms which arise cancel exactly the reductions. The purpose of this section is to provide intuitive understanding of these phenomena and to see why they are so different. We will need the spin-orbit interaction for reference:

$$H_{\rm so}=\frac{\mu_B}{2mc}\sigma\cdot(\mathbf{E}\times\mathbf{p})\ , \tag{4}$$

where μ_B is the Bohr magneton, $\mathbf{p}$ is the conduction-electron momentum operator, and $\mathbf{E}$ is the electric field arising from impurity potentials.

One-electron wave functions are two-component, Pauli spinors. We will choose the time-reversal operator to be

$$T=\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}K\ , \tag{5}$$

where K is complex conjugation. The usual presentation of BCS theory employs basis pairs:

$$\left\{e^{i\mathbf{k}\cdot\mathbf{r}_1}\begin{bmatrix}1\\0\end{bmatrix}_1, e^{-i\mathbf{k}\cdot\mathbf{r}_2}\begin{bmatrix}0\\1\end{bmatrix}_2\right\}. \tag{6}$$

(The second function is always T times the first.) We shall now prove two lemmas which will be useful in due course.

A. Lemma I

BCS theory is unchanged if every pair, (6), has its own ("private") axis of spin quantization. Instead of (6), one can use

$$\left\{e^{i\mathbf{k}\cdot\mathbf{r}_1}\begin{bmatrix}\alpha(\mathbf{k})\\ \beta(\mathbf{k})\end{bmatrix}_1,\ e^{-i\mathbf{k}\cdot\mathbf{r}_2}\begin{bmatrix}-\beta^*(\mathbf{k})\\ \alpha^*(\mathbf{k})\end{bmatrix}_2\right\}, \tag{7}$$

where α and β are arbitrary (even pathological) functions of $\mathbf{k}$, subject only to $|\alpha|^2+|\beta|^2=1$, and to the requirement that (α,β) be the same for $\mathbf{k}$ and $-\mathbf{k}$. (This last condition preserves orthogonality.) Proof of the lemma requires that the matrix element of the Fröhlich interaction between the pair (7) and any other pair

$$\left\{e^{i\mathbf{k}'\cdot\mathbf{r}_1}\begin{bmatrix}\alpha'\\ \beta'\end{bmatrix}_1,\ e^{-i\mathbf{k}'\cdot\mathbf{r}_2}\begin{bmatrix}-\beta'^*\\ \alpha'^*\end{bmatrix}_2\right\}, \tag{8}$$

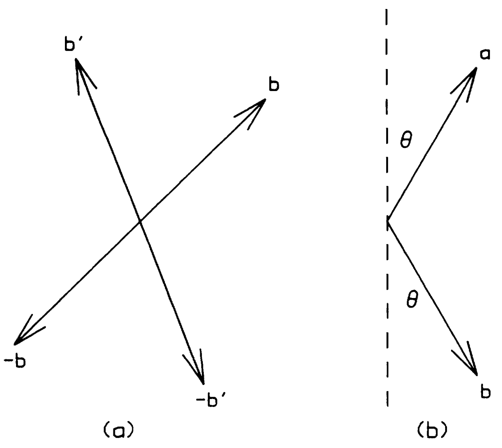

FIG. 1. (a) Two different axes of spin quantization for basis pairs $(\mathbf{k},\hat{b};-\mathbf{k},-\hat{b})$ and $(\mathbf{k}',\hat{b}';-\mathbf{k}',-\hat{b}')$. (b) Canted spins for a basis pair $(\mathbf{k},\hat{a};-\mathbf{k},\hat{b})$.

still equals $-V$ regardless of α' and β'. Assumption (iii) of Sec. I is equivalent to an attractive potential, $-V\delta(\mathbf{r}_1-\mathbf{r}_2)$; so that all that remains after the (6-dim) spatial integration is a direct term,

$$-V(\alpha'^*\alpha+\beta'^*\beta)(\alpha'\alpha^*+\beta'\beta^*)\ , \tag{9}$$

and an exchange term,

$$V(\beta'^*\alpha^*-\alpha'^*\beta^*)(\alpha'\beta-\beta'\alpha)\ . \tag{10}$$

The sum of (9) and (10) is

$$-V(|\alpha|^2+|\beta|^2)\times(|\alpha'|^2+|\beta'|^2)=-V\ . \tag{11}$$

Figure 1(a) illustrates this lemma. The spin directions, $\pm\hat{b}$ and $\pm\hat{b}'$, for the basis pairs, $\{\mathbf{k},\hat{b};\ -\mathbf{k},-\hat{b}\}$ and $\{\mathbf{k}',\hat{b}';-\mathbf{k}',-\hat{b}'\}$, can be completely different. Nevertheless, the phonon-mediated coupling which connects such basis pairs when forming a BCS condensate is still $-V$.

B. Lemma II

Canted basis pairs are states, $\{\mathbf{k},\hat{a};-\mathbf{k},\hat{b}\}$, for which $\hat{a}$ and $\hat{b}$ are not antiparallel. The axis of a canted pair, shown by the dashed line in Fig. 1(b), lies in the plane of $\hat{a}$ and $\hat{b}$ and is perpendicular to the direction which bisects the angle between $\hat{a}$ and $\hat{b}$. The canting angle θ is the angle between $\hat{a}$ and the axis. (θ is also the angle between $\hat{b}$ and the axis.) Lemma II states that the matrix element of the (simplified) Fröhlich interaction between canted pairs, one with canting angle θ and the other with θ' (generally having different axes) is

$$M_{\mathrm{cp}}=-V\cos\theta\cos\theta'\ . \tag{12}$$

Note that M_{cp} does not depend on the axis directions. In this respect, lemma II exhibits the feature of lemma I.

Proof of the lemma requires calculation of the (simplified) Fröhlich-interaction matrix element connecting an arbitrary canted basis pair $(\mathbf{k},\hat{a};-\mathbf{k},\hat{b})$,

$$\left\{ e^{i\mathbf{k}\cdot\mathbf{r}_1}\begin{bmatrix}\alpha\\ \beta\end{bmatrix}_1,\ e^{-i\mathbf{k}\cdot\mathbf{r}_2}\begin{bmatrix}\gamma\\ \delta\end{bmatrix}_2\right\}, \tag{13}$$

to another one. There is no loss of generality if we select the axis of the final pair to be along $\hat{z}$ and the canting direction along $\hat{x}$, i.e., for a canting angle θ',

$$\left\{ e^{i\mathbf{k}'\cdot\mathbf{r}_1}\begin{bmatrix}\cos\theta'/2\\ \sin\theta'/2\end{bmatrix}_1,\ e^{-i\mathbf{k}'\cdot\mathbf{r}_2}\begin{bmatrix}\sin\theta'/2\\ \cos\theta'/2\end{bmatrix}_2\right\}. \tag{14}$$

After the (6-dim) spatial integration, the required canted-pair matrix element, M_{cp}, between the two Slater determinants generates a direct term,

$$-V\left[\alpha\cos\frac{\theta'}{2}+\beta\sin\frac{\theta'}{2}\right]\times\left[\gamma\sin\frac{\theta'}{2}+\delta\cos\frac{\theta'}{2}\right], \tag{15}$$

and an exchange term,

$$V\left[\gamma\cos\frac{\theta'}{2}+\delta\sin\frac{\theta'}{2}\right]\times\left[\alpha\sin\frac{\theta'}{2}+\beta\cos\frac{\theta'}{2}\right]. \tag{16}$$

The sum of (15) and (16) is

$$M_{\mathrm{cp}}=-V(\alpha\delta-\beta\gamma)\cos\theta'\ . \tag{17}$$

Now the canting angle θ for the pair (13) is half the angle between $\hat{a}$ and $-\hat{b}$. Accordingly,

$$\cos^2\theta=\frac{1}{2}+\frac{1}{2}\left\langle\begin{bmatrix}\alpha\\ \beta\end{bmatrix}\middle|\sigma\middle|\begin{bmatrix}\alpha\\ \beta\end{bmatrix}\right\rangle\left\langle\begin{bmatrix}-\delta^*\\ \gamma^*\end{bmatrix}\middle|\sigma\middle|\begin{bmatrix}-\delta^*\\ \gamma^*\end{bmatrix}\right\rangle, \tag{18}$$

which after evaluation is

$$\cos^2\theta=|\alpha\delta-\beta\gamma|^2\ . \tag{19}$$

Consequently, on comparing (17) and (19),

$$M_{\mathrm{cp}}=-Ve^{i\phi}\cos\theta\cos\theta'\ . \tag{20}$$

If $\phi\neq0$, the phase of the $\hat{a}$ spinor in (13) can be redefined with a factor, $\exp(-i\phi)$, and then Eq. (20) reverts to Eq. (12). (Such phase adjustments can always be made so that $\alpha\delta-\beta\gamma$ is real and positive for every canted pair.)

The fact that M_{cp}, Eq. (12), is the product of $\cos\theta$ and $\cos\theta'$ is particularly noteworthy. For example, in the theory of superconductivity for a metal having a spiral spin-density wave (SDW),[9] this factorization permits an exact solution of the BCS gap equation. The canting angle θ is near zero for most of the Fermi surface, but rises to 90° for $\mathbf{k}$ states at the SDW energy gap. The triplet fraction of a canted pair $(\mathbf{k},\hat{a};-\mathbf{k},\hat{b})$, after being coherently combined with $(-\mathbf{k},-\hat{b};\mathbf{k},-\hat{a})$, is $\sin^2\theta$. The BCS gap parameter Δ becomes zero wherever (on the Fermi surface) $\theta=90°$, i.e., at the SDW energy gap. Therefore a SDW metal must exhibit zero-gap superconductivity.

