

Spin-Orbit Coupling and the Knight Shift in Nontransition-Metal Superconductors

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(Received 28 December 1964; revised manuscript received 19 March 1965)

The Knight shift K_s of nontransition-metal superconductors is discussed in terms of three contributions, namely: (a) The Van Vleck part of the contact shift attributed to the spin-orbit coupling force of the periodic potential which, in the presence of an external magnetic field, causes virtual high-energy rearrangements of conduction electrons near and inside the Fermi surface; (b) that part of the contact shift which is attributed to low-energy rearrangements of conduction electrons and affected by spin-reversing scattering; and (c) the diamagnetic orbital shift. For the calculation of (a), Wannier's theory of a Bloch electron in a magnetic field is generalized to the original Pauli Hamiltonian \mathcal{H}_0 , describing the relativistic dynamical behavior of a conduction electron in the effective periodic potential of the lattice. This leads to an effective Hamiltonian which couples only Bloch-type spinors of the same band index, but of the same and of different spin indices. With the help of the eigenfunctions of \mathcal{H}_0 , the hyperfine contact interaction is treated by perturbation theory. To arrive at simple expressions for the corresponding Knight shift and nuclear spin-relaxation time, valid for arbitrary strength of spin-orbit coupling, the energy-band function in the absence of the field is approximated by a parabola. Formulas for (b) and (c) are taken from the literature. The relative importance of the three contributions to K_s is discussed for Al, Sn, and Hg, where the Knight shift has been observed in the normal and in the superconducting states. If one assumes that spin-reversing scattering is caused merely by spin-orbit interactions at atomic imperfections such as displaced surface atoms of small particles, and not by paramagnetic impurities, one finds that in Al neither of the two spin-orbit coupling effects is sufficiently strong to account for more than $\sim 2\%$ of the residual shift $K_s(0)$. For the experimental Sn sample, (a) and (b) have the ratio 1:3 and, together with the orbital shift, can account for $\frac{2}{3}$ of the observed $K_s(0)$. For Hg, (a) and (b) are of comparable magnitude at $T=0$ and together account for more than $\frac{1}{2}$ of the observed shift $K_s(0)$.

INTRODUCTION

ALTHOUGH the original BCS theory of superconductivity uses a rather simplified effective electron-electron interaction,^{1,2} it is by now widely accepted that this theory gives the correct answer for the ground-state wave function of the many-electron system in nontransition metals—namely, that it consists of some coherent superposition of quasibound electron pairs which are in singlet spin states. Since the BCS theory is a nonrelativistic theory, spin-orbit coupling and other relativistic effects which arise from the periodic electric field of the crystal lattice are ignored. Then, each electron of a "ground pair" is in a pure spin state; one is in a spin-up state and the other is in a spin-down state. The corresponding spin susceptibility is associated with the *low-energy* rearrangement of electron spins in the vicinity $\beta_e H$ of the Fermi surface ($-\beta_e =$ Bohr magneton). In the superconducting state, it decreases with temperature as some exponential function and vanishes for the ground state.³ This prediction of the BCS theory was apparently contradicted by earlier nuclear-magnetic-resonance (NMR) measurements on Hg and Sn, where it was found that the Knight shift does not vanish as $T \rightarrow 0$.^{4,5} The contradiction occurs if one assumes that the Knight shift is merely caused by the contact part of the hyperfine interaction.

With this assumption, several distinct explanations have been offered to resolve the discrepancy.⁶ In particular, Anderson,⁷ Ferrell,⁸ and Abrikosov and Gor'kov⁹ have shown that spin-reversing scattering, arising from spin-orbit interactions at displaced surface atoms, plays an important role in small specimens.¹⁰ Consequently, NMR experiments were undertaken on two superconducting metals with small atomic numbers, V and Al.

For vanadium, a *3d* transitional metal, Noer and Knight¹¹ observed no change in the Knight shift below the transition temperature T_c . This result is attributed to the dominant role of the orbital part of the hyperfine interaction.¹² The significance of this interaction for transition metals, where it gives rise to virtual *high-energy* transitions of *d* electrons, was suggested by Kubo and Obata.¹³ The orbital paramagnetic Knight shift was first observed on V_3Ga and V_3Si by Clogston, Jaccarino,

⁶ See J. M. Blatt, *Theory of Superconductivity* (Academic Press, Inc., New York, 1964), p. 301 ff., for literature references.

⁷ P. W. Anderson, Phys. Rev. Letters **3**, 325 (1959).

⁸ R. A. Ferrell, Phys. Rev. Letters **3**, 262 (1959).

⁹ A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **42**, 1088 (1962) [English transl.: Soviet Phys.—JETP **15**, 752 (1962)].

¹⁰ Small specimens, with a dimension $d \ll \delta$ ($\delta =$ penetration depth) must be used in order to obtain a homogeneous magnetic field (Meissner effect).

¹¹ J. Noer and W. D. Knight, Rev. Mod. Phys. **36**, 177 (1964).

¹² The observed temperature dependence of the nuclear spin relaxation time, which is found to be the same in the normal and the superconducting state (Ref. 11), can, however, not be explained in terms of the orbital interaction.

¹³ R. Kubo and Y. Obata, J. Phys. Soc. Japan **11**, 547 (1956).

¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), referred to as BCS.

² P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).

³ K. Yosida, Phys. Rev. **110**, 769 (1958).

⁴ F. Reif, Phys. Rev. **106**, 208 (1957).

⁵ G. M. Andros and W. D. Knight, Phys. Rev. **121**, 779 (1961).

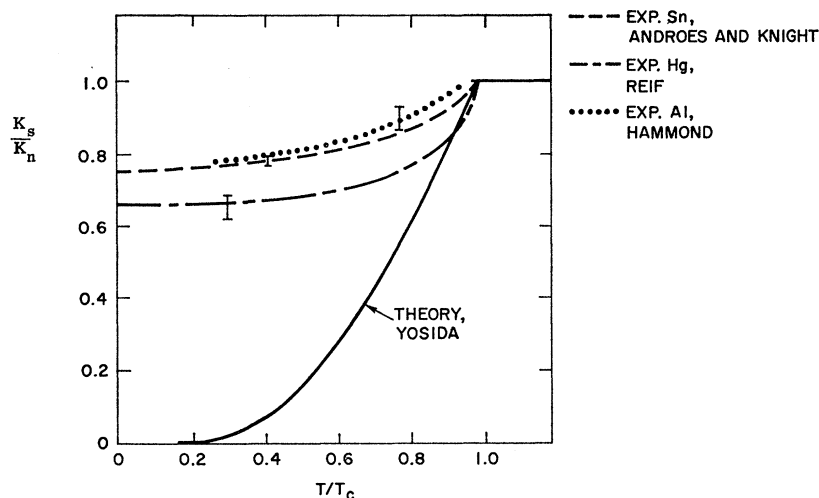


FIG. 1. Observed temperature dependence of the ratio of the Knight shift in normal and superconducting states for nontransition metals.

Gossard, and Yafet.¹⁴ These authors¹⁵ have also presented a theoretical analysis of the orbital Knight shift for the $5d$ transition metal Pt, based on the tight-binding approximation and with incorporated spin-orbit coupling. They have been able to separate the total Knight shift of Pt into its relative contributions from (1) the contact interaction with unpaired electron spins K_c , (2) the contact interaction with ion-core s electrons which are spin polarized because of their exchange interaction with unpaired conduction electrons K_{sp} , (3) the orbital interaction K_{orb} . A fourth interaction, (4) the dipolar interaction of nuclear spins with unpaired conduction electrons, gives rise to the shift K_{dip} which vanishes for cubic crystals, provided that spin-orbit coupling is ignored. Then, in a superconductor, there is only the orbital Knight shift left as $T \rightarrow 0$. Of the four contributions to the Knight shift, only the orbital shift may be considered as a "diamagnetic" effect, in the sense that it does not depend on unpaired electrons in the vicinity of the Fermi surface, but on all the electrons inside this surface.

As for Al, one is concerned with a nontransition-metal superconductor which, because of its simple electronic structure^{16,17} and its weak electron-phonon interaction, comes closer to the assumptions of the BCS theory than any other superconductor known at present. One can ignore K_{dip} (cubic symmetry), and K_{orb} is expected to be small compared with K_c . A NMR experiment on Al then provides a relevant test on the significance of spin-reversing scattering in small particles. If the lifetime of

an electron in a pure spin-up or spin-down state $\tau_s \gg \hbar/2\epsilon_0$, where the energy gap $2\epsilon_0 \sim 3.5kT_c$, the Knight shift should vanish as $T \rightarrow 0$.⁷ For Al, this condition requires $\tau_s > 10^{-11}$ sec, which is not a particularly large time,¹⁸ so that a nearly vanishing Knight shift may reasonably be expected as $T \rightarrow 0$. However, careful experimental observations by Hammond¹⁹ on Al films of 200-Å thickness show (see Fig. 1) that the Knight shift decreases by only 25% of its value at T_c (= transition temperature) as $T \rightarrow 0$. In view of this result, the question was raised by Ferrell²⁰ as to whether the spin-orbit coupling forces, arising from the periodic crystalline field and causing virtual transitions from the BCS ground state to excited states with energies $\gg 2\epsilon_0$, can produce a significant contribution to the spin susceptibility which is, as the paramagnetic orbital susceptibility of transition metals, temperature-independent and of the type known as Van Vleck or high-frequency paramagnetism. This spin-orbit coupling effect is a bulk effect, that is, it is size-independent and, therefore, should be separable from the one caused by scattering of electrons at atomic imperfections.

It is the primary purpose of this paper to calculate the effect of spin-orbit coupling, caused by the periodic electric field of the perfect lattice, on the Knight shift K_c of nontransition-metal superconductors. To this end, we calculate the high-frequency or Van Vleck-type contribution in the normal state and assume that this contribution remains unaffected by the transition to the superconducting state. As for the legitimacy of this procedure, we follow Anderson⁷ and Ferrell²⁰ in con-

¹⁴ A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters **9**, 232 (1962); Rev. Mod. Phys. **36**, 170 (1964).

¹⁵ A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964); see also, M. Shimizu and A. Katsuki, J. Phys. Soc. Japan **19**, 614 (1964).

¹⁶ W. A. Harrison, Phys. Rev. **118**, 1182 (1960), see, in particular Fig. 4 of this paper.

¹⁷ W. A. Harrison in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

¹⁸ For Na—which has the atomic number 11 as compared to 13 for Al—G. Feher and A. F. Kip [Phys. Rev. **98**, 337 (1955)] find an experimental value of 9×10^{-9} sec for the electron spin relaxation time, in fair agreement with the value of 2×10^{-9} sec obtained from Elliott's theory of electron spin relaxation due to spin-orbit scattering [Phys. Rev. **96**, 266 (1954)].

¹⁹ R. H. Hammond and G. M. Kelly, Rev. Mod. Phys. **36**, 185 (1964).

²⁰ R. A. Ferrell, University of Maryland, Technical Report No. 329 (unpublished).

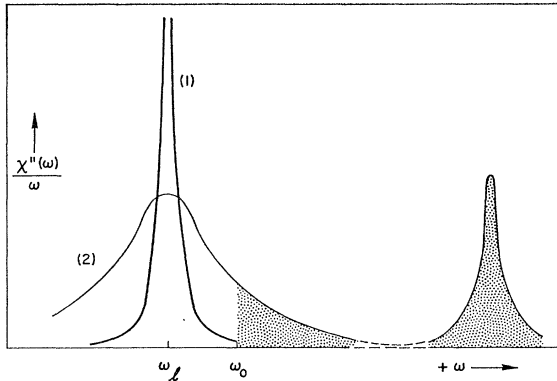


FIG. 2. Schematic sketch of the spectral decomposition of the absorptive part of the spin susceptibility. Curve 1 is a δ function centered at the Larmor frequency $\omega_l = 2|\beta_e|H$; with the Kramers-Kronig relation it yields the Pauli susceptibility of a free-electron gas. Curve 2 exhibits spin-orbit scattering and the spin-orbit coupling effect arising from the crystalline field with the broadening of the low-frequency contribution and the occurrence of a high-frequency contribution, respectively. The "paramagnetic" part of the residual Knight shift $K_s(0)$ in the superconducting state, which depends on the unpaired electron spins, is determined by the area under the curve for $\omega > \omega_0 = 2\epsilon_0/\hbar$.

