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Microscopic Theory of NMR in an Anisotropic Superfluid (^{3}He A)[*]

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Equations are derived for the motion of the magnetization and the "spin axes of the Cooper pairs," and solved for the case of unsaturated cw resonance. In general two discrete resonances are predicted, but if a special condition is met, only one occurs. The complete field dependence of the line(s) determines the gap configuration almost uniquely. The predictions are consistent with existing data and in strong conflict with Anderson's theory.

Several months after its original discovery,[1] the anomalous NMR shift in the "A phase" of liquid ^{3}He remains a source of controversy. In an earlier Letter[2] this author showed that the existence of the shift could be qualitatively understood if the system possessed the property of "broken spin-orbit symmetry"; in the presence of the nuclear dipole forces there would then be a strong correlation between the direction of total spin of any two particles and the direction of their relative orbital angular momentum.[2] If, as seems to widely believed, liquid ^{3}He A is an anisotropic BCS-type superfluid, then it is the Cooper pairs which have their spins and orbital angular momenta correlated in this way. This mechanism for the shift does not require that the total orbital angular momentum or total spin be finite, or that there be a preferred axis of quantization for the spins: The shift is therefore predicted to persist to zero field, and to occur even for the "isotropic" Balian-Werthamer[3] (BW) state. A resonance is also predicted to occur for "longitudinal" polarization of the rf field (i.e., parallel to the external field). However, this approach is clearly somewhat unsatisfactory in that the existence of a single shifted peak with the observed frequency dependence,

$$\omega^2 = \omega_L^2 + \omega_0^2(T), \tag{1}$$

and no appreciable background was taken from experiment rather than demonstrated explicitly.

A very different approach to the problem of this shift was developed by Anderson[4] under the assumption that ^{3}He A is indeed an anisotropic BCS superfluid. This approach rests fundamentally on the hypothesis of the existence of a macroscopic *total* orbital angular momentum which is coupled to the total spin and to the "reference system for the spins of the condensed pairs" (called $\hat{k}_X$ by Anderson) by some semiphenomenological energies. Among the predictions of this theory are that the shift $\omega^2 - \omega_L^2$ is a strong function of the external field and tends to zero in zero field; that there is no "longitudinal" resonance; and that the BW state shows no shift. If the last conclusion is correct, we could interpret the "B phase" of ^{3}He as a BW phase.[4]

In the present Letter I outline[5] a microscopic theory of NMR in an anisotropic BCS-type superfluid, based on a Born-Oppenheimer type of approximation. I derive general equations for the magnetization vector and a vector related to the spin of Cooper pairs at a particular point on the Fermi surface. The equations are applicable to quite general NMR situations in which field gradients can be neglected. They are solved explicitly for the case of unsaturated cw resonance, with some somewhat surprising results. The predictions of Ref. 2 are confirmed, in the sense that *if* a single resonance line (rather than two) is observed, then its frequency must satisfy Eq. (1), and that the existence of a shift is a consequence only of broken spin-orbit symmetry and holds for any field and for longitudinal rf polarization. However, we find that in general an anisotropic superfluid shows *two* discrete resonance lines neither of whose frequencies is given by Eq. (1), although the difference is noticeable only at low fields. The observation in ^{3}He A of a single line rigorously obeying Eq. (1), if it were to be confirmed by experiments at lower fields, would imply a very strong constraint on the nature of the equilibrium state. The state recently proposed by Anderson and Brinkman[6] seems to satisfy this constraint. As to the BW state, see below.

We define the total spin vector $\vec{S}$ in the usual way, and also a vector $\vec{T}(\vec{n})$, which is related to the condensation amplitude and spin axis of the Cooper pairs[5] at a point on the Fermi surface characterized by the unit vector $\vec{n}$:

$$\vec{T}(\vec{n}) = 4\pi(2\pi\hbar)^{-3}\int d^3p'\,\delta(\vec{n}-\vec{n}')a_{-p'\mu}(\tau\vec{\sigma})_{\mu\nu}a_{p'\nu} \equiv -\vec{T}(-\vec{n}),$$
$$\tau \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = 2\sigma_y/\hbar \tag{2}$$

and the components of $\vec{\sigma}$ are spin matrices. The components of $\vec{S}$ satisfy the usual commutation relations among themselves, and we also have

$$[S_i, T_j(\vec{n})] = i\hbar\epsilon_{ijk}T_k(\vec{n}) = -[S_i, T_j^{\dagger}(\vec{n})]^{\dagger}. \tag{3}$$

The commutation relations of $\vec{T}$ and $\vec{T}^{\dagger}$ are not necessary for present purposes, as will be seen.