C. Virtual scattering by spin-orbit potentials

Consider a conduction-electron wave function subject to a spin-orbit scattering interaction, Eq. (4), from a highly localized, isotropic potential centered at $\mathbf{r}=0$. A straightforward, but tedious exercise in perturbation theory leads to the following wave function for the first member of a basis pair:

$$\Psi'_{\mathbf{k}\uparrow} \cong N\left\{ e^{i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}1\\0\end{bmatrix} + g n_1(kr)\left[(\hat{k}\times\hat{r})_z\begin{bmatrix}1\\0\end{bmatrix} + [(\hat{k}\times\hat{r})_x + i(\hat{k}\times\hat{r})_y]\begin{bmatrix}0\\1\end{bmatrix}\right]\right\}, \tag{21}$$

where g is a real scattering amplitude, $n_1(\rho)$ is the spherical ($l=1$) Neumann function[10] (which is also real), and N is a normalizing factor. The hats designate unit vectors. We emphasize that the Neumann function must appear instead of a (complex) spherical Hankel function. (Basis functions in solids must satisfy the requirement, which is often ignored, that the boundary integral of the current be zero.) The basis partner of Eq. (21) is, from perturbation theory

$$\Psi'_{-\mathbf{k}\downarrow} \cong N\left\{ e^{-i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}0\\1\end{bmatrix} + g n_1(kr)\left[(\hat{k}\times\hat{r})_z\begin{bmatrix}0\\1\end{bmatrix} - [(\hat{k}\times\hat{r})_x - i(\hat{k}\times\hat{r})_y]\begin{bmatrix}1\\0\end{bmatrix}\right]\right\}. \tag{22}$$

Now, it is important to notice that Eq. (22) can be obtained directly from Eq. (21) by using the time-reversal operator, Eq. (5):

$$\Psi'_{-\mathbf{k}\downarrow} = T\Psi'_{\mathbf{k}\uparrow} . \tag{23}$$

This relation could have been anticipated since T commutes with the Hamiltonian, including the spin-orbit term, Eq. (4). Clearly, the relation (23) would still obtain for a general spin-orbit scattering potential, not necessarily highly localized nor isotropic.

Since, at any particular position $\mathbf{r}$, the spin of an electron is 100% polarized in some direction, one can calculate the polarization axis for (21) and (22) versus $\mathbf{r}$. The important result is that, at each point, the polarization directions of (21) and (22) are exactly opposite. This result follows from (23), since for an arbitrary spinor

$$\left\langle T\begin{bmatrix}\alpha\\\beta\end{bmatrix}\middle|\begin{bmatrix}\alpha\\\beta\end{bmatrix}\right\rangle = 0 ; \tag{24}$$

and two spinors are orthogonal if and only if they are antiparallel.

The final result should now be apparent. Spin-orbit scattering tilts the axis of spin quantization for a basis pair, and the tilted axis varies (in direction) from point to point. Generally at any $\mathbf{r}$, the axes of different basis pairs will differ. However, lemma I encompasses these variations, so the phonon-mediated interaction which connects basis pairs remains $-V$. T_c is not affected by spin-orbit scattering. The earlier proof of this result by Appel and Overhauser[8] was based on an analysis equivalent to lemma I and Eq. (23).

D. Virtual scattering by a magnetic solute

Consider next the wave functions of a basis pair which have been perturbed by the exchange potential, Eq. (2), caused by a magnetic impurity at $\mathbf{R}=0$. Let the direction of the (fixed) local-spin $\mathbf{S}$ be specified by a polar angle χ and an azimuthal angle ϕ. For the first member of the pair,

$$\Psi'_{\mathbf{k}\uparrow} \cong N\left\{ e^{i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}1\\0\end{bmatrix} + \frac{Jv_0mk\bar{S}}{4\pi\hbar^2}n_0(kr) \times\left[\cos\chi\begin{bmatrix}1\\0\end{bmatrix} + \sin\chi e^{i\phi}\begin{bmatrix}0\\1\end{bmatrix}\right]\right\}, \tag{25}$$

where $n_0(\rho)$ is the spherical ($l=0$) Neumann function,[10] and $\bar{S}=[S(S+1)]^{1/2}$. The wave function of the basis partner is

$$\Psi'_{-\mathbf{k}\downarrow} \cong N\left\{ e^{-i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}0\\1\end{bmatrix} - \frac{Jv_0mk\bar{S}}{4\pi\hbar^2}n_0(kr) \times\left[\cos\chi\begin{bmatrix}0\\1\end{bmatrix} - \sin\chi e^{-i\phi}\begin{bmatrix}1\\0\end{bmatrix}\right]\right\}. \tag{26}$$

It is obvious that, in this case, (26) is not T times (25). At each position $\mathbf{r}$, the polarization directions of (25) and (26) are no longer antiparallel. The spins of the basis pair are *canted,* and the canting angle θ is to first order in J,

$$\theta \approx \frac{Jv_0mk\bar{S}}{2\pi\hbar^2}n_0(kr) , \tag{27}$$

provided $\theta \ll 1$. The easiest way to derive this result is to take advantage of lemma I by choosing the $\hat{z}$ axis perpendicular to the solute spin $\mathbf{S}$. Then $\chi=90°$, and Eq. (27) follows by using (25) and (26) to obtain the Pauli spinors (at a given $\mathbf{r}$) to use in Eq. (18). The canting angle varies from point to point. Accordingly from lemma II, Eq. (12), the phonon-mediated interaction will have matrix elements given by the spatial average:

$$M_{\mathrm{cp}} = -V\langle \cos\theta(\mathbf{r})\cos\theta'(\mathbf{r})\rangle_{\mathrm{av}} . \tag{28}$$

T_c will therefore be reduced. The precise meaning of $\langle\ \rangle_{\mathrm{av}}$ will be given in Sec. IV. This result, derived here for a single magnetic solute, will be extended to the case of a finite atomic fraction c_m of solute spins in Sec. III.

The summary of this section is as follows: Spin-orbit scattering causes the spin-quantization axes of the basis pairs to *tilt.* The direction and magnitude of the tilt depend on $\mathbf{r}$ and $\mathbf{k}$. Despite these variations, lemma I shows that T_c is unaffected. Exchange scattering by magnetic solutes causes the spin polarizations of each basis pair to become *canted.* Lemma II shows that the coherent coupling between canted basis pairs is reduced, as given by Eq. (28). Consequently T_c suffers a decrease. Even though a BCS condensation utilizes singlet pairing, the exchange scattering *forces* the condensate to have a triplet contamination. This triplet fraction dilutes the pair correlation engendered by pure singlet pairing and weakens the matrix elements of the phonon-mediated attraction.

III. EIGENSTATES WITH EXCHANGE SCATTERING

As already emphasized at the end of Sec. I, we intend to include the effects of exchange scattering only to order $c_m J^2$. Two different approaches appear possible: The first method starts with a BCS condensate for the pure (superconducting) host and then employs perturbation theory to find the way exchange scattering modifies the ground and excited states. The second method begins with the normal-state basis functions and incorporates into each basis function the *virtual* admixtures caused by the magnetic interactions. *Subsequently,* the condensate is allowed to form.

It might seem at first sight that the two approaches would be equivalent. But they are not. The fundamental reason why virtual scattering and BCS condensation do not commute is that the condensation is nonperturbative; it is a nonanalytic response to the electron-phonon coupling. The BCS condensation involves diagonalization within a manifold having an approximately degenerate basis set. The BCS truncation of the manifold to within $\hbar\omega_D$ of the Fermi energy (which recognizes the retarded nature of the Fröhlich interaction) applies to the new (perturbed) basis states and not to the (original) pure-host states. This consideration is the foundation of Anderson's method.[2] The intuitive understanding of this mandate follows from the large disparity ($\sim$ three orders of magnitude) between the scattering potential within a solute's atomic cell and the binding energy of a Cooper pair. The solute potentials dominate, so the condensation process must utilize the (perturbed) basis states that are newly in force, irrespective of the size of the solute fraction c_m.

One should note that assignment of the BCS condensation to a more passive role need not always be appropriate, e.g., if the perturbation is weak and slowly varying when compared to the binding energy and size of a Cooper pair. Low-frequency electromagnetic response of a superconductor exemplifies such an exception.

It is important to prove that the two theoretical approaches described above lead to contradictory conclusions. Fortunately the published literature provides the needed analysis. The first comprehensive study of both magnetic and nonmagnetic scattering on T_c was the work of Suhl and Matthias (SM).[11] SM's theory utilized the first method described above; i.e., the BCS condensed state (for the *pure* host) was subjected to perturbation by the impurities. For nonmagnetic impurities, an exponential decrease of T_c with $1/\tau$, the impurity scattering rate, was found. See SM's Fig. 3 and Eq. (38). Subsequently Anderson's theory[2] appeared and was soon confirmed by many experiments. Thus it became clear that the theoretical *method* of SM was faulty.

Abrikosov and Gor'kov[3] (AG) treated magnetic and potential scattering simultaneously. Interestingly, their well-known result for magnetic impurities (which also included potential terms):

$$k_B(\Delta T_c) = -\pi\hbar/4\tau_s \ , \tag{29}$$

is identical to that obtained (for exchange scattering only) by SM, Eq. (29) of Ref. 11. (Only an inconsequential difference, 3.5 instead of 4 in the denominator, can be found.) The apparent acceptance of AG's theory and rejection of SM's can be attributed to the absence of a potential-scattering contribution to Eq. (29). However we have shown[1] that a very large exponential decrease of T_c, caused by potential scattering (equivalent to the decrease found by SM), is also present in AG's theory: See Eq. (25) of Ref. 1. AG "removed" the offending behavior (without notifying the reader) by an *unallowed* alteration of integration limits. The SM and AG theories for ΔT_c are essentially equivalent; so both formalisms are contradicted by the experimental verification of Anderson's predictions.