Considering the spectral decomposition of the absorptive part of the spin susceptibility, $\chi''(\omega)$ (see Fig. 2), ignoring the effect of the magnetic field on the orbital motion of the conduction electrons. For free electrons, $\chi''(\omega)/\omega$ is a δ function centered at the Larmor frequency ω_l (curve 1). Spin-orbit scattering broadens $\chi''(\omega)$ to an extent depending on τ_s (see low-frequency part of curve 2). Spin-orbit coupling caused by the periodic electric field gives rise to the high-frequency contribution of curve 2 ($\omega \gg \epsilon_0/\hbar = \omega_0$). The residual spin susceptibility and the comparable part of the contact shift in the superconducting ground state depend on the area under the curve 2 for frequencies $\omega > \omega_0$. Furthermore, in the presence of spin-orbit coupling there is a second contribution to the contact shift which has no comparable part in the spin susceptibility; it arises from electrons *inside* the Fermi surface, also because of the interplay between spin-orbit coupling and the coupling between orbital motion and magnetic field. To calculate the total Van Vleck-type contribution to K_c , we employ Wannier's powerful and compact formalism for Bloch electrons in a magnetic field (see also Kohn,²¹ Blount,²² and Roth²³). In Sec. I, Wannier's theory is properly generalized to a *relativistic* Bloch electron in a magnetic field. Thereby one is led to an effective Hamiltonian which couples only Bloch spinors of the same band index, but of different, as well as the same, spin indices. As an interesting by-product of this calculation, the correct g factor for conduction electrons is readily obtained. It may be mentioned that recently Wannier and

Upadhyaya²⁴ have derived, with a brief calculation, the field-independent susceptibility of nonrelativistic Bloch electrons and have found the same result as Roth²³ and Hebborn and Sondheimer.²⁵ With the help of the two-component wave functions for a Bloch electron in a magnetic field obtained in Sec. I, the hyperfine contact interaction is treated by perturbation theory in Sec. II. In order to arrive at meaningful and tractable expressions for the perturbation energies, we introduce what will be called the *parabolic approximation*; that is, we approximate the energy-band functions for the spin-up and the spin-down band, in the absence of the field, by parabolic functions. The corresponding conduction-electron wave functions exhibit with fair accuracy the effect of the periodic potential, including spin-orbit coupling, and will be used to derive explicit expressions for the Knight shift K_c and for the nuclear spin relaxation time T_c , valid for arbitrary strength of spin-orbit coupling. In Sec. III, the experimental situation for the three non-transition metals Hg, Sn, and Al, on which the Knight shift has been measured above and below T_c , is analyzed in terms of (a) the spin-orbit coupling effect due to the crystalline field, (b) spin-reversing scattering caused by spin-orbit interactions between conduction electrons and nonmagnetic imperfections and by exchange interactions between electrons and paramagnetic impurities, and (c) the hyperfine orbital interaction. Taking the available experimental data on the Knight shift and the nuclear spin relaxation time and using the known experimental and theoretical results on the electron structure, we find that a large fraction of the Knight shift observed on the three superconducting non-transition metals Al, Sn, and Hg can reasonably be accounted for by (a), (b), and (c).

I. RELATIVISTIC BLOCH ELECTRONS IN A MAGNETIC FIELD

As for the relativistic eigenvalue problem for Bloch electrons belonging to a simple band, one is concerned with the solution of the original Pauli equation²⁶ for a single conduction electron moving in an effective periodic potential $V(\mathbf{r})$ and a homogeneous magnetic field:

$$\left\{ \frac{\mathbf{P}^2}{2m} - \frac{\hbar e}{4m^2c^2} (\boldsymbol{\epsilon} \times \mathbf{P}) \cdot \boldsymbol{\sigma} - \frac{\hbar e}{4im^2c^2} \boldsymbol{\epsilon} \cdot \mathbf{P} - \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \mathbf{H} + \left(1 + \frac{\mathbf{P}^2}{4mc^2} \right) \left[-\frac{\hbar}{i} \frac{\partial}{\partial t} + V(\mathbf{r}) \right] \right\} \psi = 0. \quad (1)$$

In the present case, $e\boldsymbol{\epsilon} = -\partial V/\partial \mathbf{r}$ and $\mathbf{P} = \mathbf{p} - (e/c)\mathbf{A}$ is the canonical momentum of an electron in the presence

²⁴ G. H. Wannier and A. N. Upadhyaya, Phys. Rev. **136**, A803 (1964).

²⁵ J. E. Hebborn and E. H. Sondheimer, J. Phys. Chem. Solids **13**, 105 (1960).

²⁶ W. Pauli, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer-Verlag, Berlin, 1932), Vol. XXIV/I, p. 161.

²¹ W. Kohn, Phys. Rev. **115**, 809 (1959).

²² E. I. Blount, Phys. Rev. **126**, 1636 (1962).

²³ L. M. Roth, J. Phys. Chem. Solids **23**, 443 (1962).

of a vector potential \mathbf{A} giving rise to the homogeneous magnetic field \mathbf{H} . The particular gauge is of no real importance; here we take also $\mathbf{A} = \frac{1}{2}\mathbf{H} \times \mathbf{r}$ (see W).

Bloch and Wannier Spinors

To find a stationary-state solution of the gauge-invariant Pauli equation, Wannier's theory²⁷ is extended to the relativistic Hamiltonian \mathfrak{H}_0 , defined by Eq. (1), which incorporates spin-orbit coupling, the s shift or Darwin correction, and the mass-velocity correction. To this end, it is convenient to choose as basic functions the two-component Wannier spinors, given by

$$A_{m\rho}(\mathbf{r}, \mathbf{R}_l) = \exp[-\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{r} \times \mathbf{R}_l] a_{m\rho}(\mathbf{r} - \mathbf{R}_l), \quad (2)$$

where

$$a_{m\rho}(\mathbf{r} - \mathbf{R}_l) = \varphi_{m\rho}(\mathbf{r} - \mathbf{R}_l)\alpha + \chi_{m\rho}(\mathbf{r} - \mathbf{R}_l)\beta. \quad (3)$$

Here, \mathbf{R}_l is a lattice vector in a simple cubic lattice with unit cell a^3 . The Wannier spinor $A_{m\rho}$ depends on the magnetic field through the Peierls phase factor *and* through the spinor components $\varphi_{m\rho}$ and $\chi_{m\rho}$. The index ρ is the quantum number \uparrow or \downarrow which refers to the electron spin but, because of spin-orbit coupling, does not correspond to a pure spin state. In order to arrive at the basic set of relativistic wave equations for the spinors $a_{m\rho}$, which is uncoupled in the band index m , one can proceed in precisely the same fashion as Wannier does. Then, one arrives at the following set of defining equations for the Wannier spinors $a_{m\rho}$:

$$\begin{aligned} \mathfrak{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} - \mathbf{R}_l), \mathbf{r}, \boldsymbol{\sigma}] a_{m\rho}(\mathbf{r} - \mathbf{R}_l) \\ = \sum_{\rho'} \sum_{l'} \exp[\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot (\mathbf{r} \times \mathbf{R}_l + \mathbf{R}_l \times \mathbf{R}_{l'} + \mathbf{R}_{l'} \times \mathbf{r})] \\ \times \omega_{m\rho\rho'}(\mathbf{R}_l - \mathbf{R}_{l'}) a_{m\rho'}(\mathbf{r} - \mathbf{R}_{l'}). \end{aligned} \quad (4)$$

The significant difference between this set of equations and the corresponding one for the nonrelativistic case comes about because of spin-orbit coupling effects. These, in the presence of the magnetic field, cause an admixture of spinors $A_{m\rho'} (\rho' \neq \rho)$ into the quasicyclic expansion of the left-hand side of Eq. (4). The admixture is determined by the Fourier components $\omega_{m\rho\rho'}$ of the field-dependent energy-band function

$$W_{m\rho\rho'}(\mathbf{k}) = \sum_l \omega_{m\rho\rho'}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l), \quad (5)$$

which, for a finite field strength, is nondiagonal in the spin quantum numbers ρ and ρ' . To find the Bloch spinor equation implicitly contained in Eq. (4), this equation is multiplied by $\exp(i\mathbf{k} \cdot \mathbf{R}_l)$ and summed over l . By writing a field-dependent Bloch spinor in the form

$$b_{m\rho}(\mathbf{r}, \mathbf{k}) = \sum_l \exp(i\mathbf{k} \cdot \mathbf{R}_l) a_{m\rho}(\mathbf{r} - \mathbf{R}_l), \quad (6)$$

²⁷ G. H. Wannier, Rev. Mod. Phys. 34, 645 (1962), referred to as W; G. H. Wannier and D. R. Fredkin, Phys. Rev. 125, 1910 (1962).

and by using the identity

$$\begin{aligned} [\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} - \mathbf{R}_l)] b_{m\rho}(\mathbf{r}, \mathbf{k}) \\ = [\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} + i\partial/\partial\mathbf{k})] b_{m\rho}(\mathbf{r}, \mathbf{k}), \end{aligned} \quad (7)$$

one finds the defining set of equations for Bloch spinors:

$$\begin{aligned} \mathfrak{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} + i\partial/\partial\mathbf{k}), \mathbf{r}, \boldsymbol{\sigma}] b_{m\rho}(\mathbf{r}, \mathbf{k}) \\ = \sum_{\rho'} \sum_l \omega_{m\rho\rho'}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l) \\ \times \exp[-\frac{1}{2}i(e/\hbar c)\mathbf{H} \times \mathbf{R}_l \cdot \mathbf{r}] \\ \times b_{m\rho'}(\mathbf{r}, \mathbf{k} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l). \end{aligned} \quad (8)$$

This equation defines a Bloch spinor $b_{m\rho}$ which can be written in the conventional splitup form:

$$b_{m\rho}(\mathbf{r}, \mathbf{k}) = \exp(i\mathbf{k} \cdot \mathbf{r}) [u_{m\rho}(\mathbf{r}, \mathbf{k})\alpha + v_{m\rho}(\mathbf{r}, \mathbf{k})\beta], \quad (9)$$

where $u_{m\rho}$ and $v_{m\rho}$ are field-dependent functions. The periodicity of these functions in \mathbf{r} follows from the observation that on the left-hand side of Eq. (8), \mathbf{r} occurs in the periodic combination $\mathbf{r} + i\partial/\partial\mathbf{k}$ which, operating on $b_{m\rho}$, gives $i(\partial/\partial\mathbf{k})[u_{m\rho}\alpha + v_{m\rho}\beta]$; this expression is clearly periodic in \mathbf{r} . With the help of Eq. (9), Eq. (8) can be rewritten in the form

$$\begin{aligned} \mathfrak{H}_0[\mathbf{p} + \hbar\mathbf{k} - \frac{1}{2}i(e/c)\mathfrak{H} \times \partial/\partial\mathbf{k}, \mathbf{r}, \boldsymbol{\sigma}] \\ \times [u_{m\rho}(\mathbf{r}, \mathbf{k})\alpha + v_{m\rho}(\mathbf{r}, \mathbf{k})\beta] \\ = \sum_{\rho'} \sum_l \omega_{m\rho\rho'}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l) \\ \times [u_{m\rho'}(\mathbf{r}, \mathbf{k} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l)\alpha + v_{m\rho'}(\mathbf{r}, \mathbf{k})\beta]. \end{aligned} \quad (10)$$

This equation for the periodic part of the Bloch spinor can be decomposed into two simultaneous equations for the spinor components $u_{m\rho}$ and $v_{m\rho}$ and for the $\omega_{\rho\rho'}$. In the limit $H=0$, the nondiagonal components of the energy band function vanish,

$$\lim_{H \rightarrow 0} W_{\rho\rho'}(\mathbf{k}) = 0, \quad \text{for } \rho \neq \rho', \quad (11)$$

and, consequently, $\omega_{m\rho\rho'}(H=0) = 0$ for $\rho \neq \rho'$, so that Eq. (10) goes into the correct zero-field equation for the periodic part of a Bloch spinor. Assuming that the eigenvalue problem has been solved for $H=0$, we can calculate for a finite field the $u_{m\rho}$, $v_{m\rho}$, and $\omega_{m\rho\rho'}$, as power series expansions in \mathbf{H} . Before the g factor of conduction electrons is determined for arbitrary \mathbf{k} in this fashion, let us proceed to the derivation of the proper effective band Hamiltonian for relativistic Bloch electrons.

Effective Hamiltonian

For this purpose, the basic set of uncoupled equations for the $a_{m\rho}$, given by Eq. (4), is not a proper starting point. Instead, Wannier²⁷ found it convenient to begin with a relation of the form

$$\begin{aligned} [\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{r}] \exp[i\lambda(\mathbf{r})] a_{m\rho}(\mathbf{r} - \mathbf{R}_l) \\ = \exp[i\lambda(\mathbf{r})] [\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} - \mathbf{R}_l)] a_{m\rho}(\mathbf{r} - \mathbf{R}_l), \end{aligned} \quad (12)$$

which follows from Peierls' observation²⁸ that with the help of the gauge transformation

$$\mathbf{A}(\mathbf{r}) \rightarrow \mathbf{A}(\mathbf{r}) + \text{grad}\lambda(\mathbf{r}), \quad (13)$$

where

$$\lambda(\mathbf{r}) = -\frac{1}{2}(e/\hbar c)\mathbf{H} \cdot (\mathbf{r} \times \mathbf{R}_l), \quad (14)$$

the Schrödinger equations for localized functions centered at \mathbf{R}_l ($l=1, 2, 3, \dots$) can be brought into one and the same form, that is, into a set of equations cyclic in \mathbf{R}_l . If, for our case, the basic spinors are taken in the form of Eq. (2), Eq. (12) yields

$$\mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{r}, \mathbf{r}, \boldsymbol{\sigma}]A_{m\rho}(\mathbf{r}, \mathbf{R}_l) = \exp[i\lambda(\mathbf{r})] \times \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} - \mathbf{R}_l), \mathbf{r}, \boldsymbol{\sigma}]a_{m\rho}(\mathbf{r} - \mathbf{R}_l). \quad (15)$$

Into this equation, one can substitute Eq. (4) and, then, one finds a set of uncoupled equations for the $A_{m\rho}$ given by

$$\begin{aligned} \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{r}, \mathbf{r}, \boldsymbol{\sigma}]A_{m\rho}(\mathbf{r}, \mathbf{R}_l) \\ = \sum_{\rho'} \sum_{l'} \exp[\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{R}_l \times \mathbf{R}_{l'}] \\ \times \omega_{m\rho', \rho'}(\mathbf{R}_l - \mathbf{R}_{l'})A_{m\rho'}(\mathbf{r}, \mathbf{R}_{l'}). \end{aligned} \quad (16)$$