We write the Hamiltonian in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_D, \tag{4}$$

where $\hat{H}_0$ contains the "gross" terms, that is, kinetic energy, nondipole potential energy (which is assumed invariant against spin rotations), and magnetic field energy $-\gamma\vec{S}\cdot\vec{\mathcal{H}}$, where $\vec{\mathcal{H}}$ is the external field. $\hat{H}_D$ is the dipole energy: In this we keep only the terms corresponding to Cooper pairs, which then read

$$\hat{H}_D = \tfrac{2}{3}\pi\gamma^2\hbar^2\int (d\Omega/4\pi)\int (d\Omega'/4\pi)[\vec{T}^{\dagger}(\vec{n})\cdot\vec{T}(\vec{n}') - 3\hat{q}\cdot\vec{T}^{\dagger}(\vec{n})\hat{q}\cdot\vec{T}(\vec{n}')],$$
$$\hat{q} \equiv (\vec{n}-\vec{n}')/|\vec{n}-\vec{n}'|. \tag{5}$$

So long as we consider only $\hat{H}_0$, the quantities S^2 and $\vec{S}\cdot\vec{\mathcal{H}}$ are constants of the motion. Consider the energy of the state which is the equilibrium state subject to the condition that S^2 and $\vec{S}\cdot\vec{\mathcal{H}}$ have given values. We can write this as

$$E(\vec{S}) = \tfrac{1}{2}\gamma^2\chi^{-1}S^2 - \gamma\vec{S}\cdot\vec{\mathcal{H}}, \tag{6}$$

where we have assumed for simplicity that χ is independent of field (the treatment is easily modified if this is not so).

At this point one may ask whether in the ensuing argument one should not use, instead of the true (isotropic) susceptibility χ, the "susceptibility at constant $\vec{T}(\vec{n})$"[4]: This is a tensor whose principal axes depend on $\vec{T}(\vec{n})$. There is space here only to state that doing so in no way affects the results quoted below for (a) any BW state, (b) any state of the type (b) defined below, (c) longitudinal resonance, (d) T near T_c, and (e) large ω_L. For states of type (a) defined below, Eq. (14) is modified for T far from T_c and small ω_L, but this affects none of the qualitative conclusions of this Letter. These statements will be justified elsewhere.[5]

We now make a Born-Oppenheimer type of approximation[5] and assume that for motion on time scales long compared to $\hbar/\Delta$ (Δ is a typical energy gap) we may replace $\hat{H}_0$ by E, which is now to be regarded as a function of the *operator* $\vec{S}$. We define quantities

$$\vec{H} \equiv -\partial E/\partial\vec{S} = \gamma\vec{\mathcal{H}} - \gamma^2\chi^{-1}\vec{S}, \tag{7}$$

$$\vec{J}(\vec{n}) \equiv -\delta\hat{H}_D/\delta\vec{T}(\vec{n}). \tag{8}$$

Then using the commutation relations of the components of $\vec{S}$ and $\vec{T}$ [see Eq. (3)] we can write down at once the equations of motion of $\vec{S}$ and $\vec{T}(\vec{n})$. In the equation for $\vec{T}(\vec{n})$ terms arising from $[\vec{T}, \hat{H}_D]$ are of order χ relative to the others; since for nuclear magnetism χ is always very small ($\sim 10^{-7}$), we drop these. Then we obtain the simple equations

$$d\vec{S}/dt = \vec{S}\times\vec{H} + \vec{R},$$
$$\vec{R} \equiv (4\pi)^{-1}\int d\Omega[\vec{T}(\vec{n})\times\vec{J}(\vec{n}) + \text{c.c.}]; \tag{9}$$

$$d\vec{T}(\vec{n})/dt = \vec{T}(\vec{n})\times\vec{H}. \tag{10}$$

From now on we treat the macroscopic quantities $\vec{S}$, $\vec{T}(\vec{n})$, and $\vec{J}(\vec{n})$ as c-numbers (as we already did in rearranging the terms in $\vec{R}$). Equations (9) and (10) provide in principle a description of a wide variety of NMR phenomena.