Some workers have indeed noticed that a contribution to ΔT_c from potential scattering, proportional to $1/\tau$, is missing from AG's final expression. However, the enormity of the omission which, when corrected, would reduce T_c by 98% for 1% Ag or Au in Pb has apparently not been emphasized. There is no "hidden term" that can cancel such a decrease, so the theoretical method itself must be rejected. Other workers have tried to remove the offending term by transferring the BCS cutoff from the electron energy spectrum to a limitation on a sum over Matsubara temperatures, $(2n+1)\pi T_c$. There is no theoretical basis for such an artifice and, in any case, a correct ΔT_c for magnetic impurities does not emerge.

It would be dangerous indeed to suppose that the SM and AG result for exchange scattering could be valid when their methods fail so dramatically with mere potential scattering. Consequently, we now pursue a theory for magnetic scattering which incorporates exchange scattering in the normal-state basis, so as to obtain a valid manifold to treat a BCS condensation. Exchange coefficients J are typically ~ 0.1 eV, two orders of magnitude larger than the binding energy of a Cooper pair. Consequently this perturbed basis-state method *must* be utilized.

The basis states for the pure metal will be plane waves with spin up or down: α or β. They will be normalized in a volume Ω, which we keep explicit because, surprisingly, Ω will become a relevant parameter. The perturbed basis state which carries the *label* $\mathbf{k}\alpha$ is

$$\Psi_{\mathbf{k}\alpha} = N_{\mathbf{k}}\Omega^{-1/2}\left[e^{i\mathbf{k}\cdot\mathbf{r}}\alpha + \sum_{\mathbf{q}} e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}(W_{\mathbf{kq}}\beta + W'_{\mathbf{kq}}\alpha)\right] , \tag{30}$$

where, from the interaction (2),

$$W_{\mathbf{kq}}=\frac{(1/2)J\bar{S}v_0\Omega^{-1}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}}}\sum_j \sin\chi_j e^{i\phi_j-i\mathbf{q}\cdot\mathbf{R}_j} , \tag{31}$$

and

$$W'_{\mathbf{kq}}=\frac{(1/2)J\bar{S}v_0\Omega^{-1}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}}}\sum_j \cos\chi_j e^{-i\mathbf{q}\cdot\mathbf{R}_j} . \tag{32}$$

χ_j and ϕ_j are the polar and azimuthal angles of the spin $\mathbf{S}_j$ at $\mathbf{R}_j$, and the ϵ's are the electron energies of the host. The perturbed basis state for the degenerate partner of (30) is

$$\Psi_{-\mathbf{k}\beta}=N_{\mathbf{k}}\Omega^{-1/2}\left[e^{-i\mathbf{k}\cdot\mathbf{r}}\beta + \sum_{\mathbf{q}} e^{-i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}(W^*_{\mathbf{kq}}\alpha-W'^*_{\mathbf{kq}}\beta)\right] . \tag{33}$$

Equations (30)–(33) are formal only, until we cope with the singularities that appear in (31), (32), and especially in the normalizing factors $N_{\mathbf{k}}$. The states (30) and (33), which are partners in forming a BCS condensate, are degenerate because we have assumed in (viii), Sec. I that the spins $\{\mathbf{S}_j\}$ are randomly directed throughout 4π solid angle. It may be noted that (30) and (33) are the generalizations of (25) and (26) which account for all the spins $\{\mathbf{S}_j\}$ and which represent the virtual admixtures in the momentum representation.

IV. WEAKENING OF THE PHONON-MEDIATED MATRIX ELEMENTS BY VIRTUAL EXCHANGE SCATTERING

The matrix elements which cause Cooper pairing will necessarily be between *perturbed* basis pairs $(\Psi_{\mathbf{k}\alpha},\Psi_{-\mathbf{k}\beta})$ and $(\Psi_{\mathbf{k}'\alpha},\Psi_{-\mathbf{k}'\beta})$, defined by Eqs. (30)–(33). Each basis pair is, of course, a 2×2 Slater determinant. (It is important to keep in mind that the $\mathbf{k}\alpha,-\mathbf{k}\beta$ subscripts are merely labels; and that the one-electron wave functions so indicated have other spin and momentum components, as expressed by W and W'.) The computation of modified matrix elements connecting Slater-determinant pairs is sufficiently complex that we shall divide the analysis into several parts. The treatment here will be perturbative and formal. Apparent divergences will be resolved in Sec. V.

A. Virtual mixing from the *xy* component of H_m

Consider Eq. (30), but without the term involving $W'_{\mathbf{kq}}$, caused by the z component of H_m, Eq. (2). The wave function is (of course) a two-component spinor

$$\Psi_{\mathbf{k}\alpha}\approx N_k\Omega^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}1\\ \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}W_{\mathbf{kq}}\end{bmatrix} . \tag{34}$$

It is convenient to rewrite this function in terms of a normalized spinor $\hat{s}_\theta(\mathbf{r})$, which is tilted by $\theta(\mathbf{r})$ from the $\hat{z}$ axis. Accordingly,

$$\Psi_{\mathbf{k}\alpha}\approx\mathcal{N}_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\hat{s}_\theta(\mathbf{r}) , \tag{35}$$

where

$$\mathcal{N}_{\mathbf{k}}(\mathbf{r})\equiv N_{\mathbf{k}}\Omega^{-1/2}n_{\mathbf{k}}(\mathbf{r})^{-1} , \tag{36}$$

and $n_{\mathbf{k}}(\mathbf{r})$ is the normalizing factor for $\hat{s}_\theta(\mathbf{r})$:

$$n_{\mathbf{k}}(\mathbf{r})=(1+|\overline{W}|^2)^{-1/2} , \tag{37}$$

with

$$\overline{W}(\mathbf{r})\equiv\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}W_{\mathbf{kq}} . \tag{38}$$

The canting angle $\theta(\mathbf{r})$ of the unit spinor $\hat{s}_\theta(\mathbf{r})$, relative to $\hat{z}$ can be shown, using spinors such as as Eq. (14) and the $\cos\frac{1}{2}\theta$ identity, to be

$$\cos\theta(\mathbf{r})=\frac{1-|\overline{W}|^2}{1+|\overline{W}|^2} . \tag{39}$$

The degenerate partner of (34) is obtained in a similar fashion from Eq. (33):

$$\Psi_{-\mathbf{k}\beta}\approx N_{\mathbf{k}}\Omega^{-1/2}e^{-i\mathbf{k}\cdot\mathbf{r}}\begin{bmatrix}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{r}}W^*_{\mathbf{kq}}\\ 1\end{bmatrix} . \tag{40}$$

With similar definitions, (36)–(39), this perturbed state can be written

$$\Psi_{-\mathbf{k}\beta}\approx\mathcal{N}_{\mathbf{k}}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{s}_{\pi-\theta}(\mathbf{r}) , \tag{41}$$

for which the unit spinor is canted now from $-\hat{z}$ by the same angle, $\theta(\mathbf{r})$, as shown in Fig. 1(b).

A Cooper pair is synthesized from Slater determinants of partners such as (35) and (41):

$$\mathcal{D}_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{2}}\begin{vmatrix}\Psi_{\mathbf{k}\alpha}(\mathbf{r}_1) & \Psi_{\mathbf{k}\alpha}(\mathbf{r}_2)\\ \Psi_{-\mathbf{k}\beta}(\mathbf{r}_1) & \Psi_{-\mathbf{k}\beta}(\mathbf{r}_2)\end{vmatrix} . \tag{42}$$

When one employs assumption (iii) of Sec. I, the phonon-mediated interaction is equivalent to $-V\delta(\mathbf{r}_1-\mathbf{r}_2)$. Accordingly, the relevant behavior of the determinant (42) is $\mathcal{D}_{\mathbf{k}}(\mathbf{r},\mathbf{r})$. It is a straightforward exercise to show from Eqs. (35), (41), and (42) that

$$\mathcal{D}_{\mathbf{k}}(\mathbf{r},\mathbf{r})=\mathcal{N}_{\mathbf{k}}(\mathbf{r})^2\cos\theta(\mathbf{r})\left[\frac{1}{\sqrt{2}}(\alpha_1\beta_2-\beta_1\alpha_2)\right] . \tag{43}$$

In other words, $\cos\theta(\mathbf{r})$ is the relative *singlet amplitude* of the basis pair when both electrons are near $\mathbf{r}$. The $\mathbf{r}$ dependence of $\mathcal{N}_{\mathbf{k}}(\mathbf{r})^2$ reflects only the variation in electron density from point to point introduced by the heterogeneous impurity distribution. The *imputed* triplet amplitude, $\sin\theta(\mathbf{r})$, cannot be similarly derived because the exclusion principle prevents parallel-spin electrons from being at the same $\mathbf{r}$. (The triplet amplitude is inherently a *nonlocal* two-electron operator.) Nevertheless, the sum of the squares of the two amplitudes must be unity. (The triplet amplitude has of course three components; but we ignore such details here.)

