Theory of spin-orbit and many-body effects on the Knight shift

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We derive an expression for the Knight shift (K) in solids, including spin-orbit and many-body effects. We construct in $\vec{k}$ space, using the Bloch representation, the equation of motion of the Green's function in the presence of a periodic potential, spin-orbit interaction, external magnetic field, and electron-nuclear hyperfine interaction. We use a finite-temperature Green's-function method where the thermodynamic potential is expressed in terms of the exact one-particle propagator G, and we derive a general expression for K. Our result for the Knight shift is expressed as $K = K_o + K_s + K_{so}$, where K_o and K_s are the usual orbital and spin contributions to K modified by the spin-orbit and many-body contributions and where K_{so}, which is nonzero only when spin-orbit interaction is taken into account, is a new contribution to K which had been overlooked in the earlier theories. If we make simple approximations for the self-energy, our expression for K_o reduces to the earlier results. If we make drastic assumptions while solving the matrix integral equations for the field-dependent part of the self-energy, our expression for K_s is equivalent to the earlier results for the exchange-enhanced K_s but with the free-electron g factor replaced by the effective g factor. A novel feature of our analysis is that while some of the terms in K_{so} have exchange enhancement effects similar to those of K_s, except that the exchange enhancement parameters are different, the other terms in K_{so} become modified similar to K_o. Thus because of the mixed character of these terms, the exchange and correlation effects on K_{so} cannot be interpreted in an intuitive way. In order to calculate the importance of the new contribution K_{so}, we apply our theory to calculate the Knight shift of ^{207}Pb in p-type PbTe with small hole concentrations. Our results, which agree with experimental results, indicate that K_{so} is of the same order of magnitude and has the same sign as K_s and is about 3 orders of magnitude larger than K_o. Thus K_{so}, the new contribution to the Knight shift that we have calculated, is important for solids with large effective g factors and should contribute a significant fraction of their total Knight shift.

I. INTRODUCTION

A first-principles analysis of the Knight shift[1] (K) of solids is of importance from a theoretical point of view for two reasons. First, since K depends rather sensitively on both the wave functions as well as features of the band structure and Fermi surface of the metal, it provides a more detailed assessment of the applicability of methods used for band calculations than properties which depend only on the shape and dimensions of the Fermi surface. Second, it depends on a variety of mechanisms involving both single-particle and many-body effects connected with interactions among conduction electrons and between conduction and core electrons. The quantitative analysis of various pertinent mechanisms that contribute to K could thus sharpen our understanding not only of the electronic structure of solids, but also of electron-electron interaction effects in the presence or absence of magnetic fields.

It is well known[2] that the basic mechanism for contribution to the Knight shift of metals is due to the extra field produced at the nuclear site by the surplus of polarized electrons at the Fermi surface with the magnetic moments parallel to the magnetic field. Since this extra field also produces the Pauli paramagnetism, this basic mechanism may

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be termed as the spin effect. To evaluate this spin contribution to Knight shift (K_s) one needs a knowledge of the spin susceptibility (χ_s) as well as the spin density produced by the Fermi-surface electrons at the nucleus. It is also well known[3] that the electron-electron interactions enhance χ_s. In conventional treatment[4-6] of this quantity, it is tacitly assumed that electronic exchange interactions give rise to a spatially homogeneous effective magnetic field acting on the electronic spin. With this assumption, K_s becomes proportional to exchange-enhanced χ_s and a Fermi-surface average of the electron contact density. The recent theoretical calculations of K_s of metals either use relativistic wave functions constructed from many orthogonalized plane waves (OPW's) using first-order perturbation theory[7] or nonlocal pseudopotentials[8] in which the effect of electron-electron interactions in χ_s have been taken into account.[9] However, these theories do not include the exchange core-polarization effect[10,11] which can be viewed as a consequence of a spatially inhomogeneous exchange field in the core of the ion and the exchange interaction[12,13] between the polarized Fermi-surface electrons and the paired-spin electrons below the Fermi surface. Further, the requirement of achieving self-consistency between the spin density and the exchange field had also been ignored. Zaremba and Zobin[14] have formulated a linear-response theory of Knight shift in metals based on the density-functional formalism.[15,16] Their approach, which is similar to the recent theories of muon Knight shifts,[17,18] emphasizes the importance of achieving self-consistency with respect to both the charge and spin densities and includes core polarization. Recently, attempts have been made[19] within density-functional theory to treat correlation effects on spin susceptibility in many-band but nearly-free-electron-like systems, such as aluminum and magnesium. However, when band-structure effects are important it may be difficult to handle the strong local-field effects within the usual density-functional theory.