To discuss the case of unsaturated cw resonance, we notice that the definition of $\vec{R}$, together with Eqs. (5), (8), and (10), leads to

$$dR_i/dt = \sum_j \Phi_{ij} H_j, \tag{11}$$

where the elements of the 3×3 matrix Φ are bilinear functionals of $\vec{T}(\vec{n})$, $\vec{T}^*(\vec{n}')$. In the case of interest we can replace the Φ_{ij} by their value in the equilibrium state, $\Phi_{ij}^{(0)}$. It is of course essential[2] to choose this state from among the various states left degenerate by $\hat{H}_0$ so as to minimize $\langle \hat{H}_D\rangle$. Then it is easy to show that $\Phi^{(0)}$ is a symmetric matrix with positive definite eigenvalues, and $\mathrm{Tr}\,\Phi^{(0)} = -6\langle \hat{H}_D\rangle$. $\Phi_{xx}^{(0)}$ is just γ^{-2} times the Q defined in Ref. 2.

Finally, we use Eq. (7) to express $\vec{H}$ in terms of the deviation $\vec{S}'$ of $\vec{S}$ from its equilibrium value $\vec{S}_0 = \gamma^{-1}\chi\vec{\mathcal{H}}_0$, and the rf field $\vec{\mathcal{H}}_{rf}$. The resulting equation for $\vec{S}'$ is, after a Fourier transformation with respect to time,

$$(\omega^2 - \hat{\Omega}^2)\vec{S}' - i\omega(\vec{\omega}_{\mathrm{L}} \times \vec{S}') = -\gamma^{-1}\chi(\hat{\Omega}^2\vec{\mathcal{H}}_{rf} + i\,\omega\vec{\omega}_{\mathrm{L}} \times \vec{\mathcal{H}}_{rf}), \tag{12}$$

where $\vec{\omega}_{\mathrm{L}} \equiv \gamma\vec{\mathcal{H}}_0$ and $\hat{\Omega}^2$ is a 3×3 matrix defined by

$$\begin{aligned}(\hat{\Omega}^2)_{ij} \equiv \gamma^2\chi^{-1}\Phi_{ij}^{(0)} = 4\pi\gamma^4\hbar^2\chi^{-1}\,\mathrm{Re}\int(d\Omega/4\pi)\int(d\Omega'/4\pi)\{[\hat{q}\cdot\vec{T}^*(\vec{n})][\hat{q}\cdot\vec{T}(\vec{n}')]\,\delta_{ij}\\ - \hat{q}\cdot\vec{T}^*(\vec{n})\hat{q}_j T_i(\vec{n}') - [\hat{q}\times\vec{T}^*(\vec{n})]_i[\hat{q}\times\vec{T}(\vec{n}')]_j\}.\end{aligned} \tag{13}$$

From Eq. (12) we may obtain the complete absorption spectrum.[5] We shall assume that Ω^2 can be diagonalized in a frame in which $\vec{\omega}_{\mathrm{L}}$ lies along the z axis, and call its eigenvalues Ω_x^2, Ω_y^2, Ω_z^2. Then a longitudinal resonance occurs at $\omega = \Omega_z$, while the absorption of a transverse field (the usual NMR case) shows in general *two* resonances at frequencies

$$\omega^2 = \tfrac{1}{2}\{\omega_{\mathrm{L}}^2 + \Omega_x^2 + \Omega_y^2 \pm [(\omega_{\mathrm{L}}^2 + \Omega_x^2 + \Omega_y^2)^2 - 4\Omega_x^2\Omega_y^2]^{1/2}\}. \tag{14}$$

For large ω_{L} Eq. (14) (with the upper sign) agrees with Eq. (1), if we set $\omega_0^2(T) = \Omega_x^2(T) + \Omega_y^2(T)$. Deviations from Eq. (1), as well as frequency and spectral weight of the lower resonance, are determined by the quantity

$$\begin{aligned}\delta(\omega_{\mathrm{L}}, T) &\equiv \alpha[\omega_0^2/(\omega_0^2 + \omega_{\mathrm{L}}^2)]^2,\\ \alpha &\equiv \Omega_x^2\Omega_y^2/(\Omega_x^2 + \Omega_y^2)^2 \leq \tfrac{1}{4}.\end{aligned} \tag{15}$$

If we use the existing data[1,7] on ^{3}He A to determine the value of $\omega_0^2(T)$, we find that δ would have been very small ($\lesssim 0.06$) for all experiments so far carried out. It is therefore not surprising that the second line was not seen. Moreover, the existing data are probably not quite adequate[8] to set a nontrivial upper limit on the quantity α. If Eq. (1) were observed to hold rigorously for all ω_{L}, this would imply $\alpha = 0$ and hence that one of the eigenvalues in the xy plane, say Ω_y^2, is zero; this would be an extremely strong constraint on the equilibrium state. In this special case the lower mode always has zero frequency; it might, nevertheless, reduce the spectral weight in the upper mode at low fields, depending on how the anisotropy axes lock on to the rf field.[5]