The matrix element $V_{\mathbf{k}'\mathbf{k}}$ of the (simplified) Fröhlich interaction between two perturbed basis determinants is, after the first integration utilizing the δ function

$$V_{\mathbf{k}'\mathbf{k}} = -V \int \mathcal{D}^*_{\mathbf{k}'}(\mathbf{r},\mathbf{r}) \mathcal{D}_{\mathbf{k}}(\mathbf{r},\mathbf{r}) d^3r \ , \tag{44}$$

which reduces immediately, on using Eq. (43), to

$$V_{\mathbf{k}',\mathbf{k}} = -V \int \cos\theta_{\mathbf{k}'}(\mathbf{r}) \cos\theta_{\mathbf{k}}(\mathbf{r}) \mathcal{N}_{\mathbf{k}'}(\mathbf{r})^2 \mathcal{N}_{\mathbf{k}}(\mathbf{r})^2 d^3r \ . \tag{45}$$

$V_{\mathbf{k}'\mathbf{k}}$ depends explicitly on the impurity locations in view of Eqs. (31) and (36)–(39). It is of course convenient to take an impurity average at this point. Whereupon

$$\overline{V_{\mathbf{k}'\mathbf{k}}}^{\mathrm{imp}} = -V\Omega^{-1} \langle \overline{\cos\theta_{\mathbf{k}'}(\mathbf{r})}^{\mathrm{imp}} \overline{\cos\theta_{\mathbf{k}}(\mathbf{r})}^{\mathrm{imp}} \rangle_{\mathrm{av}} \ . \tag{46}$$

The angular brackets indicate a spatial average. Factorization of the impurity averages in (46) is justified by our neglect of terms which are of higher order than J^2. Equation (46) indicates the promised interpretation of Eq. (28), for which Ω had been taken to be unity.

B. Virtual mixing from the z component of H_m

Treatment of virtual mixing arising from the z component of the magnetic interaction proceeds in a fashion similar to that given above. The first wave function of a basis pair is, after inspecting Eq. (30),

$$\Psi'_{\mathbf{k}\alpha} \approx N'_{\mathbf{k}} \Omega^{-1/2} e^{i\mathbf{k}\cdot\mathbf{r}} \alpha \left[1 + \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} W'_{\mathbf{k}\mathbf{q}} \right] , \tag{47}$$

where $W'_{\mathbf{k}\mathbf{q}}$ is defined by Eq. (32). The degenerate partner is, from the terms involving β in Eq. (33),

$$\Psi'_{-\mathbf{k}\beta} \approx N'_{\mathbf{k}} \Omega^{-1/2} e^{-i\mathbf{k}\cdot\mathbf{r}} \beta \left[1 - \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{r}} W'^*_{\mathbf{k}\mathbf{q}} \right] . \tag{48}$$

The Slater determinant of this basis pair is easily evaluated when both electrons are at $\mathbf{r}$:

$$\mathcal{D}'_{\mathbf{k}}(\mathbf{r},\mathbf{r}) = N'^2_{\mathbf{k}} \Omega^{-1} \left[\frac{1}{\sqrt{2}} (\alpha_1\beta_2 - \beta_1\alpha_2) \right] F_{\mathbf{k}}(\mathbf{r}) , \tag{49}$$

where

$$F_{\mathbf{k}}(\mathbf{r}) = \left[1 + \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} W'_{\mathbf{k}\mathbf{q}} \right] \left[1 - \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{r}} W'^*_{\mathbf{k}\mathbf{q}} \right] . \tag{50}$$

If we define $\overline{W'}$

$$\overline{W'} \equiv \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} W'_{\mathbf{k}\mathbf{q}} \ , \tag{51}$$

then

$$F_{\mathbf{k}}(\mathbf{r}) = 1 - |\overline{W'}|^2 + \text{cross terms} \ . \tag{52}$$

We will argue in Appendix A that the cross terms can be neglected; so if we tentatively discard them, and note that

$$N'^2_{\mathbf{k}} = [1 + \langle |\overline{W'}|^2 \rangle_{\mathrm{av}}]^{-1} , \tag{53}$$

the singlet amplitude is reduced (from its value for a pure superconductor) by

$$\mathcal{F}_s(\mathbf{r}) = \frac{1 - |\overline{W'}|^2}{1 + \langle |\overline{W'}|^2 \rangle_{\mathrm{av}}} \ . \tag{54}$$

Observe that this amplitude reduction has the same form, Eq. (39), as that caused by spin canting in the $\hat{x}\hat{y}$ plane.

The minus sign in the numerator of Eqs. (39) and (54) is the noteworthy feature of exchange scattering. For nonmagnetic impurities the sign is positive. In this latter case, the numerator and denominator cancel; whereupon Anderson's theorem for dirty superconductors follows immediately.

When the impurity averages of $|\overline{W}|^2$ and $|\overline{W'}|^2$ are taken, it is clear from Eqs. (31) and (32) that the mean reduction in singlet amplitude from the z components of H_m will be half that caused by the xy canting components. (The average of $\sin^2\chi_j$ is $\frac{2}{3}$, whereas the average of $\cos^2\chi_j$ is $\frac{1}{3}$.) That is to say, the three Cartesian components of H_m contribute equally to the weakening of the phonon-mediated interaction. This result had to emerge, given the isotropy of the fixed-spin model.

C. Weakened phonon-mediated matrix element

In view of the foregoing observations, one can express the total pair-scattering matrix element, using Eq. (46) and the preceding subsection

$$\overline{V_{\mathbf{k}'\mathbf{k}}}^{\mathrm{imp}} \cong -\frac{V}{\Omega} \left[1 - 2Z_i \sum_{\mathbf{q}} \frac{[(1/2)J\bar{S}v_0\Omega^{-1}]^2}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}})^2} - 2Z_i \sum_{\mathbf{q}} \frac{[(1/2)J\bar{S}v_0\Omega^{-1}]^2}{(\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}'+\mathbf{q}})^2} \right] . \tag{55}$$

We have assumed that $|\overline{W}|^2$ is small enough so that a first-order expansion of the denominators in Eqs. (39) and (54) is allowed, thus accounting for the factors of 2. Z_i is the number of magnetic impurities in the volume Ω. The magnetic-impurity-spin polar-angle factors have summed to unity, as discussed above. (The J^2 contributions from subsections A and B are additive.)

It is necessary to emphasize that Eq. (55) is a formal result only. The integrations (sums) over $\mathbf{q}$ are divergent. This difficulty is common to perturbation treatments of virtual scattering. The remedy is to replace the formal terms in Eq. (55) by their accurate counterparts derived from a partial-wave analysis of the virtual scattering. This treatment is presented in Sec. V. It turns out that after this analysis is complete, a divergence involving the impurity sum remains. This difficulty is a deep one, and is overcome only by recognizing that the theory is relevant to a bound state, and that the bound-state radius provides the needed cutoff.

The physical interpretation of Eq. (55) should nevertheless be clear. Paramagnetic virtual scattering causes the singlet fraction of each determinantal basis pair to be reduced. The triplet fraction is correspondingly increased. When the phonon-mediated interaction is approximated by $-V\delta(\mathbf{r}_1 - \mathbf{r}_2)$, only the singlet fraction of each basis pair contributes to $V_{\mathbf{k}'\mathbf{k}}$. Reduction of T_c is therefore caused by the exchange-scattering-induced triplet contamination of each determinantal basis pair used to synthesize the BCS condensed state.

A BCS condensate (at $T=0$) is a stationary state, so it and its Cooper-pair components are time independent. It is not correct to say that the pairs are broken (or are being broken) by the $\mathbf{s}\cdot\mathbf{S}_i$ interactions of Eq. (2). The pairs merely have a diminished binding energy caused by the $\mathbf{s}\cdot\mathbf{S}_i$-enforced triplet contamination. The coherent amplitude of the condensate is reduced, but each basis pair remains as a component of the BCS wave function.

V. T_c REDUCTION FROM EXCHANGE SCATTERING ONLY

In the previous section we showed that the coherent matrix element, $V_{\mathbf{k}'\mathbf{k}}$, between 2×2 Slater determinants of perturbed basis pairs can be written,

$$V_{\mathbf{k}'\mathbf{k}} = -V\Omega^{-1}\langle\cos\Theta_{\mathbf{k}'}(\mathbf{r})\rangle\langle\cos\Theta_{\mathbf{k}}(\mathbf{r})\rangle \ , \tag{56}$$

where the brackets indicate both a spatial and impurity average. The indicated factorization is justified from Eq. (55) because terms of order J^4 are intentionally neglected. The canting angles, $\Theta_{\mathbf{k}}(\mathbf{r})$, in Eq. (56) include the canting action caused by all components of the spin Hamiltonian H_m (including the z component). It is possible to show that the reduction in singlet amplitude from the z components, given by Eq. (54), corresponds to a canting (of otherwise antiparallel spins) along the $\hat{z}$ direction. Accordingly, from Eqs. (39) and (54)

$$\langle\cos\Theta_{\mathbf{k}}(\mathbf{r})\rangle \cong 1-2|W_{\mathbf{k}}|^2 \ , \tag{57}$$

where $|W_{\mathbf{k}}|^2$ is the relative probability contained in the virtual spherical waves surrounding the magnetic solutes (compared to the plane-wave part).

In order to compute $|W_{\mathbf{k}}|^2$ we return to Eq. (25), where the virtual exchange scattering has been expressed in terms of $l=0$ partial waves. However, we must include the spherical waves surrounding each magnetic solute at $\{\mathbf{R}_j\}$:

$$\Psi_{\mathbf{k}\alpha} \sim \Omega^{-1/2}\left\{ e^{i\mathbf{k}\cdot\mathbf{r}}\alpha - \frac{Jv_0 m\bar{S}}{4\pi\hbar^2}\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_j}\left[\frac{\cos k|\mathbf{r}-\mathbf{R}_j|}{|\mathbf{r}-\mathbf{R}_j|}\right](\alpha\cos\chi_j+\beta e^{i\phi_j}\sin\chi_j)\right\} \ . \tag{58}$$

We have used,[10] $n_0(\rho) = -\cos(\rho)/\rho$. In order to evaluate the integral over each spherical wave, we cut off the radial integral at R, defined by

$$\Omega = \frac{4\pi}{3}R^3 \ . \tag{59}$$

Since the number of impurities is $Z_i = nc_m\Omega$, it follows that

$$|W_{\mathbf{k}}|^2 = nc_m\left[\frac{Jv_0 m\bar{S}}{4\pi\hbar^2}\right]^2\int_0^R\left[\frac{\cos kr}{r}\right]^2 4\pi r^2 dr \ . \tag{60}$$

[We have used the postulated isotropy of the impurity-spin directions. Cross terms linear in J, which occur in the normalization of (58), drop out because the impurity positions are random.] The integral is trivial, i.e., $2\pi R$, whereupon (with $nv_0=1$),

$$|W_{\mathbf{k}}|^2 = \frac{J^2 m^2 \bar{S}^2 c_m R}{8\pi n\hbar^4} \ . \tag{61}$$

The appearance here of R, $\sim\Omega^{1/3}$, is of extraordinary importance, because it is just this feature which leads to the unique predictions of the present theory. It is worth noting that the $\mathbf{k}$ dependence of $|W_{\mathbf{k}}|^2$ has disappeared, and so $\langle\cos\Theta\rangle$, Eq. (57), is also independent of $\mathbf{k}$.