This equation can readily be rewritten in terms of Bloch-type spinors

$$\begin{aligned} B_{m\rho}(\mathbf{r}, \mathbf{k}) = b_{m\rho}[\mathbf{r}, \mathbf{k} - \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{r}] \\ = \sum_l \exp(i\mathbf{k} \cdot \mathbf{R}_l)A_{m\rho}(\mathbf{r}, \mathbf{R}_l), \end{aligned} \quad (17)$$

the components of which are *not* identical to Harper functions²⁹ because of the field dependence of the $A_{m\rho}$ beyond that given by the Peierls phase factor, that is, because of the field dependence of the $\varphi_{m\rho}$, $\chi_{m\rho}$. Multiplication of Eq. (16) with $\exp(i\mathbf{k} \cdot \mathbf{R}_l)$ summation over l yields

$$\begin{aligned} \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{r}, \mathbf{r}, \boldsymbol{\sigma}]B_{m\rho}(\mathbf{r}, \mathbf{k}) \\ = \sum_{\rho'} \sum_l \exp(i\mathbf{k} \cdot \mathbf{R}_l)\omega_{m\rho', \rho'}(\mathbf{R}_l) \\ \times B_{m\rho'}[\mathbf{r}, \mathbf{k} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l]. \end{aligned} \quad (18)$$

With the help of this equation, one proceeds directly to the effective band Hamiltonian if an eigenfunction of the original Pauli Hamiltonian is written in the form

$$\psi_\rho(\mathbf{r}) = C \sum_{\rho'} \int_{\Omega^*} f_{\rho\rho'}(\mathbf{k})B_{m\rho'}(\mathbf{r}, \mathbf{k})d\mathbf{k}, \quad (19)$$

where C is a constant and where $\Omega^* = (2\pi/a)^3$ is the volume of the elementary Brillouin zone. Because of spin-orbit coupling effects, Bloch-type spinors $B_{m\rho}$ from both bands are admixed into an eigenfunction ψ_ρ . The admixture depends on the amplitude functions $f_{\rho\rho'}$ for $\rho \neq \rho'$; it must vanish if the spin-orbit coupling

strength vanishes. When \mathcal{H}_0 is applied to an eigenfunction ψ_ρ , one finds, after a shift of the momentum variable \mathbf{k} to $\mathbf{k} - \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l$,

$$\begin{aligned} \mathcal{H}_0\psi_\rho(\mathbf{r}) = C \sum_{\rho'} \sum_{\rho''} \sum_l \int_{\Omega^*} f_{\rho\rho'}[\mathbf{k} - \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l] \\ \times \omega_{m\rho', \rho''}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l)B_{m\rho''}(\mathbf{r}, \mathbf{k})d\mathbf{k}. \end{aligned} \quad (20)$$

If the amplitude function $f_{\rho\rho'}(\mathbf{k})$ can be Fourier analyzed, it is easily seen that

$$f_{\rho\rho'}(\mathbf{k} - \mathbf{k}_0) = \exp(-i\mathbf{k}_0 \cdot \partial/\partial\mathbf{k})f_{\rho\rho'}(\mathbf{k}). \quad (21)$$

With the help of this equation and the Pauli equation for the stationary state, Eq. (20) becomes

$$\begin{aligned} \sum_{\rho'} \sum_{\rho''} W_{m\rho', \rho''}[\mathbf{k} - \frac{1}{2}i(e/\hbar c)\mathbf{H} \times \partial/\partial\mathbf{k}] \\ \times f_{\rho\rho'}(\mathbf{k})B_{m\rho''}(\mathbf{k}) = E_\rho \sum_{\rho'} f_{\rho\rho'}(\mathbf{k})B_{m\rho'}(\mathbf{k}), \end{aligned} \quad (22)$$

where E_ρ is an eigenvalue of \mathcal{H}_0 . Let us now interchange the spin indices ρ'' and ρ' on the left-hand side and, furthermore, assume that the $B_{m\rho}$ are linear-independent; then one arrives at the simultaneous set of eigenvalue equations

$$\sum_{\rho''} W_{m\rho', \rho''}(\mathbf{K})f_{\rho\rho''}(\mathbf{k}) = E_\rho f_{\rho\rho'}(\mathbf{k}), \quad (23)$$

where the operator $\mathbf{K} = \mathbf{k} - \frac{1}{2}(e/\hbar c)\mathbf{H} \times \partial/\partial\mathbf{k}$. The four components $W_{m\rho\rho'}(\mathbf{K})$ represent the effective band Hamiltonian for a relativistic Bloch electron in a magnetic field; the $W_{m\rho\rho'}(\mathbf{k})$ are given by Eq. (5) and can be found as power series expansions in H from Eq. (8). The first-order term of this expansion determines the g factor³⁰ (see Appendix A).

II. KNIGHT SHIFT AND NUCLEAR SPIN RELAXATION

The total hyperfine interaction between the conduction electrons and the nuclear magnetic moments, located at lattice points \mathbf{R}_l , is given by³¹:

$$\mathcal{H}_1 = \mathcal{H}_c + \mathcal{H}_{\text{orb}} + \mathcal{H}_{\text{dip}}, \quad (24)$$

where

$$\mathcal{H}_c = \sum_{l,j} \mathcal{H}_c(l,j) = -8\pi/3 \sum_{l,j} \mathbf{u}_e(\mathbf{r}_j) \cdot \mathbf{u}_n(\mathbf{R}_l)\delta(\mathbf{r}_j - \mathbf{R}_l) \quad (25)$$

³⁰ For a detailed theoretical discussion of the g factor in solids, the reader is referred to Y. Yafet, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14.

³¹ A. H. Bethe, in *Handbook of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXXV/I, p. 193; here one finds a formal derivation of the total hyperfine interaction whereby it is shown how its various contributions arise as lowest order relativistic corrections, linear in μ_n , from the relativistic theory of two interacting particles.

²⁸ R. Peierls, *Z. Physik* **80**, 763 (1933).

²⁹ P. J. Harper, *Proc. Phys. Soc. (London)* **A68**, 879 (1955).

is the contact interaction, and where³²

$$\mathcal{H}_{\text{orb}} = \frac{|e|}{mc} \sum_{i,j} \mathbf{u}_n(\mathbf{R}_i) \cdot \frac{\mathbf{r}_j - \mathbf{R}_i}{|\mathbf{r}_j - \mathbf{R}_i|^3} \times \left[\gamma \mathbf{p} + \left(\frac{\hbar \gamma^2}{4mc^2} \right) \boldsymbol{\sigma}_j \times \left(\frac{\partial V}{\partial \mathbf{r}_j} \right) \right] - \mathcal{H}_c \quad (26)$$

is the orbital interaction. The dipolar interaction \mathcal{H}_{dip} will not be considered here, since, for most metals, it is small compared with \mathcal{H}_c and \mathcal{H}_{orb} . Furthermore, it depends on the number of unpaired electron spins. In particular, for the noncubic metals Sn and Hg, the observed anisotropic Knight shifts, which are partly caused by \mathcal{H}_{dip} , amount to only a few percent of the total shift.³³ \mathcal{H}_{orb} , the spin-orbit interactions between nuclear spins and electron orbits, differs from its standard form (see Ref. 31) where the spin-orbit interaction between electron spins and electron orbits is ignored. Equation (26) contains the usual convergence factor, $\gamma(r) = [1 + (E - V)/2mc^2]^{-1}$, which can be omitted if Bethe's prescription is used in calculating expectation values of \mathcal{H}_{orb} .

Since for the three superconducting metals, Al, Sn, and Hg, the hyperfine contact interaction is the dominant source of Knight shift and nuclear spin relaxation, we shall treat both in some detail, with emphasis on spin-orbit coupling effects, first the effect arising from the crystalline field and then the one caused by scattering.⁷⁻⁹ As for the orbital interaction, its relative importance for the three nontransition metals will be discussed with the help of recent work by Hebborn³⁴ and Yafet.³⁵

Spin-Orbit Coupling and K_c

In the representation found in Sec. I for Bloch electrons in a magnetic field, the contact interaction between a single nucleus with moment \mathbf{u}_n located at the origin of a simple cubic lattice, with dimensions $-G\alpha/2 \leq x, y, z \leq G\alpha/2$, and the system of $N = G^3$ conduction electrons, is treated as a small perturbation. Then, from the corresponding thermodynamic perturbation expansion for the free energy F of electrons and nucleus, the first-order term F_1 is taken for the calculation of the Knight shift, $K_c = -F_1/\mathbf{u}_n \cdot \mathbf{H}$. We write

$$F = F_0 + F_1 + \dots, \quad (27)$$

³² See, e.g., Ref. 15, p. A658.

³³ T. J. Rowland, Acta Met. I, 731 (1953); F. Reif, Phys. Rev. 102, 1417 (1956); a large anisotropic Knight shift, however, has recently been observed by R. R. Hewitt and B. F. Williams [Phys. Rev. Letters 12, 21b, (1964)] on Bi. The physical origin for this experimental result is not dipolar interaction, but the long-range part of the orbital interaction which makes the corresponding part of K_{orb} proportional to g^2 , whereas $K_{\text{dip}} \propto gg_0$ [$g_0 = 2$, free electron g factor; g = effective g factor; this conclusion can be drawn from the work of Yafet (Ref. 35)].

³⁴ J. E. Hebborn, Proc. Phys. Soc. (London) 80, 1237 (1962).

³⁵ Y. Yafet, J. Phys. Chem. Solids 21, 99 (1961).

where F_0 is the free energy of nucleus and conduction electrons in the presence of the external field, and where

$$F_1 = \text{Tr} \{ \rho_N(1, 2, \dots, N) \sum_j \mathcal{H}_c(0, j) \}. \quad (28)$$

Here ρ_N is the electron density matrix operator. Since $\mathcal{H}_c(0, j)$ is a one-electron operator and since electron-electron interactions are ignored to the extent that they are not incorporated in the effective local potential $V(\mathbf{r})$, F_1 is given by

$$F_1 = \sum_{i,\rho} (i\rho | \mathcal{H}_c(0, \mathbf{r}) | i\rho) [\exp(E_{i\rho} - \zeta)/kT + 1]^{-1}. \quad (29)$$

In order to determine F_1 , correct to first order in \mathbf{H} , the expectation value of the contact interaction between eigenfunctions $\psi_{i\rho}$ of \mathcal{H}_c is calculated to this order in the field strength. To this end, let us write the conduction electron wave function in the form of Eq. (19);

$$\psi_{i\rho} = C \sum_{\rho'} \int c_{\rho\rho'} [f_{i;0}(\mathbf{k}) + H^\alpha f_{i;\alpha}(\mathbf{k})] \times [b_{m\rho';0}(\mathbf{r}, \mathbf{k}) + H^\alpha b_{m\rho';\alpha}(\mathbf{r}, \mathbf{k})], \quad (30)$$

where $f_{i;0}$ is an eigenfunction of $W_{\rho\rho;0}(\mathbf{K})$. The normalization constant C and the coefficients $c_{\rho\rho'}$ are determined as in ordinary perturbation theory. It is assumed that

$$\int_{\Omega^*} (f_{i;0} f_{i;\alpha}^* + f_{i;0}^* f_{i;\alpha}) d\mathbf{k} = 0.$$

A corresponding relation is assumed for the Bloch functions $b_{m\rho;0}$ and $b_{m\rho;\alpha}$. Then, from the condition

$$\int_{\Omega^*} |f_{i;0}|^2 d\mathbf{k} = 1 \quad \text{and from} \quad \sum_{\rho'} |c_{\rho\rho'}|^2 = 1, \quad (31)$$

one has

$$c_{\rho\rho'} = d_{\rho\rho'} / (1 + |d_{\rho\rho'}|^2) = c_{\rho\rho'}^*, \quad (\rho \neq \rho'), \quad (32)$$

where $d_{\uparrow\uparrow}$ and $d_{\uparrow\downarrow}$ are given by Eqs. (A19) and (A20), respectively. The constant C is determined by the normalization condition for Bloch spinors in the absence of the field. With

$$\sum_{\rho'} \int_{\Omega} |b_{m\rho';0}(\mathbf{r}, \mathbf{k})|^2 d\mathbf{r} = 1,$$

and with

$$\lim_{H \rightarrow 0} \int_{\Omega} |\psi_{i\rho}(\mathbf{r})|^2 d\mathbf{r} = 1, \quad (33)$$

where $\Omega = \alpha^3$, one has $C = (\Omega^*)^{1/2}$. Knowing the coefficients C and $c_{\rho\rho'}$, we take the wave function $\psi_{i\rho}$, given by Eq. (30), and calculate the expectation value of the hyperfine interaction. To first order in $H = H_z$, it is

given by³⁶

$$\begin{aligned}
\langle i\rho | \mathcal{H}_c(0, r) | i\rho \rangle &= - (8\pi/3) \mu_{n,z} \beta_e (1/\Omega^*) \\
&\times \left\{ \sum_{\rho'} \sum_{\rho''} c_{\rho\rho'}^* c_{\rho\rho''} \int_{\Omega^*} d\mathbf{k} \int_{\Omega^*} d\mathbf{k}' f_{i;0}^*(\mathbf{k}) f_{i;0}(\mathbf{k}') \right. \\
&\times [u_{m\rho';0}^*(\mathbf{k}) u_{m\rho'';0}(\mathbf{k}') - v_{m\rho';0}^*(\mathbf{k}) v_{m\rho'';0}(\mathbf{k}')] \\
&+ H \sum_{\rho'} \sum_{\rho''} c_{\rho\rho'} \int_{\Omega^*} d\mathbf{k} \int_{\Omega^*} d\mathbf{k}' f_{i;0}^*(\mathbf{k}) f_{i;0}(\mathbf{k}') \\
&\times [u_{m\rho';z}^*(\mathbf{k}) u_{m\rho'';0}(\mathbf{k}') + u_{m\rho';0}^*(\mathbf{k}) u_{m\rho'';z}(\mathbf{k}') \\
&\left. - v_{m\rho';z}^*(\mathbf{k}) v_{m\rho'';0}(\mathbf{k}') - v_{m\rho';0}^*(\mathbf{k}) v_{m\rho'';z}(\mathbf{k}') \right\}. \quad (34)
\end{aligned}$$

Here, $u_{m\rho;0}(\mathbf{k}) = u_{m\rho;0}(r=0, \mathbf{k})$. In the first term on the right-hand side of Eq. (34) we have omitted the term linear in $H f_{i;0}$ since it does not contribute to F_1 . If the expression (34) for the expectation value of the contact interaction is inserted into Eq. (29), one has, to first order in H , the exact expression for the free-energy correction F_1 caused by the contact interaction between the conduction electron system and a single nucleus.