There are also additional mechanisms such as orbital hyperfine interaction and spin-orbit interaction which contribute to the Knight shift of metals. The contribution of orbital hyperfine interaction in the absence of many-body effects has been fairly well understood.[20,21] In the calculation of the spin-orbit contribution to Knight shift of metals,[22] the spin-orbit interaction was included to second order in the terms involving the electron-nuclear contact interaction which resulted in an anisotropy of Knight shift even in cubic metals. However, many-body effects were also neglected in these calculations.

It is well known that the spin-orbit interaction has a profound effect on the energy eigenstates of multivalley semiconductors, but Sapoval,[23] who was the first to obtain an expression for the Knight shift of semiconductors, ignored this property. Bailey[24] ignored Yafet's treatment of the hyperfine coupling[25] showing that the hyperfine Hamiltonian does not involve the effective *g* factors. Sapoval and Leloup[26] derived a theory of the Knight shift in degenerate multivalley semiconductors, considering the spin-orbit interaction and the relativistic effects on the hyperfine coupling. They considered the spinor character of the wave function and the nontensorial nature of the *g* matrix and showed that, except for a spherical valley, the Knight shift is not proportional to the Pauli paramagnetic susceptibility. However, they did not consider the many-body effects on these contributions. Adler *et al.*[27] have developed a $\vec{k}\cdot\vec{p}$ band model to calculate the Knight shift of $Pb_{1-x}Sn_xTe$ in which the spin-orbit interaction is included through the effective *g* factor, but they have also ignored the many-body effects. It may be noted that in these calculations, the effective *g* factors depend on the choice of the basis functions (in particular, on their phase). Unfortunately, a convention[28] is necessary to obtain the sign of the conduction-electron *g* factor, thus introducing an ambiguity in the expression for Knight shift.

It is clear from the foregoing remarks that only the theory of Knight shift in simple metals in the absence of spin-orbit and many-body effects is well known. Although attempts have been made to include the spin-orbit and other relativistic effects, none of these obtain all the contributions to *K*. In fact, hitherto it has been thought that the entire effect of spin-orbit interaction on *K* is incorporated through a modification of the *g* factor and through a change in the orbital contribution via modification of the one-particle eigenstates. Similarly, it has been assumed that the entire effect of electron-electron interaction is to enhance the spin susceptibility appearing in the spin contribution to *K*. The complete effect of the electron-electron interaction on *K* starting from first principles, particularly for many-band systems and for strong spin-orbit interaction, has not been investigated. The present work was carried out as an attempt in this direction, and we believe that we have been able to derive a satisfactory theory for *K*.

Our approach is different from the earlier methods in the sense that we have used a finite-temperature Green's-function formalism where the thermodynamic potential (Ω) for an interacting electron system in the presence of a periodic potential, spin-orbit interaction, external magnetic field, and electron-nuclear hyperfine interaction is expressed in terms of the exact one-particle propagator G. We have constructed in $\vec{k}$ space, using the Bloch representation, the equation of motion of the Green's function in the presence of the magnetic and hyperfine fields and evaluated Ω and hence K.

The expression for Knight shift for interacting electrons in solids, which we shall derive, is of the form

$$K = K_o + K_s + K_{so} \ , \tag{1.1}$$

where K_o and K_s are the counterparts of the usual orbital and spin contributions to K, modified by the spin-orbit and many-body interactions,[29] and K_{so} is an additional important contribution to K due to the effect of spin-orbit coupling on the orbital motion of interacting Bloch electrons. In our theory the effects of exchange and correlation on each of the three components of K have been explicitly calculated. If we make simple approximations for the self-energy, our expression for K_o reduces to the earlier results. If we make drastic assumptions while solving the matrix integral equations for the field-dependent part of the self-energy, our expression for K_s is equivalent to the earlier results for the exchange-enhanced K_s but with the free-electron g factor replaced by the effective g factor, a result which has been intuitively used but not yet rigorously derived. An important aspect of our work is the analysis of exchange and correlation effects on K_{so}, which are more subtle and cannot be included in an intuitive way. We show that K_{so}, which has been hitherto neglected, is of the same order of magnitude as K_s and much larger than K_o for solids with large g factors. We apply our theoretical results to p-type PbTe as an example and present what we believe to be the most complete calculation of K in a solid which analyzes all the contributions carefully.