A. Determination of the R cutoff

It may seem (at first) disconcerting that Eq. (61) depends on R, which is related to Ω through Eq. (59). Were we dealing with an unbound-state problem, such an R dependence would indicate an incorrect formulation of the physical question. However, we are concerned with a *bound* state of Cooper pairs in a BCS condensate.

Suppose one were treating a hydrogen atom in the presence of strong scatterers randomly distributed throughout space. One would be entitled to use a quasi-plane-wave basis, as we have done here. Again, the relative probability assigned to the (standing) spherical waves surrounding the scattering centers would dominate the plane-wave components if Ω were taken large enough. However, only those scattering centers within a Bohr radius of the proton are relevant to the ground state; so one should limit Ω to the space occupied by the ground-state wave function.

The foregoing conclusion is extremely interesting: The effective Hamiltonian arena depends on the outcome of the bound-state calculation, i.e., the Hamiltonian must be selected to be self-consistent with its own solution. Such a logical structure is not unprecedented and, for example, finds an analog in renormalization-group theory.

In the present problem the appropriate value of R will be (approximately) the BCS coherence length ξ_0. A more accurate relation follows from the pair-correlation amplitude which, from Appendix D of BCS,[5] falls exponentially as $\exp(-r/\pi\xi_0)$. Accordingly, after squaring this amplitude, we set

$$R = \tfrac{1}{2}\pi\xi_0 \ . \tag{62}$$

ξ_0 is related to T_c. From Eq. (5.50) of BCS,[5]

$$\xi_0 = 0.18\frac{\hbar v_F}{k_B T_c} \ . \tag{63}$$

With Eqs. (3), (57), and (61)–(63) together with the density of states per spin (per unit volume),

$$N_0 = m^2 v_F/2\pi^2\hbar^3 \ , \tag{64}$$

where v_F is the Fermi velocity, and with

$$l_s = v_F\tau_s \ , \tag{65}$$

the mean free path for exchange scattering only, one readily finds

$$\langle\cos\Theta\rangle = 1-\frac{\pi\xi_0}{2l_s} \ . \tag{66}$$

This mean canting-angle cosine, associated with triplet contamination (caused by exchange scattering), is a very useful theoretical result, even though its validity is limited to the dilute limit. A generalization of Eq. (66) is given in Sec. V C.

B. Initial slope of the T_c decrease

The BCS T_c equation still applies after a modification of the effective coupling constant according to Eq. (56):

$$\lambda_{\text{eff}}=\lambda\langle\cos\Theta\rangle^2 , \tag{67}$$

where the BCS λ is N_0V. Accordingly, the BCS T_c equation is now,

$$k_BT_c=1.13\hbar\omega_D e^{-1/\lambda_{\text{eff}}} . \tag{68}$$

The change in T_c relative to T_{c0} (for the pure metal) can easily be calculated to first order in the impurity concentration c_m, which is equivalent to first order in $1/\tau_s$. From Eqs. (63) and (65)–(68)

$$k_B(\Delta T_c)\cong-\frac{0.57\hbar}{\lambda\tau_s} . \tag{69}$$

(The numerical coefficient is 0.18π.) This equation for the initial slope of ΔT_c is (in magnitude) similar to the traditional one, Eq. (29), but analytically it is profoundly different. The factor $1/\lambda$ shows that the initial slope (versus $1/\tau_s$) *depends* on the superconductor and, consequently, is *not* a universal constant. Weak superconductors "lose their T_c" more rapidly than strong ones.

It should be noticed that λ is the BCS coupling constant, and differs from a similar parameter λ_E employed in strong-coupling theory. A relation between λ and λ_E can be derived by equating T_c from the BCS equation to T_c given, say, by McMillan's equation[12] with $\mu^*=0$ [i.e., Coulomb interactions are ignored—assumption (vi) of Sec. I]. The relation so derived is

$$\lambda\approx\frac{\lambda_E}{1.04+1.54\lambda_E} . \tag{70}$$

If $\lambda_E=0.5$, $\lambda=0.28$. Needless to say, Eqs. (66) and (69) apply only in the dilute limit, i.e., for $\xi_0/l_s\ll1$.

That the (theoretical) initial slope of ΔT_c cannot be a universal constant was noticed by Jarrel,[13] who calculated T_c numerically from the Eliashberg-Migdal equations (incorporating the effects of magnetic impurities) for nine values of λ_E. His initial slope, dT_c/dc, varies with λ_E in close accord with the analytic prediction of Eq. (69), upon using the $\lambda_E\rightarrow\lambda$ conversion, Eq. (70).

C. Fall of T_c versus $1/\tau_s$ from T_{c0} to zero

We need to generalize Eq. (66) so that T_c can be predicted for an extended range of solute concentration. Consider a basis state $\Psi'_{\mathbf{k}\uparrow}$ at the point $\mathbf{r}$, as was done in Sec. II D. The canting angle at $\mathbf{r}$ will have contributions from all of the spherical waves (surrounding each solute spin within the range R). The vector sum of these contributions constitutes a random walk on the surface of a hemisphere beginning at the pole, $\theta=0$. Since the maximum canting angle is $\theta=90°$, the equator is a (reflecting) boundary. This random walk (or diffusion) problem is solved in Appendix B. The solution leads to

$$\langle\cos\Theta\rangle=\frac{1}{2}+\frac{1}{2}\left[1+5\left[\frac{u}{2}\right]^2\right]^{-1}e^{-2u} , \tag{71}$$

where

$$u\equiv\pi\xi_{\text{eff}}/2l_s . \tag{72}$$

We have replaced ξ_0 by ξ_{eff} for reasons which will soon be apparent. Equation (71) agrees with Eq. (66) when $u\ll1$, as it must. The large-u limit is particularly interesting for it satisfies another rigorous requirement:

$$\lim_{u\rightarrow\infty}\langle\cos\Theta\rangle=\tfrac{1}{2} . \tag{73}$$

The reduction in singlet fraction of a canted pair, from Sec. II B or Eq. (43) is $\cos^2\Theta$. Consequently, the limit (73) means that the singlet fraction can fall only to 25%. This lower limit is just the expected singlet fraction for a pair of electrons having *random* spin orientations. Accordingly λ_{eff}, Eq. (67), can fall only to $\frac{1}{4}\lambda$; i.e., T_c can fall only to $T_{c0}\exp(-3/\lambda)$. (For $\lambda=0.25$, $T_c/T_{c0}\rightarrow10^{-5}$, which is essentially zero.)

When the conduction electrons have a mean free path l which is smaller than the coherence length ξ_0 (for a pure superconductor), the effective coherence length is reduced. A random-walk analysis during the coherence time ξ_0/v_F leads to[14]

$$\xi_{\text{eff}}\approx\sqrt{l\xi_0} . \tag{74}$$

One needs an interpolation formula that smoothly connects both limits, $l<\xi_0$ and $l>\xi_0$. Such an expression can be found easily:

$$\xi_{\text{eff}}\approx\xi_0\left[\frac{l^2}{l^2+\xi_0^2}\right]^{1/4} . \tag{75}$$

T_c can now be calculated from Eqs. (67) and (68), with $\langle\cos\Theta\rangle$ given by Eqs. (71) and (72), and ξ_{eff} determined from Eq. (75). The required ξ_0 is still Eq. (63), which depends explicitly on the T_c being calculated. An iterative procedure converges rapidly. One may first use $T_c\sim T_{c0}$ in Eq. (63), calculate T_c as just described, and repeat using the computed T_c in Eq. (63), etc.

If spin-disorder scattering *only* is taken into account, then $l=l_s$, Eq. (65). T_c versus $1/\tau_s$ is shown in Fig. 2 for four λ values between 0.15 and 0.30. The calculated curves apply to a metal having $\Theta_D=300$ K and $v_F=1.0\times10^8$ cm/sec. These calculations have neglected the influence of (spin-independent) potential scattering arising from the paramagnetic solutes. This influence is dramatic, and is one of the new predictions of the theory, to be elaborated in Sec. VII.

One should not conclude from the curves in Fig. 2 that we have violated our resolve to employ only J^2 effects in the theory. T_c is simply a highly nonlinear, transcendental function of the spin-disorder scattering cross section.