In its general form given above, $\langle i\rho | \mathcal{H}_c | i\rho \rangle$ is not in a suitable form for a quantitative discussion of spin-orbit coupling effects. Therefore, at this point we introduce what will be called the *parabolic* approximation. The energy band function in the absence of the field is approximated by the relation

$$W_{\rho\rho;0}(\mathbf{k}) = (\hbar^2/2m^*) |\mathbf{k}|^2. \quad (35)$$

This equation is to be considered as a rough interpolation formula for the energy of Bloch states within the occupied part of the Brillouin zone, *not* as the nearly free-electron approximation. For $W_{\rho\rho;0}$, the effect of the lattice, and thus of spin-orbit coupling, is contained in m^* , which depends in second and higher order on some characteristic parameter for the spin-orbit coupling strength. The energy levels $E_{i;0}$ of $(\hbar^2/2m^*)\mathbf{K}^2$, where $\mathbf{K} = \mathbf{k} - \frac{1}{2}(e/\hbar c)\mathbf{H} \times \partial/\partial\mathbf{k}$, are highly degenerate, as they are for free electrons. For Bloch electrons, the *correct* eigenvalues $E_{i\rho}$ of $W_{\rho\rho'}(\mathbf{K})$ are also degenerate, but each degenerate level is broadened into a band, as one knows from the work of Kohn³⁷ and Blount.²² Here, this broadening is ignored because (a) the correct effective Hamiltonian $W_{\rho\rho'}$ is replaced by its zero-order term $W_{\rho\rho;0}$ (small fields), and (b) the energy band function in zero field is taken in the parabolic approximation

³⁶ I am indebted to Dr. Y. Yafet for pointing out that the second term on the right-hand side of this equation leads to a contribution to the contact shift which depends on all occupied states.

³⁷ W. Kohn, Proc. Phys. Soc. (London) **72**, 301 (1958); see also A. D. Brailsford, *ibid.* **A70**, 275 (1957) and G. E. Zil'berman, Zh. Eksperim. i Teor. Fiz. **32**, 296 (1957) [English transl.: Soviet Phys.—JETP **5**, 208 (1957)]. It has been pointed out by Kohn and Blount, for example, that at low fields this broadening is small compared with Landau splitting when the classical trajectories in \mathbf{k} space do not touch each other, which is the case if the Fermi surface does not come close to the surface of the Brillouin zone.

[Eq. (35)]. Then, with the gauge³⁸ $\mathbf{A} = \{0, Hx, 0\}$, the eigenvalues of $(\hbar^2/2m^*)\mathbf{K}^2$ are given by

$$E_{i;0} = E(n, \kappa_z) = (\hbar^2 s/m^*) (n + \frac{1}{2}) + \kappa_z^2/2m^*, \quad (36)$$

and the corresponding eigenfunctions have the form

$$\begin{aligned}
f_{i;0} &= f(n, \kappa_y, \kappa_z; \mathbf{k}) \\
&= [A_n(s)/(\Omega^*)^{1/3}] \exp[(i/s)k_x k_y] \\
&\quad \times \exp(-k_x^2/2s) H_n(k_x/s^{1/2}) \\
&\quad \times \delta(1 - k_z/\kappa_z) \delta(1 - k_y/\kappa_y), \quad (37)
\end{aligned}$$

where

$$s = eH/\hbar c, \quad A_n(s) = (\pi^{1/2} s^{1/2} n! 2^n)^{-1/2}, \quad (38)$$

and where $H_n(x)$ is the Hermite polynomial of n th degree. The subindex i stands for the three orbital quantum numbers n , κ_y , and κ_z . The amplitude function (37) is the Fourier transform of the Landau wave function

$$\begin{aligned}
g(n, \kappa_y, \kappa_z; \mathbf{r}) &= \frac{s^{1/2} A_n(s) i^n}{\Omega^{1/3}} \exp[i(\kappa_y y + \kappa_z z)] \\
&\quad \times \exp[-(\frac{1}{2}s)(x - x_0)^2] H_n[s^{1/2}(x - x_0)], \quad (39)
\end{aligned}$$

where $x_0 = -\kappa_y/s$ (see Appendix B).

With the help of the parabolic approximation, the Knight shift can be brought into a simple form which clearly demonstrates the spin-orbit coupling effect. For this purpose, the expression (37) for the amplitude function is substituted into the matrix element given by Eq. (34), then the δ functions are integrated out, and it is taken into account that the z part of the contact interaction ($H = H_z$) has vanishing matrix elements between Bloch spinors with different spin quantum numbers; the final expression for the contact interaction is given by

$$\langle i\rho | \mathcal{H}_c | i\rho \rangle = - (8\pi/3) \mu_{n,z} \sum_{\rho'} |c_{\rho\rho'}|^2 (F_{\rho'} + H G_{\rho'}), \quad (40)$$

where

$$\begin{aligned}
F_{\rho'}(n, \kappa_y, \kappa_z) &= (\Omega^*)^{-1/3} \int_{-\pi/a}^{+\pi/a} dk_x \int_{-\pi/a}^{+\pi/a} dk_x' \\
&\quad \times \exp\left[\left(\frac{i\kappa_y}{s}\right)(k_x' - k_x)\right] h_n\left(\frac{k_x}{s^{1/2}}\right) h_n\left(\frac{k_x'}{s^{1/2}}\right) \\
&\quad \times [u_{m\rho';0}^*(k_x, \kappa_y, \kappa_z) u_{m\rho';0}(k_x', \kappa_y, \kappa_z) \\
&\quad - v_{m\rho';0}^* v_{m\rho';0}], \quad (41)
\end{aligned}$$

and where

$$\begin{aligned}
G_{\rho'}(n, \kappa_y, \kappa_z) &= (\Omega^*)^{-1/3} \int_{-\pi/a}^{+\pi/a} dk_x \int_{-\pi/a}^{+\pi/a} dk_x' \\
&\quad \times h_n\left(\frac{k_x}{s^{1/2}}\right) h_n\left(\frac{k_x'}{s^{1/2}}\right) \{ \exp[(i\kappa_y/s)(k_x' - k_x)] \\
&\quad \times [u_{m\rho';z}^*(k_x, \kappa_y, \kappa_z) u_{m\rho';0}(k_x', \kappa_y, \kappa_z) \\
&\quad - v_{m\rho';z}^* v_{m\rho';0}] + \text{complex conj.} \}. \quad (42)
\end{aligned}$$

³⁸ It is convenient to choose this gauge, and not the $\frac{1}{2}(\mathbf{H} \times \mathbf{r})$ gauge, since it allows for simple Fourier transformations between coordinate and momentum representations.

The functions h_n are defined by the equation

$$h_n(k_x/s^{1/2}) = A_n(s) \exp(-k_x^2/s) H_n(k_x/s^{1/2}). \quad (43)$$

Let us substitute this expression for the contact interaction and the energy eigenvalues of the parabolic approximation

$$E_{i\rho} = E(n, \kappa_z) \mp \frac{1}{2} g(n, \kappa_z) \beta_e H, \quad (44)$$

[upper (lower) sign for $\rho = \uparrow (\downarrow)$]

into Eq. (29) for the free-energy correction. Then the Knight shift $K_c = -F/\mu_n H_z$ is given by

$$K_c = \frac{8\pi}{3} \left(\frac{\Omega^{1/3}}{2\pi} \right)^2 \beta_e \sum_{\rho} \sum_n \int_{-sa/2}^{sa/2} dk_y \int_{-\pi/a}^{+\pi/a} dk_z \times \frac{\sum_{\rho'} |c_{\rho\rho'}|^2 [(1/H)F_{\rho'}(n, \kappa_y, \kappa_z) + G_{\rho'}(n, \kappa_y, \kappa_z)]}{\exp\{[E(n, \kappa_z) \mp \frac{1}{2} g(n, \kappa_z) \beta_e H - \zeta]/kT\} + 1}. \quad (45)$$

This expression for the Knight shift is correct, in the parabolic approximation, for small magnetic fields and for arbitrary strength of spin-orbit coupling. The first part of K_c depends on F_{ρ} , which has opposite signs for "spin-up" ($\rho = \uparrow$) and "spin-down" ($\rho = \downarrow$) electrons. Therefore, only the unpaired spin electrons in the vicinity of the Fermi surface contribute. The first part exhibits spin-orbit coupling via three parameters, namely: the "dressed" g factor $g(n, \kappa_z)$, the coefficients $c_{\rho\rho'}$ which determine the admixture of Bloch functions from both the spin-up and spin-down band into a conduction-electron wave function, and the components $u_{m\rho;0}$ and $v_{m\rho;0}$ of a Bloch spinor in the absence of the field. All occupied states contribute to the second part of the Knight shift. It depends on that part of G_{ρ} which has equal sign for $\rho = \uparrow$ and $\rho = \downarrow$ and which vanishes in the absence of spin-orbit coupling. The first-order corrections $H_z u_{m\rho;0}$ to the field-independent Bloch functions occurring in G_{ρ} are calculated in Appendix C. At $T=0$, the Fermi-Dirac step function leads to the formula

$$K_c = (8\pi/3) \beta_e \sum_{\rho, \rho'} \sum_i |c_{\rho\rho'}|^2 [(1/H)F_{\rho'} + G_{\rho'}], \quad (46)$$

where \sum_i represents the number of states given by

$$\sum_i = \frac{\Omega^{2/3}}{4\pi^2} \sum_n \int_{-sa/2}^{+sa/2} dk_y \int_{-\pi/a}^{+\pi/a} dk_z. \quad (47)$$

The upper limit for the oscillator quantum number n depends on ρ ; one has

$$\bar{n}_{\rho} = \frac{\zeta \pm \beta_e g H / 2}{\hbar^2 s / m^*}. \quad (48)$$

Here g is defined as the mean value of $g(n, \kappa_z)$ over eigenstates with energies $E(n, \kappa_z) = \zeta$. The function F_{ρ} is of interest only at the Fermi surface, where

$$F_{\rho} = |u_{m\rho;0}(k_{\zeta})|^2 - |v_{m\rho;0}(k_{\zeta})|^2.$$

Writing G_{ρ} in terms of the series expansion (C1) and observing that, when $H \rightarrow 0$, the number of states \sum_i goes into $\sum_k = \int \rho(E) dE$, where $\rho(E)$ is the density of states in the parabolic approximation, we obtain the Knight shift in the form

$$K_c = \frac{16\pi}{3} \frac{\beta_e^2 g g_0}{4} \rho(\zeta) \sum_{\rho} |c_{\uparrow\rho}|^2 [|u_{m\rho;0}(k_{\zeta})|^2 + |v_{m\rho;0}(k_{\zeta})|^2] + \frac{16\pi}{3} \beta_e \sum_{\mathbf{k}} \sum_{\rho} |c_{\uparrow\rho}|^2 \times \{ \sum_{m' \neq m} \sum_{\rho' \neq \rho} A_z(m, \rho, \mathbf{k}; m', \rho', \mathbf{k}) \times [u_{m\rho;0}^* u_{m'\rho';0} - v_{m\rho;0}^* v_{m'\rho';0}] + \text{compl conj} \}. \quad (49)$$

Here $\rho(\zeta)$ is the density of states at the Fermi surface, $g_0 = 2$, and, in the second term, $u_{m\rho;0} = u_{m\rho;0}(\mathbf{r}=0; k)$. If spin-orbit coupling is ignored, $g = g_0$, $c_{\rho\rho'} = 0$ for $\rho \neq \rho'$, and $v_{m\rho;0} = 0$, so that the first part of K_c becomes equal to the original expression of Townes, Herring, and Knight.³⁹ The second part vanishes since $A_z(\rho \neq \rho_i) = 0$ for this case. For the special case where spin-orbit coupling is weak, g depends in first order and $|c_{\rho\rho'}|^2$ and $|u_{m\rho;0}|^2$ in second order on a smallness parameter $\lambda_{\zeta}/\Delta E_{\zeta}$, where λ_{ζ} is an average spin-orbit coupling energy for Bloch electrons at the Fermi surface and where ΔE_{ζ} is an average energy gap between conduction band states at the Fermi surface and excited states to which the orbital angular momentum connects. The second part of K_c is proportional to $\lambda(E)/[\Delta E(E)]^2$; it depends on the coefficients A_z , which are defined as coefficients in the series expansion (A4) for the first-order correction to the zero-field Bloch spinor $b_{m\rho;0}$. These coefficients are calculated in Appendix C; it is seen that A_z is proportional to an energy denominator times a matrix element which is of a form similar to the g factor. If one assumes that the corresponding spin-orbit contribution is positive, the total spin-orbit contribution to the Knight shift is given by

$$K_c^{\text{so}} = \left[\delta g(\zeta) + \int_0^{\zeta} \frac{\rho(E)}{\rho(\zeta)} \frac{\lambda(E)}{[\Delta E(E)]^2} dE \right] K_c. \quad (50)$$

It is this part of K_c which remains unaffected when a metal becomes superconducting, and $T \rightarrow 0$. The g shift δg is of the magnitude $\lambda_{\zeta}/\Delta E_{\zeta}$, but its sign cannot be predicted, even in this case of small spin-orbit coupling. We mention that for the three nontransition metals the second term in the bracket of Eq. (50) is of the order

$$(n/\Delta E_{\text{c.b.}})/\rho(\zeta) \simeq 1, \\ \frac{(n/\Delta E_{\text{c.b.}})}{\rho(\zeta)} \simeq 1,$$

³⁹ C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

if one assumes one conduction electron per atom and if $\Delta E_{e,b} \sim 3$ eV. (n = concentration of conduction electrons; $\Delta_{e,b}$ = average energy gap of conduction-band electrons.)