The planning of the paper is as follows. In Sec. II, we construct in $\vec{k}$ space, using the Bloch representation, the equation of motion of the Green's function in the presence of a magnetic field. In Sec. III, we derive an expression for the Knight shift for an interacting electron system in the presence of a periodic potential, spin-orbit interaction, external magnetic field, and electron-nuclear hyperfine interaction. In Sec. IV, we carefully analyze the exchange and correlation effects on each component of K and compare our results with the earlier results. In Sec. V, we apply our theoretical results to calculate the Knight shift of p-type PbTe and show that K_{so} is of the same order as K_s and much larger than K_o. We also compare our results with experimental results. In Sec. VI, we summarize and discuss our results.

II. EFFECTIVE EQUATION OF MOTION IN BLOCH REPRESENTATION

The exact one-particle propagator $G(\vec{r},\vec{r}\,',\zeta_l)$ for an interacting electron system in the presence of a periodic potential $V(\vec{r})$, spin-orbit interaction, external magnetic field $\vec{B}$, and electron-nuclear hyperfine interaction satisfies the equation

$$(\zeta_l - H)G(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l) + \int d\vec{r}\,''\Sigma(\vec{r},\vec{r}\,'',\vec{B},\vec{M},\zeta_l)G(\vec{r}\,'',\vec{r}\,',\vec{B},\vec{M},\zeta_l) = \delta(\vec{r}-\vec{r}\,') \ , \tag{2.1}$$

where Σ is the proper self-energy operator, ζ_l is the complex energy

$$\zeta_l = \frac{(2l+1)i\pi}{\beta} + \mu \ , \tag{2.2}$$

and H is the one-particle Hamiltonian[29]

$$H = \frac{1}{2m}\left[\vec{p} + \frac{e\vec{A}}{c}\right]^2 + V(\vec{r}) + \frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times\left[\vec{p}+\frac{e}{c}\vec{A}\right] + \frac{\hbar^2}{8m^2c^2}\nabla^2 V + \tfrac{1}{2}g_0\mu_0\vec{B}\cdot\vec{\sigma}$$
$$+\sum_j\left[-\frac{1}{N}\vec{M}_j\cdot\vec{B} + \mu_0\left[-\frac{\vec{M}_j\cdot\vec{\sigma}}{r_j^3} + \frac{3(\vec{\sigma}\cdot\vec{r}_j)(\vec{M}_j\cdot\vec{r}_j)}{r_j^5} + \frac{8\pi}{3}\vec{\sigma}\cdot\vec{M}_j\delta(\vec{r}_j) + \frac{2\vec{M}_j\cdot\vec{r}_j\times[\vec{p}+(e/c)\vec{A}]}{\hbar r_j^3}\right]\right] . \tag{2.3}$$

In Eq. (2.3), $\vec{A}(\vec{r})$ is the vector potential, $\vec{\sigma}$ is the Pauli spin matrix, g_0 is the free-electron g factor, μ_0 is the electron Bohr magneton, $\vec{M}_j$ is the nuclear moment of the jth nucleus, and $\vec{r}_j$ is the coordinate of the electron relative to the jth nucleus. The first five terms are the well-known terms for the one-electron Hamiltonian in an external magnetic field including spin and spin-orbit interaction, the sixth term is the nuclear Zeeman term, the seventh and eighth terms are the interaction terms due to nuclear and electron-spin magnetic moments and have the form of a dipole-dipole interaction energy, the ninth term is the magnetic hyperfine contact interaction, and the tenth term describes the interaction of the electronic orbital moment with the nuclear magnetic moment.

In the absence of the magnetic field, both G and Σ have the symmetry

$$G(\vec{r}+\vec{R},\vec{r}\,'+\vec{R},\zeta_l)=G(\vec{r},\vec{r}\,',\zeta_l) \tag{2.4}$$

and

$$\Sigma(\vec{r}+\vec{R},\vec{r}\,'+\vec{R},\zeta_l)=\Sigma(\vec{r},\vec{r}\,',\zeta_l) , \tag{2.5}$$

where $\vec{R}$ is the crystal translation vector. The vector potential in the Hamiltonian destroys this symmetry, but both G and Σ can be written as the product of a "Peierls phase factor" and a part which has the above symmetry.[30,31] In the symmetric gauge ($\vec{A}=\frac{1}{2}\vec{B}\times\vec{r}$), we have