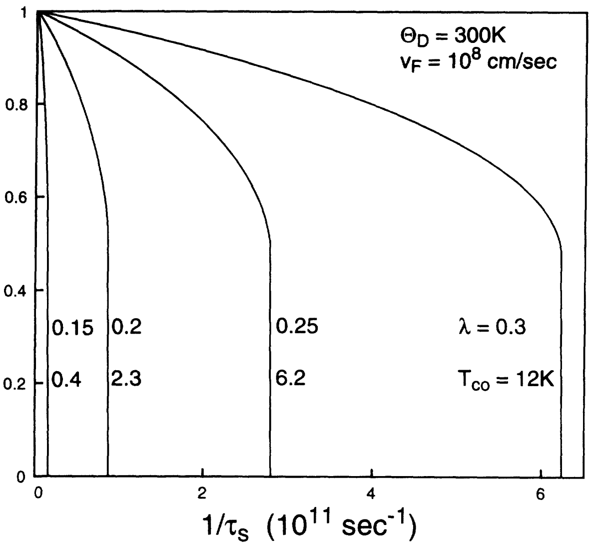

FIG. 2. Variation of T_c with magnetic-solute concentration (measured in terms of the spin-disorder scattering rate, $1/\tau_s$) for four BCS weak-coupling superconductors. ($T_{c0}=1.13\theta_D e^{-1/\lambda}$.)

which we treat only to order J^2. (Multiple scattering from solutes is also ignored.) The nonanalytic nature of the superconducting transition forces a linear influence, $1/\tau_s$, to exhibit a highly nonlinear consequence T_c.

VI. COMPENSATION OF THE PARAMAGNETIC-IMPURITY EFFECT BY ORDINARY IMPURITIES

We consider now a superconductor which has ordinary impurities as well as magnetic impurities. The scattering potential from an impurity at $\mathbf{R}_j$ can be represented by the interaction

$$H_0=Pv_0\delta(\mathbf{r}-\mathbf{R}_j)\ . \tag{76}$$

P is typically ~ 1 eV. If the solute fraction is c_0, the scattering rate is

$$\frac{1}{\tau_0}=\frac{2\pi P^2 N_0 c_0}{n\hbar}\ , \tag{77}$$

and is $\sim 10^{13}-10^{14}\ \text{sec}^{-1}$ for $c_0=0.01$ [depending on the solute residual resistivity ($\rho_0=m/ne^2\tau_0$) caused by potential scattering]. ρ_0 is frequently in the $1-10\ \mu\Omega\,\text{cm}/\%$ range. The ratio of (77) to $1/\tau_s$, the corresponding rate for exchange scattering, will often be between 20 and 200.

As discussed in Sec. I, potential scattering *by itself* does not significantly alter T_c.[2] The widely held misbelief that this insensitivity remains valid, even when exchange scattering is also present, stems from AG's work[3] (which sought to include both potential and exchange scattering). Their finding, Eq. (29), does not depend on τ_0.

However, it is apparent from Eq. (75) that potential scattering profoundly affects the paramagnetic-impurity effect. The total mean free path l, given by

$$\frac{1}{l}=\frac{1}{l_s}+\frac{1}{l_0}\ , \tag{78}$$

(with $l_0\equiv v_F\tau_0$) is needed to evaluate ξ_{eff}. Since l and ξ_{eff} decrease as the solute fraction c_0 increases, the number of magnetic solutes that influence a Cooper pair in the BCS condensate becomes smaller. Accordingly, potential scattering counteracts the T_c decline caused by exchange scattering.

The algorithm for calculating $T_c(\tau_s,\tau_0)$, already described following Eq. (75), remains unchanged. One merely uses l from Eq. (78). Figure 3 shows the recovery of T_c towards its initial value, T_{c0}, which results from adding nonmagnetic impurities. The solid curve is for a magnetic-solute fraction that reduces T_c (from $T_{c0}=3.6$ K) by 150 mK. The dashed curve is for a magnetic-solute fraction which (when acting alone) reduces T_c by 1.3 K. The horizontal axis is the potential-scattering rate, which is proportional to the nonmagnetic-solute concentration.

Experimental study of magnetic compensation must recognize that superconductors do not accurately obey assumptions (ii) and (v) of Sec. I. The gap parameter Δ is generally not isotropic. A consequence of an anisotropic Δ is that T_{c0} will be larger than what one would (otherwise) expect if the mean value of Δ occurred everywhere on the Fermi surface.[2] Accordingly, when impurities are *initially* added to a pure superconductor, a small decrease in T_c results because scattering tends to average the Δ's for the initial and final **k** states. T_c levels off when $1/\tau_0$ exceeds $\Delta/\hbar$.[15] Subsequently, T_c may change gradually with further additions of nonmagnetic solute because assumption (v) is only an approximation. In view of these

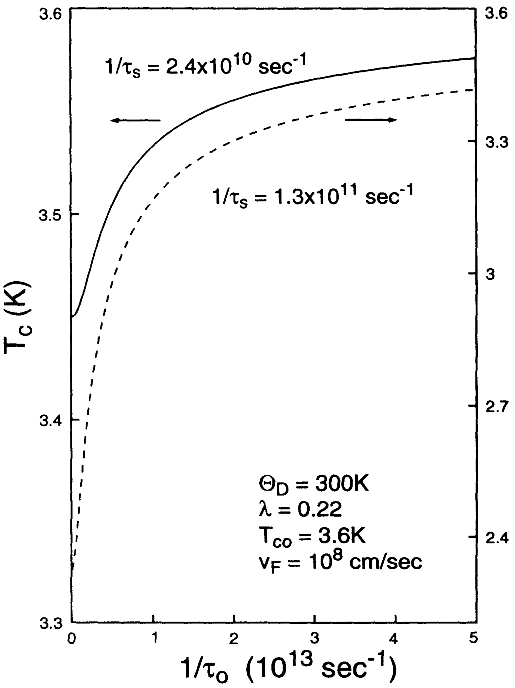

FIG. 3. Compensation of T_c with doping by a nonmagnetic solute (measured in terms of the potential-scattering rate, $1/\tau_0$) for two alloys having magnetic-solute concentrations which reduce T_c from T_{c0} by 150 mK and 1.3 K.

two latter effects, $T_c(\infty,\tau_0)$ must be measured so that the magnetic-impurity effect,

$$\Delta T_c(\tau_s,\tau_0) \equiv T_c(\tau_s,\tau_0) - T_c(\infty,\tau_0) , \tag{79}$$

represents the T_c change caused only by exchange scattering (appropriate to each concentration of nonmagnetic solute).

Merriam, Liu, and Seraphim[16] discovered that adding dilute concentrations of Pb or Sn to In significantly reduced the paramagnetic-impurity effect caused by a small (~ 5 ppm) concentration of Mn. T_c changes caused by Pb or Sn (alone) were first determined accurately.[17] The Mn concentration chosen was intentionally small in order to stay well below the solubility limit, which is ~ 60 ppm.[18] The ΔT_c data of Merriam, Liu, and Seraphim, defined according to Eq. (79), are shown in Fig. 4 for ten samples of In-Mn-Pb. The theoretical curve shown involves just one adjustable parameter, τ_s, in order that $\Delta T_c = -42.5$ mK, the observed value without Pb. $\tau_0(c_0)$ for Pb in In was determined from the measured residual resistivity. Observe that the compensation for 2 at. % Pb is about 80%.

Data for In-Mn-Sn samples were similar, and were measured to verify that the compensation effect did not depend on the third element.[16] Merriam, Liu, and Seraphim also determined the initial slope of the T_c decrease, Sec. V B, by measuring ΔT_c of 18 dilute In-Mn alloys with c_m in the 1–10 ppm range. The observed slope was large, i.e., characteristic of magnetic solutes having a local moment, when compared to the initial slope, say, for Al-Mn, which is 30 times smaller. (Presumably, Mn does not carry a moment in Al.)

Boato, Bugo, and Rizzuto[19] have also studied the In-Mn-Pb system. They measured four samples having 50-ppm Mn. The largest ΔT_c was -21 mK (for $c_{\rm Pb}=0$), and the maximum compensation was $\sim 25\%$.

It is clear that compensation of the paramagnetic-impurity effect, predicted theoretically in this paper, should be subjected to further experimental study, especially in systems devoid of metallurgical difficulties. The Th-Gd system, with nonmagnetic solutes such as Ti or Zr, is a promising one.[20] (La-Gd would also appear to be a favorable system if it were possible to control the occurrence of dhcp and fcc phases.)

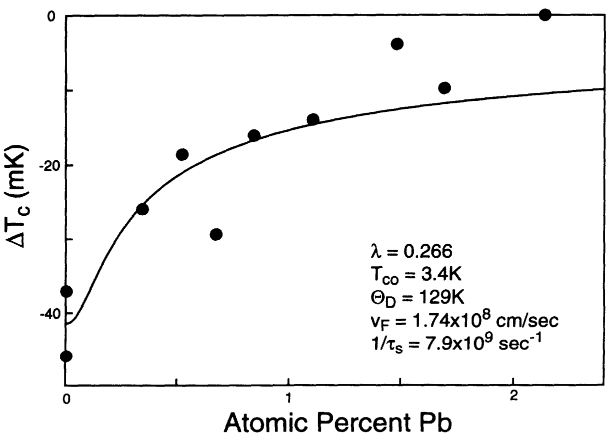

FIG. 4. Compensation of T_c in In-Mn-Pb vs Pb concentration for 5-ppm Mn. Data are due to Merriam, Liu, and Seraphim, Ref. 16. $1/\tau_s$ was adjusted in the theoretical curve so that $\Delta T_c = -42.5$ mK without any Pb.

Compensation of the paramagnetic impurity effect has also been observed as a consequence of radiation damage.[21] Pure In and In + 400 ppm Mn foils were irradiated with Ar ions. 90% of the 2.2 K decrease in T_c (caused by the Mn) was suppressed by an Ar fluence of 2.2×10^{16} cm^{-2}.

VII. SELF-COMPENSATION OF THE PARAMAGNETIC-IMPURITY EFFECT

In the previous section we treated the recovery of T_c caused by the addition of nonmagnetic solutes. The compensation results merely from the extra limitation of the mean free path, which reduces the number of magnetic solutes that influence a Cooper pair in a BCS condensate (as elaborated in Sec. V C).