Spin-Orbit Coupling and T_1

In metals the pertinent relaxation mechanism for nuclear spins consists in an energy exchange with conduction electrons, caused by the hyperfine contact interaction \mathcal{H}_c . The corresponding relaxation time T_1 is determined by the transition probability P_{nm} of a nucleus between two spin states n and m , in a fashion well defined by statistical mechanics (see Hebel and Slichter^{40,41}). In order to calculate P_{nm} , the contact interaction is conveniently written in the form

$$\mathcal{H}_c(0, \mathbf{r}) = -(8\pi/3)\beta_e\beta_n\delta(\mathbf{r})[I_x\sigma_z + \frac{1}{2}(I_+\sigma_- + I_-\sigma_+)], \quad (51)$$

where $\mathbf{u}_n = \beta_n \mathbf{I}$, and $I_{\pm} = I_x \pm iI_y$. In the representation of Sec. I, the transition probability for a nucleus from state n to m and for an electron from state (i, ρ) to (i', ρ') is given by

$$P_{n,i,\rho;m,i',\rho'} = \frac{2\pi}{\hbar} \left(\frac{8\pi}{3} \beta_e \beta_n \right)^2 \times \sum_{\alpha, \alpha' = z, \pm} (n | I_{\alpha} | m) (m | I_{\alpha'} | n) \times (i\rho | \delta(\mathbf{r}) \sigma_{\alpha} | i'\rho') (i'\rho' | \delta(\mathbf{r}) \sigma_{\alpha'} | i\rho) \times \delta(E_{i\rho} + E_n - E_{i'\rho'} - E_m), \quad (52)$$

where E_n is the energy of a nucleus in state n . Summing this expression for all initial and final electron states and taking into account the statistical occupation of each state with the Fermi-Dirac function $f(E_{i\rho})$, we have the total transition probability per unit time

$$P_{nm} = \sum_{i,i'} \sum_{\rho,\rho'} P_{n,i,\rho;m,i',\rho'} f(E_{i\rho}) [1 - f(E_{i'\rho'})]. \quad (53)$$

To evaluate this expression, let us introduce the parabolic approximation for which $E_{i\rho}$ is given by Eq. (44) and for which \sum_i is given by Eq. (47). Then, to lowest order in H , one has

$$(i\uparrow | \sigma_+ \delta(\mathbf{r}) | i'\downarrow) = \frac{1}{\Omega^*} \int_{\Omega^*} d\mathbf{k} \times \int_{\Omega^*} d\mathbf{k}' h_n(k_x/s^{1/2}) h_n'(k_x'/s^{1/2}) \delta(1 - k_z/\kappa_z) \times \delta(1 - k_y/\kappa_y) \delta(1 - k_z'/\kappa_z') \delta(1 - k_y'/\kappa_y') \times \sum_{\rho,\rho'} \sqrt{2} c_{\uparrow\rho}^* c_{\downarrow\rho'} u_{m\rho;0}(\mathbf{k}) u_{m\rho';0}(\mathbf{k}'). \quad (54)$$

⁴⁰ L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).
⁴¹ C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963).

Since σ_+ and σ_- are Hermitian conjugates, we also know the matrix element of $\sigma_+ \delta(\mathbf{r})$. The third element, i.e., that of $\sigma_z \delta(\mathbf{r})$, gives no contribution to W_{mn} , if one assumes $E_{i\rho} = E_{i'\rho'}$. This assumption, however, is well justified since $E_m - E_n \ll kT$. Then, taking into account the δ -function character of $f(1-f)$, eliminating with its help the integration over κ_z , and eliminating the integration over κ_z' with the help of the δ function in the transition probability [Eq. (52)], we have

$$P_{mn} = a_{00} \sum_{\alpha, \alpha' = \pm} (n | I_{\alpha} | m) (m | I_{\alpha'} | n), \quad (55)$$

where the sum excludes the term $\alpha = \alpha'$, and where a_{00} defines T_1 .⁴² The *low-field* relaxation time is given by

$$\frac{1}{T} = 2a_{00} = \frac{4\pi}{\hbar} \left(\frac{8\pi}{3} \beta_e \beta_n \right)^2 kT \left[\frac{V^{2/3} (2m^*)^{1/2} - 2}{4\pi^2 \hbar} \right]^2 \times \int \int d\kappa_y d\kappa_y' \sum_{n,n'} [\zeta - (\hbar^2 s/m^*) (n + \frac{1}{2}) + g\beta_e H]^{-1} \times [\zeta - (\hbar^2 s/m^*) (n' + \frac{1}{2}) - g\beta_e H]^{-1} \times |(i\uparrow | \sigma_+ \delta(\mathbf{r}) | i'\downarrow)|^2. \quad (56)$$

Here the matrix element of $\sigma_+ \delta(\mathbf{r})$ is given by Eq. (54), with $\mathbf{k} = \{k_x, \kappa_y, \kappa_z(n)\}$ and with n determined by $E(n, \kappa_z) - g\beta_e H = \zeta$. If one assumes that at the Fermi surface, the matrix element is constant (i.e., independent of the direction of \mathbf{k}), the summation over n and the integration over κ_y can be performed; this leads to the density of states per unit volume,

$$\rho(\zeta) = (2m^*)^{3/2} \zeta^{1/2} / 4\pi^2 \hbar^3,$$

and to the relaxation rate

$$\frac{1}{T_1} = \frac{4\pi}{\hbar} \left(\frac{8\pi}{3} \beta_e \beta_n \right)^2 \rho^2(\zeta) kT \times |\sqrt{2} \sum_{\rho,\rho'} c_{\uparrow\rho}^* c_{\downarrow\rho'} u_{m\rho;0}^*(k_{\zeta}) u_{m\rho';0}(k_{\zeta})|^2. \quad (57)$$

When spin-orbit coupling is neglected, only the term with the factor $|c_{\uparrow\rho}^* c_{\downarrow\rho}| = 1$ contributes to the relaxation rate; then Eq. (57) becomes a well-known result (see Ref. 41, p. 126). For weak spin-orbit coupling, $1/T_1$ has a contribution quadratic in $\lambda/\Delta E$. Assuming arbitrary strength of spin-orbit coupling, we find, from Eqs. (49) and (57), the proper low-field Korringa relation for noninteracting electrons.^{43,44}

⁴² Coherent relaxation of two nuclei is ignored.

⁴³ For an external field H large compared with the local field (~ 10 G) but small compared with $\hbar c/ek_{\zeta}^2$ (so that $s/k_{\zeta} \ll 1$), the high-field Korringa relation contains a factor 2.

⁴⁴ To incorporate electron-electron interactions, the right side is multiplied by Pines' factor (see Ref. 41). The electron-phonon interaction has no effect on the spin susceptibility [J. J. Quinn, Ref. 17, p. 58; P. A. Wolf, Phys. Rev. **120**, 814 (1960)]; its effect on the density of states in T_1 is not known but is likely to be temperature-independent, as indicated by the experimental fact $T_1 T = \text{const}$ for Al and $1^\circ < T < 1000^\circ \text{K}$ (J. J. Spokas and C. P. Slichter, Phys. Rev. **113**, 1462, 1959).

As for the effect of spin-orbit coupling on the nuclear spin relaxation in a superconductor, the theory of Hebel and Slichter remains formally unchanged. The reason is that the spin-orbit coupling term in \mathcal{H}_0 has the symmetry of the Bravais lattice so that a ground pair occupies the states $(m, \mathbf{k}, \uparrow)$ and $(m, -\mathbf{k}, \downarrow)$ related by time-reversal symmetry. The corresponding BCS wave functions lead, aside from a constant factor, to the same nuclear spin relaxation time as that of the original theory. Therefore, for a given temperature $T < T_c$, the ratio of the relaxation times in the normal and the superconducting state, T_{1n}/T_{1s} , is not affected by the spin-orbit coupling force arising from the periodic crystalline field.

Spin-Reversing Scattering

Besides the spin-orbit coupling effects which were considered above and found to be of the Van Vleck type, there is another effect which gives rise to a *broadening* of the low-frequency contribution of the absorptive part $\chi''(\omega)$ of the spin susceptibility (see Fig. 2) and which therefore affects K_{cs} , namely spin-reversing scattering. This effect has been discussed in the literature⁷⁻⁹ and more recently also the nuclear spin relaxation time T_{1s} has been calculated by Griffin and Ambegoakar,⁴⁵ including spin-reversing scattering. Here we shall merely summarize the results, so that we can assess the relative importance of both the total effect arising from the crystalline field and the one caused by spin-reversing scattering.

The first quantitative result for the spin susceptibility of small particles, where surface scattering plays an important role, was derived by Anderson.⁷ He introduced exact one-electron states, the scattered states ψ_n, ϵ_n , and then calculated the perturbation theoretical expression for the susceptibility in terms of the matrix elements $S_{nn'} = (\psi_n | \sigma_z | \psi_{n'})$. The energy dependence of these elements is taken from the function $\chi''(\omega) \propto (1 + \omega^2 \tau_s^2)^{-1}$, where τ_s is a spin lifetime. The final result is given by

$$\lim_{T \rightarrow 0} (\chi_s / \chi_n) = 1 - 2\epsilon_0 \tau_s / \hbar, \quad \hbar / \tau_s \gg \epsilon_0, \quad (58)$$

$$= \hbar / 6\epsilon_0 \tau_s, \quad \hbar / \tau_s \ll \epsilon_0.$$

Anderson's consideration ignores the effect of spin-reversing scattering on the energy gap and on the density of states for quasiparticle excitations in a superconductor. Nevertheless, Eq. (58) will be approximately correct, since the major contribution to the second-order perturbation expression for χ_s comes from matrix elements $S_{nn'}$ with energy differences larger than ϵ_0 (Fig. 2). The corresponding density of states, however, remains unaffected by spin-reversing scattering, $\rho_s(E_n) \simeq \rho_s(E_k)$ for $E \gg 2\epsilon_0$. Therefore, Anderson's result is in nearly quantitative agreement with the corresponding

⁴⁵ A. Griffin and V. Ambegoakar, Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, August, 1964 (to be published).

one of Abrikosov and Gor'kov,⁹ although these authors, with the help of their Green's-function formalism* for impure superconductors, take all the effects of scattering into account. It is necessary to do so in a calculation of the ratio of the nuclear spin relaxation time in the normal and the superconducting state. Here, it is the squared quasiparticle density of states, in particular, near the gap edge, which causes the enhancement of $1/T_{1s}$, and not the matrix element $S_{nn'}$. In other words, it appears that the expression, which Hebel and Slichter derive for the nuclear spin relaxation time with the help of the BCS theory, remains approximately valid for superconductors with spin-reversing scattering centers, provided the actual gap is taken for $2\epsilon_0(T)$ and the actual density of states is used for ρ_s . A correct formal theory of T_{1s} will be published by Griffin and Ambegoakar.⁴⁵

As for the crucial parameter τ_s , the average spin lifetime, a rough estimate can be made if it is limited by spin-orbit scattering at displaced surface atoms. Then, in the Born approximation, τ_s is determined by the square of the matrix element

$$M_{k, k'; \rho, \rho'} = \left(b_{m\rho}(\mathbf{r}, \mathbf{k}) \left| V_p(\mathbf{r}) \right. \right. \\ \left. \left. + \frac{\hbar}{4m^2 c^2} \partial V_p / \partial \mathbf{r} \times \mathbf{p} \cdot \boldsymbol{\sigma} \right| b_{m\rho'}(\mathbf{r}, \mathbf{k}') \right). \quad (59)$$

Here, the spin-orbit coupling term connects the large spinor components of $b_{m\rho}$ and $b_{m\rho'}$, and the perturbing potential V_p connects the small spinor component of $b_{m\rho}$ with the large spinor component of $b_{m\rho'}$. The first contribution is of the order of $\lambda/\Delta E$ times the matrix element for ordinary scattering from a screened Coulomb potential. The second contribution is of the same magnitude, if one makes the reasonable assumption that $(b_{m\rho} | V_p | b_{m\rho}) \approx \Delta E$.⁴⁶ Then $\tau_s \propto (\Delta E/\lambda)^2$ and, since the ordinary scattering time τ_r , which determines the residual resistance is determined by $(b_{m\rho}(\mathbf{r}, \mathbf{k}) | V_p | b_{m\rho}(\mathbf{r}, \mathbf{k}'))$, one may consider $(\lambda/\Delta E)^2$ to be the probability of a spin flip in a single scattering event. For a film with thickness d , we have $\tau \simeq d/v_f$, where v_f is the average Fermi velocity, and thus $\tau_s \simeq (d/v_f)(\Delta E/\lambda)^2$.