We shall quote some values of Ω_i^2 for various states of interest, confining ourselves to temperatures near T_c where $\vec{T}(\vec{n})$ is directly proportional to the vector $\vec{d}(\vec{n})$ defined by BW.[3] The absolute values of Ω_i^2 depend on unknown factors,[9] so we shall quote values of $C_i \equiv \Omega_i^2/\Omega_0^2$, where

$$\Omega_0^2 \equiv 4\pi\gamma^4\hbar^2 \times \tfrac{3}{4}\int(d\Omega/4\pi)\,|\vec{T}(\vec{n})|^2. \tag{16}$$

The maximum possible value of $\sum_i C_i$ is then 1. We confine ourselves to the case of p-wave pairing:

(a) $\vec{d}(\vec{n}) = (\tfrac{3}{2})^{1/2}\hat{z}\times\vec{n}$; $C_x = C_y = \tfrac{1}{10}$, $C_z = \tfrac{4}{5}$;

(b) $\vec{d}(\vec{n}) = (\tfrac{3}{2})^{1/2}\hat{y}(x + iz)$; $C_x = C_z = \tfrac{1}{5}$, $C_y = 0$;

(c) $d_z(\vec{n}) = n_z$, $d_x = -\tfrac{1}{4}n_x + (\tfrac{15}{16})^{1/2}n_y$,
$d_y = -\tfrac{1}{4}n_y - (\tfrac{15}{16})^{1/2}n_x$;
$C_x = C_y = 0$, $C_z = \tfrac{1}{2}$.

State (a) is the best (from the point of view of the dipole energy) of the class of equal-spin-pairing[3] states which are degenerate in the weak-coupling approximation. State (b) is the best of the subclass of this which is said by Anderson and Brinkman[6] to minimize the spin-fluctuation energy. State (c) is the best BW state: See below. Clearly we have $C_y = 0$ not only for state (b) but more generally for any state of the form $\hat{y} f(\vec{n})$, where f is a scalar function (e.g., an $l=3$ spherical harmonic).

In writing down the state (c) as the "best" BW state we have argued as follows. In zero external field the dipole energy of the BW state is minimized if we start from the configuration $\vec{d}=\vec{n}$ and then rotate $\vec{d}(\vec{n})$ through the angle $\cos^{-1}(-\frac{1}{4})$ about an arbitrary axis. We have assumed that in a finite field we should choose this axis to be the z axis, since the number of $S_z=0$ pairs is slightly less than the number of $S_z=\pm 1$ pairs and it is therefore more important to correlate the latter. Then we see that the resultant state does not show a "transverse" shift but does show a large longitudinal shift. Hence it is possible that ^{3}He B is in a BW phase,[4] and we can test this hypothesis by a longitudinal NMR experiment.

We conclude: (1) The phenomenon of shifting of the resonance(s) is quite insensitive to whether or not there exists a $\hat{k}_\chi$ in Anderson's[4] sense, or a finite total angular momentum; thus, contrary to Ref. 4, a shift will occur for longitudinal polarization (even for the BW state) and will in no case tend to zero as $\vec{\mathcal{H}}_0 \to 0$. (2) The shift cannot be ascribed to an effective internal field lying in the xy plane, since at low external fields the motion of $\vec{S}'$ is more nearly linear than circular [see Eq. (12)]. (3) Existing experimental data on ^{3}He A probably cannot determine the nature of the configuration unambiguously, but lower-field data will go a long way towards doing so. (4) ^{3}He B may be in a BW state, and this can be tested by longitudinal NMR experiments.

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New Mössbauer-Effect Measurements on the System Fe:*Cu*

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High-field ($H \leq 60$ kG) and low-temperature ($T \geq 25$ mdeg K) Mössbauer-effect measurements of the Kondo system Fe:*Cu* are reported. The comparison of these results with bulk susceptibility data leads to a polarization, of antiferromagnetic sign, of the electron gas in the Kondo state.

The true nature of the Kondo effect is far from being understood; this is so for the theoretical[1] as well as for the experimental[2] side of the problem. For simplicity one may, as far as the experimental situation is concerned, divide the measurements into macroscopic and microscopic ones. For the macroscopic the situation is reasonably simple. The properties like resistivity,