A similar reduction in l can arise from the potential scattering associated with the magnetic solutes themselves. One needs only to replace c_0 by c_m in Eq. (77). Accordingly, both terms in Eq. (78) are proportional to c_m. Self-compensation is a dramatic effect because the potential-scattering cross section is generally 20–200 times larger than that for exchange scattering.

Figure 5 compares $T_c(c_m)$ for magnetic solutes having potential to exchange-scattering ratios of 0, 20, 50, and 100. The critical value of c_m, where T_c plummets to zero can be larger than that when only exchange scattering occurs by more than an order of magnitude. It is clear from Fig. 5 why serious attempts[22] to predict the size of the magnetic-impurity effect could not succeed; the relevance of potential scattering had not yet been recognized. The potential-scattering cross section depends, of course, on both the solute and the host, so similar

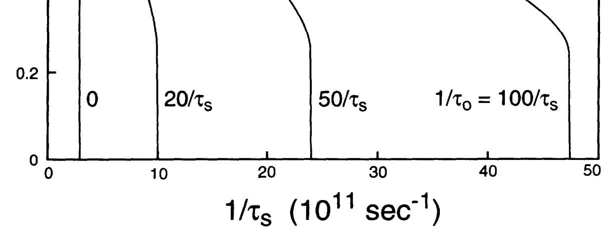

FIG. 5. Self-compensation of T_c in a superconductor for which the potential to exchange-scattering ratio is 20, 50, and 100. The curve labeled 0 is the expected T_c variation without self-compensation. (The magnetic-solute concentration is proportional to $1/\tau_s$.)

behavior in a variety of hosts (for the same magnetic solute) cannot be anticipated.

An important feature of the self-compensated $T_c(c_m)$ curves of Fig. 5 is that they exhibit significant positive curvature over a considerable range prior to their fall towards zero. In contrast, the curves of Fig. 2, where only exchange scattering occurs, have negative curvature throughout. Many examples of $T_c(c_m)$ data with positive curvature have been noted.[23] Some workers have suggested that solutes which exhibit positive curvature do not have local moments, but rather introduce only spin fluctuations. In view of the likely occurrence of self-compensation, illustrated in Fig. 5 for a model with fixed local spins, the curvature of $T_c(c_m)$ should not be used as an indicator of transient spin fluctuations.

VIII. CONCLUSIONS AND DISCUSSION

A. Recapitulation

The fundamental imperative recognized in this work stems from the fact that exchange potentials of paramagnetic impurities are two orders of magnitude larger than the gap parameter Δ of a Cooper pair. Consequently the quantum mechanics of the scattering must be appropriately solved *prior* to the BCS condensation (viz., Sec. III). The normal-state wave functions must be perturbed only to terms linear in the exchange constant J, so that one can continue to specify states meaningfully with $\mathbf{k}\alpha, -\mathbf{k}\beta$ labels. That is, the plane-wave parts of Eqs. (30) and (33) must retain sufficient amplitude to implement a pairing algorithm.

Were one to use instead exact eigenstates (for a sample having a large volume), then all one-electron states would have zero mean spin polarization. *Any* pair selected would, on average, be 75% triplet and 25% singlet, i.e., the same average values for two electrons in the normal state.

The scattered spherical waves surrounding each magnetic impurity, cf. Eq. (58), create spin canting of the basis pairs and lead to a reduced $V_{\mathbf{k}'\mathbf{k}}$, Eq. (56). The $1/r$ dependence of the spherical waves requires introduction of a radial cutoff (Sec. V A). Fortunately a natural cutoff is at hand in a bound-state problem. For a BCS superconductor the appropriate cutoff is $\sim\pi\xi_{\text{eff}}/2$. ξ_{eff}, Eq. (75), depends on both ξ_0 and the mean free path l. As T_c decreases with increasing magnetic-solute concentration, ξ_0 increases and allows an ever expanding number of magnetic solutes to weaken each Cooper pair. This expansion accelerates the fall of T_c near the critical concentration, as shown in Fig. 2. The T_c decrease is nevertheless continuous. In this connection one must remember that although ξ_0 is a function of T_c, it is essentially independent of T for a given T_c. Tinkham[24] evaluated Eq. (5.45) of BCS,[5] and showed that the shape and range of Cooper-pair correlation functions for $T=0$ and T_c are similar. Accordingly, the BCS relation between ξ_0 and T_c, Eq. (63), has been adopted in this study.

The decrease in ξ_{eff}, which occurs whenever the mean free path l becomes shorter than ξ_0, leads to two effects. Since the number of magnetic solutes that can influence each Cooper pair decreases when ξ_{eff} decreases, caused either by nonmagnetic impurities, other disorder (e.g., radiation damage), or by potential scattering of the magnetic solutes themselves, T_c acquires a significant compensation, counteracting the imputed decrease that would result from exchange scattering only. Observed compensation by nonmagnetic solutes, illustrated in Fig. 3, has been reported[16] for In-Mn-Pb (Fig. 4) and In-Mn-Sn systems. Compensation caused by radiation damage[21] has also been found.

Self-compensation, Fig. 5, can strikingly reduce the paramagnetic-impurity effect and increase substantially the value of the critical concentration at which T_c falls (essentially) to zero. Also, self-compensation can cause positive curvature of T_c versus $1/\tau_s$ in the intermediate solute concentration range (preceding the rapid fall of T_c to zero).

Finally, a unique feature of the theory is that the initial slope of T_c versus $1/\tau_s$, Eq. (69), is inversely proportional to the BCS electron-phonon interaction strength, λ.

B. Dynamic magnetic-impurity effect

As already emphasized in the Introduction, a more realistic model for treating the paramagnetic-impurity effect would allow the local spins $\{\mathbf{S}_i\}$ to be quantum mechanical (instead of classical and fixed). Each $\mathbf{S}_i$ has $2S+1$ magnetic sublevels which must be included in the Hilbert space of the superconductor. Adoption of this expanded freedom leads obviously to an expansion in theoretical "bookkeeping" activities. We have carried out that task and report here just the final result and the physical origin of the change.

A tractable theory is possible only if one assumes that the $2S+1$ magnetic sublevels for each solute spin are degenerate. This simplification is equivalent to neglecting $\mathbf{S}_i \cdot \mathbf{S}_j$ interactions (arising, say, from indirect exchange), and is analogous to the random-orientation postulate, (viii), of the fixed-spin model.

Each term of a normal-state basis function cf. Eq. (58), should include a $Z=(2S+1)^N$-component spin function for the N solute spins in the volume Ω. The matrix element $V_{\mathbf{k}'\mathbf{k}}$ of the phonon-mediated interaction is to be calculated, as usual, between antisymmetrized basis pairs $(\mathbf{k}\alpha, -\mathbf{k}\beta)$ and $(\mathbf{k}'\alpha, -\mathbf{k}'\beta)$. Each element of a basis pair is a $4Z$-component vector (which recognizes the freedom of the two conduction-electron spins and the Z components of the solute-spin system). One must note, once again, that $\mathbf{k}\alpha, -\mathbf{k}\beta$ are labels used to catalog wave functions of considerable complexity.

The coherent matrix element, $V_{\mathbf{k}'\mathbf{k}}$, is nonzero only to the extent that the $(\mathbf{k}\alpha, -\mathbf{k}\beta)$ and $(\mathbf{k}'\alpha, -\mathbf{k}'\beta)$ basis pairs have overlap in their $4Z$-component spin functions. On account of the spin admixtures in the basis pairs caused by the magnetic Hamiltonian, Eq. (2), $V_{\mathbf{k}'\mathbf{k}}$ will have an exchange term as well as a direct term. For the fixed-spin model, the exchange terms double the loss to $V_{\mathbf{k}'\mathbf{k}}$ resulting from the σ_x and σ_y direct terms. σ_z leads only to a reduction in the direct term, but it is twice as large as the direct-term reduction for σ_x and σ_y. The σ_x and σ_y terms (for the dynamic model) are associated with transitions between sublevels of the $\{\mathbf{S}_i\}$ solutes; and it turns out that the exchange terms are then zero to order J^2. All other details remain the same. The net result is that the magnetic-impurity effect for the dynamic-spin model can be found from the fixed-spin model merely by letting

$$J^2S(S+1)\rightarrow\tfrac{2}{3}J^2S(S+1)\ . \tag{80}$$

It is sometimes put forward that the magnetic-impurity effect is associated with an absence of time-reversal symmetry. The Hamiltonian for the fixed-spin model does indeed lack time-reversal symmetry. However, the Hamiltonian of the dynamic-spin model *has* time-reversal symmetry. The magnetic-impurity effect should rather be attributed to the spin-canting of basis pairs, as elaborated in Sec. II D, which occurs whether or not the solute Hamiltonian, Eq. (2), has time-reversal symmetry.

Inclusion of Coulomb interactions in this theoretical approach should be an interesting exercise. Also of interest would be extension of the method for Kondo impurities and for solutes that can be described by an Anderson Hamiltonian.[25] It seems likely that other topics in inhomogeneous superconductivity may need to be reexamined.

ACKNOWLEDGMENTS

This work was originally undertaken in response to a challenge by Professor J. Appel to illuminate the physics of impure superconductors. We have benefited from conversations with D.M. Ginsberg and Lance DeLong. Finally, this research was possible because of the financial support of the National Science Foundation, Materials Theory Program.