If the spin lifetime τ_s is limited by the exchange interactions between a conduction electron and magnetic impurities, one also expects τ_s to be one to two orders of magnitude larger than τ_r , the reason being that non-exchange interactions, i.e., Coulomb interactions, are always smaller than comparable exchange interactions.^{47, 48} In a concrete case, namely Zn-Mn alloys,

⁴⁶ The major contribution to this matrix element comes from the core region of the perturbing potential where $V_p(\mathbf{r}) \simeq V(\mathbf{r})$ for a displaced surface atom.

⁴⁷ A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 39, 1781 (1960) [English transl.: Soviet Phys.—JETP 12, 1243 (1961)].

⁴⁸ P. W. Anderson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 169.

the s - d exchange integral $|J|$, indicated by the resistance change when magnetic ordering occurs, is $\sim 1.5 \times 10^{-12}$ erg or $\sim \frac{1}{10}$ of the Fermi energy for zinc⁴⁹; in another case, that of dilute Cu-Fe alloys, the observed resistance minimum is accounted for by Kondo's theory,⁵⁰ if $|J| \sim 2.5 \times 10^{-12}$ erg.

Orbital Interaction and Knight Shift

In the special case where spin-orbit coupling is ignored, one takes $\gamma \mathbf{p}$ in Eq. (26), instead of the bracket, and then \mathcal{H}_0 on the right-hand side of this equation must be omitted, since K_c is exactly compensated for by the shift arising from the spin-orbit coupling term alone. Ignoring spin-orbit coupling, Hebborn³⁴ has derived an exact expression for K_{orb} ; including it, Yafet³⁵ has worked out K_{orb} for a small number of degenerate conduction electrons. In both cases, \mathcal{H}_{orb} is conveniently split into a long-range part, where, in Eq. (26), \mathbf{r}_j is outside the unit cell centered at \mathbf{R}_l , and the residual short-range part, which is periodic in \mathbf{r}_j . Some results of these authors are as follows:

The long-range contribution $K_{\text{orb}}(l)$ consists of a diamagnetic part, caused by the interaction between nuclear moments and diamagnetic surface currents, which give rise to the induced magnetic moment $\mathbf{M} = \chi_d(l)\mathbf{H}$, and a Van Vleck-type paramagnetic part arising from the interaction between nuclear moments and the orbital magnetic moments of the conduction electrons given by Eqs. (A5) and (A6). For a small number of degenerate electrons, the total $K_{\text{orb}}(l)$ is approximately given by

$$K_{\text{orb}}(l) \simeq (4\pi - D)[\chi_d(l) + (\beta_e^2/2)g(g - g_0)\rho(\zeta)], \quad (60)$$

where we take $\chi_d(l) = \chi_{\text{LP}} = -e^2 k_t / 12\pi m^* c$, i.e., the Landau-Peierls susceptibility, and where D is the demagnetizing factor. The short-range contribution $K_{\text{orb}}(s)$ plays a significant role in transition metals,¹⁵ because of its paramagnetic (Van Vleck-type) contribution which is ignored here. Its diamagnetic contribution is difficult to assess, except for Bloch bands which can be treated in the tight binding approximation, then it is approximately given by the diamagnetic core susceptibility of the metal ions.⁵¹ For simple metals like Al, however, one knows from the work of Kohn and Kjeklaas⁵² (Li, Na) that χ_{LP} alone gives too large a value for the total diamagnetic susceptibility. Short of a calculation of this type, we take the total orbital shift in the form

$$K_{\text{orb}} = (4\pi - D)[\chi - \beta_e^2(g_0 g / 2)\rho(\zeta)], \quad (61)$$

where χ is the total observed magnetic susceptibility.⁵³

⁴⁹ E. W. Collins, F. T. Hedcock, and Y. Muto, Phys. Rev. **134**, A1521 (1964).

⁵⁰ J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

⁵¹ R. Peierls, Z. Physik **80**, 763 (1933).

⁵² T. Kjeklaas and W. Kohn, Phys. Rev. **105**, 806 (1957).

⁵³ As for an evaluation of $K_{\text{orb}}(s)$, in a fashion similar to the calculation of K_c in Sec. II, the calculation is straightforward if one uses the parabolic approximation. In the limit $H=0$, one has $\langle i\rho | \mathcal{H}_{\text{orb}}(s) | i\rho \rangle = 0$, since the two contributions from \mathcal{H}_c

III. DISCUSSION OF THE EMPIRICAL DATA

For this purpose, the total Knight shift of a non-transition-metal superconductor is written in the form⁵⁴

$$K_s = K_{\text{orb}} + K_c^{\text{so}}(\lambda/\Delta E) + K_c^{\text{sr}}(\tau_s \epsilon_0 / \hbar). \quad (62)$$

Here, the orbital shift, K_{orb} , and the Van Vleck part of the contact shift K_c^{so} are assumed to be temperature-independent and to remain unchanged by the transition. The third term of K_s is given by

$$K_c^{\text{sr}} = (\chi_s/\chi_n)(K_c - K_c^{\text{so}})_n, \quad (63)$$

where χ_s/χ_n is the temperature-dependent ratio of the spin susceptibility determined by the spin lifetime

$$1/\tau_s = 1/\tau_s^{\text{so}} + 1/\tau_s^{\text{ex}}.$$

τ_s is limited by spin-orbit scattering at nonmagnetic imperfections and by exchange scattering at paramagnetic impurities. We wish to discuss the relative importance of the different contributions to K_s for Al, Sn, and Hg, where the Knight shift has been measured in the normal and the superconducting state.

This discussion is confronted with some serious difficulties. First, we do not know the signs of the two different contributions to K_c^{so} . However, it appears unlikely that the two terms nearly cancel one another, since the first is determined by spin-orbit parameters at the Fermi surface, whereas all occupied states contribute to the second. For the following discussion, it is assumed that $K_c^{\text{so}}/K_c \simeq \lambda/\Delta E$. Second, there are no quantitative values for bulk parameters, such as the average spin-orbit coupling energy λ of electrons at and inside the Fermi surface and the corresponding energy gap ΔE , nor for impurity parameters such as the spin lifetime τ_s^{so} or, if magnetic impurities are present, the exchange integral J . Furthermore, in none of these three metals has electron-spin resonance, from which one could obtain some information regarding $\lambda/\Delta E$ and τ_s , been observed. A convenient theoretical estimate of $\lambda/\Delta E$ would presume the knowledge of Bloch functions in the orthogonalized-plane-wave (OPW) approximation, where⁵⁵

$$b_m(\mathbf{r}, \mathbf{k}) = \text{PW} + \text{AO} = \sum_n C_{mn}[(\text{PW}, n) - \sum_t C_{tn} \varphi_t]. \quad (64)$$

Here, AO = atomic orbital, (PW, n) is a plane wave with wave vector $\mathbf{k} + \mathbf{K}_n$ ($\mathbf{K}_n = 2\pi$ times vector in the reciprocal lattice), and φ_t is an atomic orbital in the potential $V(\mathbf{r})$. The spin-orbit matrix elements between the φ_t 's can, in a good approximation, be determined from the tabulated atomic energy levels. These elements and the

($=\mathcal{H}_c(s)$) and from the spin-orbit coupling term, cancel one another. To first order in H , there occurs the paramagnetic Van Vleck term, i.e., interband matrix elements of the orbital angular momentum, and an "intra-band" diamagnetic term.

⁵⁴ Equation (62) also holds if there is a significant contact interaction with ion-core s electrons; then K_c is to be replaced by $K_c + K_{\text{sp}}$.

⁵⁵ See V. Heine, Proc. Roy. Soc. (London) **240**, 354 (1957).

constants C_{mn} and C_{ln} determine λ . Finally, the experimental Knight shift results do not allow for a clear-cut interpretation because of the complex temperature dependence⁵⁶ and field dependence⁵⁷ of the energy gap in the small particles used in NMR experiments. These dependences have not been measured directly on either of the samples on which the NMR phenomena have been observed; however, all authors^{4,5,19} have been aware of this difficulty. Because of the reasons given above, the following discussion is of a qualitative nature only.

Aluminum

As for its electronic structure, aluminum is the simplest and most carefully studied multivalent metal.^{16,55} Furthermore, because of its small atomic number and its weak electron-phonon interaction, it comes close to the assumptions of the nonrelativistic BCS theory. Why, then, does the Knight shift observed by Hammond¹⁹ decrease by only 25% of its value at T_c , as $T \rightarrow 0$? The orbital shift is calculated from Eq. (61) with $D=0$, and with the help of susceptibility values tabulated by Knight.⁵⁸ By taking χ =total bulk susceptibility and approximating the paramagnetic term in Eq. (61) by the bulk spin susceptibility, we find that K_{orb} amounts to 9% of the observed shift in the normal state (see Table I). The characteristic parameter for the two spin-orbit coupling effects, $\lambda/\Delta E \ll 1$, since (a) in an OPW wave function for a conduction electron in Al, the plane-wave part has a much larger amplitude than

the orbital part, and (b) the spin-orbit matrix elements between atomic orbitals are small. Assuming that $\frac{9}{10}$ and $\frac{1}{10}$ of the squared amplitude $|b_m(\mathbf{k})|^2$ inside the core, where the spin-orbit interaction is strong, corresponds to PW and AO, respectively, and that a very rough measure for the spin-orbit energy of the $2p$ orbitals in AO is provided by the multiple splitting ($3s^3P_1 - 3s^3P_2$) = 1741 cm^{-1} (Al IV⁵⁹), we have $\lambda \simeq 0.022$ eV. With a band gap $\Delta E = 3$ eV, one clearly sees that both of the spin-orbit coupling effects give a negligible contribution to the Knight shift at $T=0$. The estimated spin lifetime τ_s^{so} is larger by a factor 10^3 than the experimental value $\tau_s(\text{expt}) \simeq 0.5 \times 10^{-12}$ sec, necessary to account for Hammond's result with Eq. (58). Such a small value of the spin lifetime in Al can be explained by the presence of paramagnetic impurities, a possibility suggested by Matthias.⁶⁰ If, in fact, the oxide layer on the surface of an aluminum film is paramagnetic, so that with each surface scattering event an exchange interaction occurs, then the value $\tau_s(\text{expt})/\tau_s \simeq 10^{-3}$ is a reasonable number. It is mentioned above that the relevant exchange integral is one to two orders of magnitude smaller than the corresponding Coulomb integral. Furthermore, the small (20-30%) enhancement of the nuclear spin relaxation rate $1/T_{1s}$ below T_c observed by Hammond,¹⁹ and also observed in a systematic study of side effects on T_{1s} by Masuda and Redfield,⁶¹ is compatible with the experimental value of τ_s , which corresponds to the Abrikosov-Gor'kov parameter $\rho_0 \simeq 4$, as can be seen from the work of Griffin and Ambegoakar.⁴⁵ From the observed temperature dependence of T_{1s} , Masuda and Redfield find in their sample a reduction of the energy gap by a factor $\frac{1}{2}$ with particle sizes between 200 and 700 Å. Such a reduction is consistent with the effect of magnetic impurities on the energy gap of bulk superconductors. Correspondingly, a reduction in T_c is to be expected. Hammond,¹⁹ for his thin-film sample, did not observe a T_c significantly different from the bulk T_c of pure Al. This must not be a contradiction to the assumption of a paramagnetic oxide layer at the film surface, since an increase of T_c with decreasing size parameter has been observed for Al by Douglass and Meservey⁵⁶ (the phenomenon is attributed to differential contraction of substrate and film, i.e., to strains within the film).

Tin

Apparently no band structure calculation has been performed for β tin which crystallizes in a slightly deformed diamond lattice. From the experimental investigation of various electronic-transport phenomena in a magnetic field, it is known that the Fermi surface (F.S.) of Sn, containing 4 valence electrons, is rather complex; it is partly open and extends over a number of Brillouin

TABLE I. Estimated Knight-shift values for nontransition-metal superconductors.

Metal	Al	Sn	Hg
K_n in percent ^a (expt)	0.162	0.709	2.5
K_{orb}/K_n	0.09	0.06	0.03
$\lim_{T \rightarrow 0} K_s/K_n$ (expt)	0.75 ^b	0.76 ^c	0.66 ^d
particles	films	pellets	spheres
	$d \sim 200$ Å	$d \sim 50$ Å	$d \sim 500$ Å
$2\epsilon_0(0)$ in 10^{-4} eV (expt)	3.14 ^e	12.0 ^e	16.5 ^f
Spin-orbit energy λ in eV	0.022	0.36	0.48
$K_c^{so}/K_c \simeq \lambda/\Delta E$	0.008	0.12	0.16
	$(\Delta E = 3 \text{ eV})$		
v_f in 10^{-7} cm/sec (expt)	13 ^g	5.4 ^h	10 ⁱ
$\tau_r \sim d/v_f$ in 10^{-14} sec	1.6	0.93	5
$\tau_s^{so}/\tau_r = (\Delta E/\lambda)^2$	1.9×10^4	70	39
ρ_0 (A - G parameter ^j)	9.2×10^{-3}	1.1	0.27
χ_s/χ_n^j ($T=0$)	0.007	0.45	0.11
K_c^{st}/K_c ($T=0$)	0.007	0.36	0.22
$K_s(\text{calc}^k)/K_n$ ($T=0$)	0.11	0.51	0.40

^a Reference 61. ^b Reference 19. ^c Reference 5. ^d Reference 4. ^e Reference 59. ^f S. Berman and D. M. Ginsberg, Phys. Rev. **135**, A306 (1964). ^g E. Fawcett, Ref. 62. ^h Estimated. ⁱ Reference 9. ^k Equation (62).

⁵⁶ D. H. Douglass, Jr., and R. Meservey, Phys. Rev. **135**, A19 (1964).

⁵⁷ R. Meservey and D. H. Douglass, Phys. Rev. **135**, A24 (1964); P. G. DeGennes and M. T. Tinkham, Physics **1**, 107 (1964).

⁵⁸ W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, pp. 114, 116, Table II, column 3.

⁵⁹ C. E. Moore, Natl. Bur. Std. (U.S.) Circ. 467, Vol. 1, (1949).

⁶⁰ Private communication.

⁶¹ Y. Masuda and A. G. Redfield, Phys. Rev. **133**, A944 (1964).

zones.⁶² The Hall coefficient is small and changes sign with temperature.⁶³ Since the Knight shift does not depend on the curvature of a surface of constant energy, but only on $|\partial E/\partial \mathbf{k}|$, we estimate an average spin-orbit energy λ for electrons and holes in unfilled bands by assuming that one-half of the amplitude of $\sum_m |b_m(\mathbf{r}, \mathbf{k})|^2$ corresponds to the AO part of the OPW wave function. A rough estimate for the spin-orbit energy of AO is provided by the multiplet splitting $\frac{1}{2}(5s^3D_1 - 5s^3D_3) = 4311.6 \text{ cm}^{-1}$ (Sn V⁶⁴). This number, $\sim 0.54 \text{ eV}$, is of the same magnitude as the one found by Herman, Kuglin, Cuff, and Kortum⁶⁵ in a more reliable estimate of the spin-orbit energy for a p -like valence-band edge of gray tin, 0.71 eV . Taking this value, we have calculated K_e^{so} and τ_s^{so} given in Table I. The spin lifetime $\tau_s^{so} \simeq 10^{-12}$ sec for this particular sample. The two spin-orbit coupling effects are of comparable magnitude and, together with K_{orb} , account for most of the residual Knight shift ($T \rightarrow 0$). Furthermore, the sizable Van Vleck type contribution K_e^{so} which arises from the spin-orbit force of the periodic crystalline field can well account for the observation of Androes and Knight that there is no strong dependence on the experimental particle size.

Mercury

The electronic structure of solid mercury, which crystallizes in a rhombohedrally deformed bcc lattice, is apparently not known. The measured Hall constant at 213°K is -8.7×10^{-25} Gaussian units, comparable with that of gold at room temperature. The observed Knight shift is large compared with that of other heavy metals, like Pb and Tl, which have an even larger hyperfine coupling constant. To estimate roughly a spin-orbit coupling energy, let us assume that a large fraction of the conduction electron wave functions, say one-half, corresponds to the PW part of the OPW wave function, and that the spin-orbit energy of the AO part is given by $\frac{1}{2}(6s^3D_1 - 6s^3D_3) = 7777.3 \text{ cm}^{-1}$ (Hg III⁶⁶). The corresponding values of K_e^{so} , τ_s^{so} , etc., are found in Table I. The orbital shift K_{orb} is calculated from Eq. (61) with the help of susceptibility values tabulated by Knight.⁶⁸ It is seen that the spin-orbit coupling effect arising from the crystalline field is as important as spin-orbit scattering. The least reliable assumption here is that one-half of the OPW function corresponds to the plane-wave part. If, instead, inside the core, where spin-orbit coupling is strong, three-fourths and one-fourth of the squared amplitude of the OPW functions for conduction electrons correspond to the PW and the

AO parts, respectively, then $K_e^{so}/K_n \simeq 0.08$ and, for $d = 500 \text{ \AA}$, $K_e^{so}/K_n \simeq 0.03$. With these numbers, the calculated residual shift amounts to only 10% of the total shift in the normal state. Therefore, at present, our poor knowledge concerning the electronic structure of solid Hg does not allow for a quantitative estimate of $K_s(T=0)$; one can merely say that such a value lies between 10 and 50%. The earlier experimental results of Knight, Androes, and Hammond⁶⁷ for the Knight shift in superconducting Hg at 2°K and in a magnetic field of 5000 G, $K_s/K_n \sim 0.20$, cannot be dismissed as due to a decrease of K_s in high magnetic fields.⁶⁸

IV. CONCLUSIONS

It is seen from Table I (Sec. III) that the effect of spin-orbit coupling, arising from the periodic crystalline field, on the residual Knight shift $K_s(0)$ of the three nontransition-metal superconductors Al, Sn, and Hg is as important as the effect of spin-orbit scattering at displaced surface atoms of small particles. The two different spin-orbit coupling effects are separable because the average spin lifetime τ_s^{so} is size-dependent. Although the two spin-orbit coupling effects account for a substantial portion of the residual Knight shift observed in Sn and Hg, they play only a minor role in Al. To account for the observed residual shift with τ_s , it must be smaller by a factor of 10^3 than τ_s^{so} . Such a small τ_s can occur in small particles with a paramagnetic oxide surface layer, so that in each surface scattering event a conduction electron undergoes an exchange interaction with paramagnetic imperfections. Then, one can also understand the small enhancement of the nuclear spin relaxation rate observed in small Al particles. It is emphasized that the true residual Knight shift, i.e., the shift in the bulk material which, aside from the orbital shift, is determined by the spin-orbit coupling effect considered in Sec. II, can be observed only if the nuclear spin relaxation rate exhibits below T_c the same enhancement as that in bulk Al. This also follows from Sec. II, where it is pointed out that *the spin-orbit coupling effect arising from the crystalline field affects the residual Knight shift but does not affect the ratio of the nuclear spin relaxation rate in the superconducting and the normal state*. On the other hand, it is known that spin-reversing scattering affects both the residual Knight shift and the nuclear spin relaxation rate. Therefore, in a light nontransition-metal superconductor, where spin-orbit coupling can be ignored (Al), the proper enhancement of the nuclear spin relaxation rate provides a sensitive criterion for the absence of magnetic imperfections. In a heavy nontransition-metal superconductor, where spin-orbit coupling is important, the corresponding enhancement is determined by τ_s^{so} ,

⁶² E. Fawcett, Ref. 17, p. 197; T. Olsen, Ref. 17, p. 237; A. V. Gold and M. G. Priestley, Phil. Mag. **5**, 1089 (1960); E. S. Borovik, Izv. Akad. Nauk (USSR) **19**, 429 (1955).

⁶³ Landolt-Boernstein Tables, edited by K. H. and A. M. Hellwege (Springer-Verlag, Berlin, 1959), Vol. 6/L.

⁶⁴ Reference 59, Vol. III.

⁶⁵ F. Herman, C. D. Kuglin, K. F. Cuff, and L. Kortum, Phys. Rev. Letters **11**, 540; F. Herman, LMSC report 895374, Sec. 4 (unpublished).

⁶⁶ Reference 59, Vol. III.

⁶⁷ W. D. Knight, G. M. Androes, and R. H. Hammond, Phys. Rev. **104**, 1 (1956).

⁶⁸ F. Reif, Phys. Rev. **106**, 208 (1957).

whereas the residual shift is determined by both spin-orbit scattering and the bulk spin-orbit coupling effect depending on λ .

ACKNOWLEDGMENTS

It is a pleasure to thank Professor W. Kohn for many stimulating and helpful discussions on the entire subject matter of this paper and Dr. R. Hammond for innumerable valuable discussions on NMR phenomena. I am indebted to Professor Ferrell for some stimulating conversations, to Professor Ambegoakar and Dr. Griffin for a copy of their unpublished report, and to Dr. Y. Yafet for correcting a serious error in Eq. (49).

ADDENDUM

Assuming that both the spin-orbit interaction and the orbital interaction between electrons and magnetic field can be treated as a small perturbation with respect to the periodic Hamiltonian $\mathcal{H}_0 = p^2/2m + V(\mathbf{r})$, Y. Yafet has calculated the spin density at the nucleus with standard second-order perturbation theory. The corresponding correction to the contact shift depends on all occupied states. From his perturbation-theoretic expression for the spin density at the nucleus, it is concluded that the corresponding contact shift is positive, if the inner bands involve large energy denominations and if the amplitudes of the conduction-electron wave functions at the nucleus are much larger than those of higher lying bands. Then, the result, which he considers to be an overestimate, is given by

$$K_c^{so}/K_0 = [\lambda/(\Delta E)^2]n/\rho(\dot{r}).$$

APPENDIX A

g Factor

Strictly speaking, one must distinguish between the g factor for a Bloch electron in the state (m, \mathbf{k}) of a simple (i.e., orbitally nondegenerate) band of a crystal with inversion center, and the g factor for an exact eigenstate of \mathcal{H}_0 , denoted by (i) . The former, $g(m, \mathbf{k})$, measures the splitting linear in H which occurs between a spin-up state $(m, \mathbf{k}, \uparrow)$ and the corresponding spin-down state, whereby the effect of the magnetic field on the orbital motion is ignored. The latter, $g(i)$, is defined as that part of the energy difference between a spin-up state (i, \uparrow) and the corresponding spin-down state of \mathcal{H}_0 which is linear in H . To determine $g(m, \mathbf{k})$, the $b_{m\rho}$ and $W_{m\rho\rho'}$ are written as a power series expansion in H :

$$\begin{aligned} b_{m\rho}[\mathbf{r}, \mathbf{k} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l] \\ = b_{m\rho;0} + H^\alpha b_{m\rho;\alpha} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l \\ \cdot (\partial/\partial \mathbf{k})b_{m\rho;0} + \dots, \quad (\text{A1}) \end{aligned}$$

$$\begin{aligned} W_{m\rho\rho'}(\mathbf{k}) = W_{m\rho\rho';0} + H^\alpha W_{m\rho\rho';\alpha} + \dots, \\ (\alpha = x, y, z), \quad (\text{A2}) \end{aligned}$$

where the $b_{m\rho;0}$ are Bloch spinors in zero field and where the $W_{m\rho\rho;0}$ are the corresponding energy band functions; these are spin-degenerate because we assume inversion symmetry. The series expansion for $b_{m\rho}$ and the one for $\omega_{m\rho\rho'}$, which is found from Eqs. (5) and (A2), are substituted into Eq. (8). Taking the scalar product of this equation with $b_{m\rho';0}$, we obtain to first order in H^α the equation

$$\begin{aligned} (b_{m\rho';0} | \mathcal{H}_0(\mathbf{A}=0) | b_{m\rho;\alpha}) H^\alpha \\ + (b_{m\rho';0} | - (e/2mc)\mathbf{p} \cdot \mathbf{H} \times (\mathbf{r} + i\partial/\partial \mathbf{k}) | b_{m\rho;\alpha}) \\ + (b_{m\rho';0} | (\hbar/4m^2c^2)(\partial V/\partial \mathbf{r}) \cdot [-\frac{1}{2}(e/c)\mathbf{H} \\ \times (\mathbf{r} + i\partial/\partial \mathbf{k})] \cdot \boldsymbol{\sigma} | b_{m\rho;0}) + (b_{m\rho';0} | (\hbar/4im^2c^2) \\ \times (-e/2c)(\partial V/\partial \mathbf{r}) \cdot \mathbf{H} \times (\mathbf{r} + i\partial/\partial \mathbf{k}) | b_{m\rho;0}) \\ + (b_{m\rho';0} | \beta_e \boldsymbol{\sigma} \cdot \mathbf{H} | b_{m\rho;0}) \\ = W_{m\rho\rho;0} H^\alpha (b_{m\rho';0} | b_{m\rho;\alpha}) + \sum_{\rho''} W_{m\rho\rho'';\alpha} H^\alpha \\ \times (b_{m\rho';0} | b_{m\rho'';0}) + \sum_l \omega_{m\rho\rho;0}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l) \\ \times [(-ie/2\hbar c)\mathbf{H} \times \mathbf{R}_l \cdot (b_{m\rho';0} | \mathbf{r} | b_{m\rho;0}) \\ + (e/2\hbar c)\mathbf{H} \times \mathbf{R}_l \cdot (b_{m\rho';0} | \partial/\partial \mathbf{k} | b_{m\rho;0})]. \quad (\text{A3}) \end{aligned}$$

The spinor $b_{m\rho;\alpha}$, which is periodic in \mathbf{r} , is written in terms of the complete set of Bloch spinors,

$$b_{m\rho;\alpha}(\mathbf{r}, \mathbf{k}) = \sum_{m', \rho', \mathbf{k}'} A_\alpha(m, \rho, \mathbf{k}; m', \rho', \mathbf{k}') b_{m\rho;0}(\mathbf{k}'). \quad (\text{A4})$$

Then the first term on the left and on the right cancel one another. From Eq. (A3), and for $\rho = \rho'$ and $\rho \neq \rho'$, one finds the result given by

$$\begin{aligned} \sum_{\alpha=x,y,z} W_{m\rho\rho;\alpha} H^\alpha = (b_{m\rho;0} | \beta_e \boldsymbol{\sigma} \cdot \mathbf{H} | b_{m\rho;0}) \\ + (b_{m\rho;0} | -\frac{1}{2}(e/c)(\hbar/4im^2c^2)(\partial V/\partial \mathbf{r}) \\ \cdot \mathbf{H} \times (\mathbf{r} + i\partial/\partial \mathbf{k}) | b_{m\rho;0}), \quad (\text{A5}) \end{aligned}$$

$$\begin{aligned} \sum_{\alpha} W_{m\rho\rho';\alpha} H^\alpha = (b_{m\rho';0} | -\frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{r} + i\partial/\partial \mathbf{k}) \\ \cdot [\mathbf{p}/m + (\hbar/4m^2c^2)\boldsymbol{\sigma} \times \partial V/\partial \mathbf{r}] | b_{m\rho;0}) \\ + i \sum_l \omega_{m\rho\rho;0}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l) \frac{1}{2}(e/\hbar c)\mathbf{H} \times \mathbf{R}_l \\ \cdot (b_{m\rho';0} | \mathbf{r} + i\partial/\partial \mathbf{k} | b_{m\rho;0}). \quad (\text{A6}) \end{aligned}$$