APPENDIX A

Section IV B concerns the basis-pair spin canting caused by the z component of the magnetic Hamiltonian, Eq. (2). The Slater determinant, evaluated at $\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}$, Eq. (49), involves term linear in $W'_{\mathbf{kq}}$, Eq. (32), and its complex conjugate; and these terms were dropped following Eq. (52). The concern is that these terms, linear in J, combine with similar ones when $V_{\mathbf{k'k}}$, the matrix element of the phonon-mediated interaction between two Slater determinants, is calculated. Since $\mathbf{k}$ and $\mathbf{k}'$ will differ in such a product, there will be two simple poles (rather than a second-order pole) when the $\mathbf{q}$ integrations are evaluated. It is possible to make use of assumption (i), electron-hole symmetry, together with the $\hbar\omega_D$ BCS cutoff algorithm to show that the dropped terms would lead to corrections of order $(\hbar\omega_D/E_F)^2$.

However, a more satisfactory reason exists for dropping the terms in question. Singlet superconductivity requires that a basis pair $(\mathbf{k}\alpha,-\mathbf{k}\beta)$ be combined with equal amplitude and phase to the basis pair $(-\mathbf{k}\alpha,\mathbf{k}\beta)$. (This combination is automatic in elementary BCS theory and happens without explicit attention.) Accordingly the determinant $\mathcal{D}'_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)$, Eq. (49), will be combined with the determinant $\mathcal{D}'_{-\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)$ when implementing the pairing algorithm. When this combination is made in advance, as is permissible, one can show that the cross terms arising from both determinants, evaluated at $\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}$, cancel identically.

APPENDIX B

Consider the wave function (58). Without the scattered spherical waves from the solute spins $\{\mathbf{S}_i\}$, the spin polarization at any point $\mathbf{r}$ would be in the $\hat{z}$ direction. However, when the β (spin-down) components of (58) are superposed, the polarization direction is rotated. The effect of the incremental rotations caused by the Z_i solute spins can be likened to a random walk on the surface of a unit sphere. Such a sequence is analogous to a diffusion problem om a spherical surface for which all of the diffusing particles start from the "North" pole at $t=0$.

Suppose $M(\theta,t)d\omega$ is the probability of finding the unit polarization vector in the solid angle $d\omega$ at time t. (θ is the polar angle; the azimuthal angle does not appear on account of axial symmetry.) The diffusion equation is, accordingly:

$$\frac{\partial M}{\partial t}=\frac{D}{\sin\theta}\times\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial M}{\partial\theta}\right]\ , \tag{B1}$$

where D is the diffusion constant. This equation has the general solution

$$M(\theta,t)=\sum_{l=0}^{\infty}c_l e^{-l(l+1)Dt}P_l(\cos\theta)\ , \tag{B2}$$

where $\{P_l(x)\}$ are the Legendre polynomials; and $\{c_l\}$ are coefficients to be determined by the initial condition at $t=0$, which is

$$M(\theta,0)=2\delta(\cos\theta-1)\ . \tag{B3}$$

The factor 2 occurs because the "volume" element is $\frac{1}{2}\sin\theta\,d\theta$. By standard procedures one finds

$$c_l=2l+1\ , \tag{B4}$$

so that the solution (for the surface of a sphere) is

$$M(\theta,t)=\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)Dt}P_l(\cos\theta)\ . \tag{B5}$$

If one were interested in the mean value, $\langle\cos\theta\rangle$, versus time

$$\langle\cos\theta\rangle=\int_0^{\pi}M(\theta,t)\cos\theta(\tfrac{1}{2}\sin\theta\,d\theta)\ . \tag{B6}$$

Only the term involving $P_1(\cos\theta)$ survives the integration, and one finds

$$\langle\cos\theta\rangle=e^{-2Dt}\ . \tag{B7}$$

The mean decays from unity (at $t=0$) according to a single exponential.

The actual problem at hand involves the canting angle of two spins, initially antiparallel. Consequently, the maximum canting angle is $\frac{1}{2}\pi$. If the first spin passes the equator, the second spin passes in the opposite direction. Thus the problem is equivalent to diffusion on the surface of a hemisphere (with the equator being a reflecting boundary). The solution, which is confined to the interval $[0,\frac{1}{2}\pi]$, can be written immediately from symmetry, since the second spin starts from the "South" pole.

$$M(\theta,t)=\sum_{l=0}^{\infty}\frac{1}{2}(2l+1)e^{-l(l+1)Dt}\times[P_l(\cos\theta)+P_l(-\cos\theta)]\ . \tag{B8}$$

The factor $\frac{1}{2}$ occurs because the normalized volume element is now $\sin\theta\,d\theta$. The odd-l Legendre polynomials cancel, the even-l add, so

$$M(\theta,t)=\sum_{n=0}^{\infty}(4n+1)e^{-2n(n+1)Dt}P_{2n}(\cos\theta)\ . \tag{B9}$$

Our interest is the average, $\langle\cos\theta\rangle$, which is now,

$$\langle\cos\theta\rangle=\int_0^{\pi/2}M(\theta,t)\cos\theta\sin\theta\,d\theta\ . \tag{B10}$$

All n's contribute to $\langle\cos\theta\rangle$, unlike the case for a complete sphere, Eq. (B7). The required integrals are known:[26]

$$\int_0^1 P_{2n}(x)P_1(x)dx=\frac{(-1)^n(2n)!}{2^{2n+1}(1-2n)n!(n+1)!}\ . \tag{B11}$$

Accordingly,

$$\langle\cos\theta\rangle=\frac{1}{2}+\sum_{n=1}^{\infty}\frac{(-1)^{n+1}(4n+1)(2n)!}{2^{2n+1}(2n-1)n!(n+1)!}\times e^{-2n(2n+1)Dt}\ . \tag{B12}$$

Observe that as $t\to\infty$, $\langle\cos\theta\rangle\to\frac{1}{2}$, which is the correct average for a uniform distribution on the surface of a hemisphere.

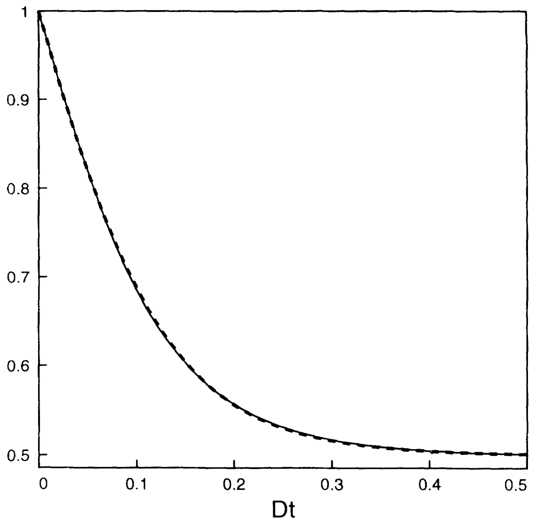

FIG. 6. Comparison of the exact $\langle\cos\theta\rangle$ vs time with an analytical fit (dashed) for diffusion on the surface of a hemisphere. Equation (71) is based on the analytical fit. (D is the surface diffusion coefficient.)

The variation of $\langle\cos\theta\rangle$ with Dt is shown by the solid curve in Fig. 6, and was computed numerically from Eq. (B12). We found (by trial and error) an excellent analytical fit, which is the dashed curve in Fig. 6. The function found is

$$\langle\cos\theta\rangle=\tfrac{1}{2}+\tfrac{1}{2}[1+5D^2t^2]^{-1}e^{-4Dt}\ . \tag{B13}$$

This function leads to Eq. (71) through the substitution, $2Dt=u$, which is required so that Eq. (71) agrees with Eq. (66).

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[1] Yong-Jihn Kim and A. W. Overhauser, Phys. Rev. B **47**, 8025 (1993).

[2] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).

[3] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1961) [Sov. Phys. JETP **12**, 1243 (1961)].

[4] B. T. Matthias, H. Suhl, and E. Corenzwit, J. Phys. Chem. Solids **13**, 156 (1961).

[5] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[6] H. Fröhlich, Proc. R. Soc. London, Ser. A **215**, 291 (1952).

[7] M. A. Jensen and H. Suhl, in *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. II B, p. 183.

[8] J. Appel and A. W. Overhauser, Phys. Rev. B **29**, 99 (1984).

[9] A. W. Overhauser and L. L. Daemen, Phys. Rev. Lett. **61**, 1885 (1988).

[10] Leonard I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1968), p. 85, $n_0(\rho)=-\cos\rho/\rho, n_1(\rho)=-\sin\rho/\rho-\cos\rho/\rho^2$.

[11] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1959).

[12] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[13] Mark Jarrel, in *International Workshop on Quantum Simulations of Condensed Matter Phenomena, Los Alamos, New Mexico, August 1989*, edited by J. D. Doll and J. E. Gubernatis (World Scientific, Singapore, 1990), p. 141, Fig. 1 inset. The $\lambda_E\to\lambda$ conversion should differ slightly from Eq. (70) since Jarrel used an Einstein-mode spectral density, whereas McMillan modeled the phonon spectrum of Nb.

[14] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966) pp. 220 and 225.

[15] David Markowitz and Leo P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[16] M. F. Merriam, S. H. Liu, and D. P. Seraphim, Phys. Rev. **136**, A17 (1964).

[17] D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta. Metall. **9**, 861 (1961).

[18] G. Boato, M. Bugo, and C. Rizzuto, Nuovo Cimento **45**, 226 (1966).

[19] G. Boato, G. Gallinaro, and C. Rizzuto, Phys. Rev. **148**, 353 (1966).

[20] Lance DeLong (private communication).

[21] A. Hofmann, W. Bauriedl, and P. Ziemann, Z. Phys. B **46**, 117 (1982), Fig. 5.

[22] A. B. Kunz and D. M. Ginsberg, Phys. Rev. B **22**, 3165 (1980).

[23] Eberhard Wassermann, Z. Phys. **220**, 6 (1969).

[24] Michael Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), p. 66, Fig. 2-12.

[25] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[26] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980), p. 820, formula 7.221, 2.