The first expression is the spin magnetic moment plus a term which arises from the Darwin correction and which has the same sign for the spin-up and the spin-down band. The second represents the exact expression for the orbital magnetic moment of an arbitrary state (m, \mathbf{k}) and can be considered as the generalization of the band edge value for the g factor which results from the procedure of Luttinger and Kohn.⁶⁹ Equation (A6) has

⁶⁹ J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

been derived before by Roth²³ and by Blount.²² The derivations given in their papers are, however, much more involved than the one presented here. To obtain an *explicit* expression for $g(m, \mathbf{k})$ one may merely follow the diagonalization procedure of Cohen and Blount.⁷⁰

As for the g factor $g(i)$ for an eigenstate of \mathcal{H}_0 , let us consider the effective Hamiltonian for small magnetic fields. Then, to first order in H , the four simultaneous equations (23) become (the band index m is omitted):

$$W_{\uparrow\uparrow;0}(\mathbf{K})f_{\uparrow\uparrow}(\mathbf{k}) + H^\alpha W_{\downarrow\uparrow;\alpha}(\mathbf{K})f_{\downarrow\uparrow}(k) = E_\uparrow f_{\uparrow\uparrow}(\mathbf{k}) \quad (\text{A7})$$

and, similarly,

$$H^\alpha W_{\uparrow\downarrow;\alpha}f_{\uparrow\downarrow} + W_{\downarrow\downarrow;0}f_{\downarrow\downarrow} = E_\downarrow f_{\downarrow\downarrow}, \quad (\text{A8})$$

$$W_{\uparrow\uparrow;0}f_{\downarrow\uparrow} + H^\alpha W_{\downarrow\uparrow;\alpha}f_{\downarrow\uparrow} = E_\downarrow f_{\downarrow\uparrow}, \quad (\text{A9})$$

$$H^\alpha W_{\uparrow\downarrow;\alpha}f_{\downarrow\downarrow} + W_{\downarrow\downarrow;0}f_{\downarrow\downarrow} = E_\downarrow f_{\downarrow\downarrow}. \quad (\text{A10})$$

For the special case where the first-order terms in H^α are also ignored, the eigenvalues of Eqs. (A7) and (A9) are degenerate, $E_\uparrow = E_\downarrow$, for each state (i) and, furthermore, the corresponding amplitude functions $f_{\uparrow\uparrow}$ and $f_{\downarrow\uparrow}$ can only differ by a constant factor, independent of H . This factor must be determined by the spin-orbit coupling strength since, if it is neglected, $f_{\downarrow\uparrow}$ must be zero. The next step is to consider the nondiagonal components of the effective Hamiltonian as a small perturbation which is allowed, even for the case of strong spin-orbit coupling, provided the magnetic field is sufficiently small. Consequently, one may write the following perturbation expansions in $|\mathbf{H}|^{71}$:

$$W_{\rho\rho'}(\mathbf{K}) = W_{\rho\rho';0}(\mathbf{K}) + HW_{\rho\rho';1}(\mathbf{K}) + \dots, \quad (\text{A11})$$

$$E_\rho = E_0 + HE_{\rho;1} + \dots, \quad (\text{A12})$$

$$f_{\rho\rho'}(\mathbf{k}) = c_{\rho\rho'}[f_0(\mathbf{k}) + Hf_1(\mathbf{k}) + \dots], \quad (\text{A13})$$

where f_0 stands for an eigenfunction $f_{i;0}$ of $W_{\rho\rho;0}$. It is assumed that these functions form a complete orthonormal set so that f_1 can be written as a series expansion

$$f_1(\mathbf{k}) = \sum_j A_1(j) f_{j;0}(\mathbf{k}). \quad (\text{A14})$$

Then, proceeding as in stationary perturbation theory, we obtain from Eqs. (A7) and (A8) two equations for $c_{\uparrow\uparrow}$ and $c_{\downarrow\uparrow}$, namely,

$$[(i|W_{\uparrow\uparrow;1}|i) - E_{\uparrow;1}]c_{\uparrow\uparrow} + (i|W_{\downarrow\uparrow;1}|i)c_{\downarrow\uparrow} = 0, \quad (\text{A15})$$

$$(i|W_{\uparrow\downarrow;1}|i)c_{\uparrow\downarrow} + [(i|W_{\downarrow\downarrow;1}|i) - E_{\downarrow;1}]c_{\downarrow\downarrow} = 0, \quad (\text{A16})$$

where $|i\rangle = f_{i;0}$ [i.e., an eigenfunction of $W_{\rho\rho;0}(\mathbf{K})$]. A corresponding pair of equations for $c_{\downarrow\downarrow}$ and $c_{\downarrow\uparrow}$ can be derived from Eqs. (A9) and (A10). The secular equation for $c_{\uparrow\uparrow}$ and $c_{\downarrow\uparrow}$ yields for the coefficient of that part of the eigenvalue E_ρ which is linear in H [see Eq. (A12)] the value

$$E_{\uparrow;1} = \pm [(i|W_{\downarrow\uparrow;1}|i)(i|W_{\uparrow\downarrow;1}|i) + (i|W_{\uparrow\uparrow;1}|i)^2]^{1/2}, \quad (\text{A17})$$

⁷⁰ M. H. Cohen and E. I. Blount, *Phil. Mag.* **5**, 115 (1960).

⁷¹ $W_{\rho\rho';1}$ is defined with the help of the direction cosines of H so that $HW_{\rho\rho';1} = H^\alpha W_{\rho\rho';\alpha}$.

where it is taken into account that

$$(i|W_{\uparrow\uparrow;1}|i) = -(i|W_{\downarrow\downarrow;1}|i). \quad (\text{A18})$$

The positive root is chosen for $E_{\uparrow;1}$, so that $\beta_e \boldsymbol{\sigma} \cdot \mathbf{H}$ (where $\beta_e = -|e|\hbar/2mc$) has a positive expectation value for a "spin-up" electron, provided $\boldsymbol{\sigma}$ is parallel to the field. In a similar fashion, one calculates $E_{\downarrow;1}$, takes the negative root $E_{\downarrow;1}(1) [= E_{\uparrow;1}(+)]$, and has $E_{\uparrow;1} - E_{\downarrow;1} = g(i)|\beta_e|H$. From Eqs. (A15)–(A17), one has

$$\frac{c_{\uparrow\downarrow}(i)}{c_{\uparrow\uparrow}(i)} = -\frac{(i|W_{\uparrow\downarrow;1}|i)}{(i|W_{\uparrow\uparrow;1}|i) + E_{\uparrow;1}(+)}, \quad (\text{A19})$$

and, correspondingly,

$$\frac{c_{\downarrow\uparrow}(i)}{c_{\downarrow\downarrow}(i)} = -\frac{(i|W_{\uparrow\downarrow;1}|i)}{(i|W_{\downarrow\downarrow;1}|i) + E_{\uparrow;1}(-)}. \quad (\text{A20})$$

APPENDIX B

Fourier Transforms⁷²

In the coordinate representation, the solution of the Schrödinger equation,

$$(1/2m^*)[\mathbf{p} - (e/c)\mathbf{A}(\mathbf{r})]^2 g(\mathbf{r}) = E g(\mathbf{r}), \quad \mathbf{A} = \{0, H_x, 0\}, \quad (\text{B1})$$

is given by Eqs. (36) and (37) of Sec. II. In the momentum representation, the solution of the eigenvalue problem

$$(\hbar^2/2m^*)[\mathbf{k} - (e/c\hbar)\mathbf{A}(\mathbf{r})]^2 f(\mathbf{k}) = E f(\mathbf{k}), \quad (\text{B2})$$

where the operator $\mathbf{r} = i\hbar\partial/\partial\mathbf{k}$, is given by Eqs. (36) and (39). We wish to prove that $g(\mathbf{r})$ and $f(\mathbf{k})$ are the correct Fourier transforms of one another,

$$f(n, \kappa_y, \kappa_z; \mathbf{k}) = (1/2\pi)^{3/2} \int_{\Omega} g(n, \kappa_y, \kappa_z; \mathbf{r}) \times \exp[-i\mathbf{k} \cdot \mathbf{r}] d\mathbf{r}. \quad (\text{B3})$$

To this end, $g(\mathbf{r})$, given by Eq. (39), is substituted on the right-hand side. Then, with the integral representation of the δ function,

$$\int_{-a/2}^{+a/2} \exp[iz(\kappa_z - k_z)] dz = \delta(1 - k_z/\kappa_z), \quad (\mathbf{k} = \text{wave vector}), \quad (\text{B4})$$

Eq. (B3) becomes

$$f(\mathbf{k}) = (1/2\pi)^{3/2} s^{1/2} A_n \Omega^{1/2} \delta(1 - k_y/\kappa_y) \delta(1 - k_z/\kappa_z) \times \int_{-a/2}^{+a/2} \exp[-(s/2)(x - x_0)^2] \exp(-ik_x x) \times H_n[(s)^{1/2}(x - x_0)] dx. \quad (\text{B5})$$

For the calculation of the integral over x , let us assume here that a is a length sufficiently large to guarantee the

⁷² I am indebted to Dr. B. Roos for his help with Appendix B.

proper limit values for the integrals below. We take the generating function for the Hermite polynomials,

$$\exp(-t^2 + 2ty) = \sum_0^\infty H_n(y) (t^n/n!), \quad (B6)$$

and evaluate

$$J = \int_{-a/2}^{+a/2} \sum_0^\infty \exp[-(s/2)(x-x_0)^2] \exp(-ik_x x) \times \exp[-t^2 + 2t(\sqrt{s})(x-x_0)] dx. \quad (B7)$$

With

$$\int_{-\infty}^\infty \exp\{-\frac{1}{2}s^{1/2}x - (s^{1/2}x_0 + 2t - ik_x/s^{1/2})^2\} dx = (2\pi/s)^{1/2}, \quad (B8)$$

the result is given by

$$J = (2\pi/s)^{1/2} \exp(-ik_x x_0) \exp(-k_x^2/2s) \times \sum_0^\infty \frac{(it)^n}{n!} H_n(k_x/\sqrt{s}). \quad (B9)$$

With Eqs. (B9) and (B5), one readily arrives at $f(n, \kappa_y, \kappa_z; \mathbf{k})$ given by Eq. (37).

APPENDIX C

Calculation of $b_{m\rho; z}(\mathbf{r}, \mathbf{k})$

In order to calculate the spinor $b_{m\rho; z}$ which represents the first-order correction in the field $H = H_z$ to the Bloch function $b_{m\rho; 0}(\mathbf{r}, \mathbf{k})$ and which can be written in terms of the complete set of field-independent Bloch spinors, Eq. (A4), one takes Eq. (8) and inserts the power series

expansions form $b_{m\rho}$ and $\omega_{m\rho\rho'}$ [see Eqs. (A1) and (A2)]. Then one equates, as in ordinary first-order perturbation theory, the coefficients of H_z , takes the inner product with $b_{m'\rho'; 0}(\mathbf{r}, \mathbf{k}'')$, and arrives at the following equation for the coefficients A_z of the expansion (A4):

$$A_z(m, \rho, \mathbf{k}; m', \rho', \mathbf{k}) = [W_{m\rho\rho; 0}(\mathbf{k}) - W_{m'\rho'\rho'; 0}(\mathbf{k})]^{-1} \times \{ (b_{m'\rho'; 0}(\mathbf{k}) | \beta_e \sigma_z | b_{m\rho; 0}(\mathbf{k})) + (b_{m'\rho'; 0}(\mathbf{k}) | -\frac{1}{2}(e/c)[\mathbf{r} + i\partial/\partial\mathbf{k}]_x \pi_y - (\mathbf{r} + i\partial/\partial\mathbf{k})_y \pi_x | b_{m\rho; 0}(\mathbf{k})) + i \sum_l \omega_{m\rho\rho; 0}(\mathbf{R}_l) \exp(i\mathbf{k} \cdot \mathbf{R}_l) \frac{1}{2}(e/\hbar c) \times b_{m'\rho'; 0}(\mathbf{k}) | R_{l; x}(\mathbf{r} + i\partial/\partial\mathbf{k})_y - R_{l; y}(\mathbf{r} + i\partial/\partial\mathbf{k})_x | b_{m\rho; 0}(\mathbf{k})) \}, \quad (m \neq m'), \quad (C1)$$

where

$$\pi = \mathbf{p} + \hbar/(4mc^2) \boldsymbol{\sigma} \times \partial V/\partial \mathbf{r}. \quad (C2)$$

On the right-hand side of Eq. (C1) occur only matrix elements which are nondiagonal in the band index. The corresponding elements which are diagonal in m , but nondiagonal in ρ' , determine the g factor, as can be seen from Eqs. (A5) and (A6). In general—that is, for arbitrary strength of spin-orbit coupling—there is no relation in sign and magnitude between the diagonal matrix elements ($m = m'$) determining the g factor and the nondiagonal matrix elements ($m \neq m'$) which determine the A 's and thereby the function G_ρ . For the calculation of the Knight shift, one is interested in that part of G_ρ which has equal sign for “spin-up” and “spin-down” electrons. It is determined by those coefficients $A_z(m, \rho, \mathbf{k}; m', \rho', \mathbf{k})$ for which $m \neq m'$ and $\rho \neq \rho'$.