$$G(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l)=e^{i\vec{h}\cdot\vec{r}\times\vec{r}\,'}\tilde{G}(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l) \tag{2.6}$$

and

$$\Sigma(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l)=e^{i\vec{h}\cdot\vec{r}\times\vec{r}\,'}\tilde{\Sigma}(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l) , \tag{2.7}$$

where

$$\vec{h}=\frac{e\vec{B}}{2\hbar c} \tag{2.8}$$

and the quantities $\tilde{G}$ and $\tilde{\Sigma}$ satisfy crystal translational symmetry. Substituting Eqs. (2.3), (2.6), and (2.7) in (2.1), commuting the differential operator through the Peierls phase factor, and then multiplying on the left by $e^{-i\vec{h}\cdot\vec{r}\times\vec{r}\,'}$, we obtain

$$\Bigg\{\zeta_l-\frac{1}{2m}[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^2-V(\vec{r})-\frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]-\frac{\hbar^2}{8m^2c^2}\nabla^2V-\tfrac{1}{2}g_0\mu_0\vec{B}\cdot\vec{\sigma}$$
$$+\sum_j\Bigg[\frac{1}{N}\vec{M}_j\cdot\vec{B}-\mu_0\Bigg(-\frac{\vec{M}_j\cdot\vec{\sigma}}{r_j^3}+\frac{3(\vec{\sigma}\cdot\vec{r}_j)(\vec{M}_j\cdot\vec{r}_j)}{r_j^5}+\frac{8\pi}{3}\vec{\sigma}\cdot\vec{M}_j\delta(\vec{r}_j)$$
$$+2\epsilon_{\alpha\beta\gamma}M_j^{\alpha}r_j^{\beta}\frac{[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^{\gamma}}{\hbar r_j^3}\Bigg)\Bigg]\Bigg\}\tilde{G}(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l)$$
$$+\int d\vec{r}\,''e^{i\vec{h}\cdot(\vec{r}\,'\times\vec{r}+\vec{r}\times\vec{r}\,''+\vec{r}\,''\times\vec{r}\,')}\tilde{\Sigma}(\vec{r},\vec{r}\,'',\vec{B},\vec{M},\zeta_l)\tilde{G}(\vec{r}\,'',\vec{r}\,',\vec{B},\vec{M},\zeta_l)=\delta(\vec{r}-\vec{r}\,')e^{-i\vec{h}\cdot\vec{r}\times\vec{r}\,'} , \tag{2.9}$$

where $\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor of the third rank and we follow Einstein summation convention. We can write the equation of motion in a Bloch representation, i.e., in terms of the basis functions

$$\psi_{n,\vec{k},\rho}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}U_{n,\vec{k},\rho}(\vec{r}) , \tag{2.10}$$

where $U_{n,\vec{k},\rho}$ is a periodic two-component function, n is the band index, $\vec{k}$ is the reduced wave vector, and ρ is the spin index. Here $\psi_{n,\vec{k},\rho}(\vec{r})$ are the eigenfunctions of the Hamiltonian of the noninteracting electrons in the absence of the external magnetic field and the hyperfine interactions [$\vec{B}=0$, $\vec{M}=0$ in Eq. (2.3)]. The index ρ, $\rho=1$ or 2, distinguishes the two independent eigenfunctions $\psi_{n,\vec{k},1}$ and $\psi_{n,\vec{k},2}$ which belong to a general wave vector $\vec{k}$ and energy $E_n(\vec{k})$ if the crystal has inversion symmetry. Using the Bloch representation, Eq. (2.9) can be written as

$$
\begin{aligned}
&\sum_{n'',\rho'',\vec{k}',\vec{k}''} \int d\vec{r}\,d\vec{r}\,'d\vec{r}\,''e^{-i\vec{k}\cdot\vec{r}}U^{\dagger}_{n,\vec{k},\rho}(\vec{r}) \\
&\quad\times\Bigg\{\zeta_l-\frac{1}{2m}[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^2-V(\vec{r})-\frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]-\frac{\hbar^2}{8m^2c^2}\nabla^2V \\
&\qquad-\tfrac{1}{2}g_0\mu_0\vec{B}\cdot\vec{\sigma}+\sum_j\Bigg[\frac{1}{N}\vec{M}_j\cdot\vec{B}-\mu_0\Bigg(-\frac{\vec{M}_j\cdot\vec{\sigma}}{r_j^3}+\frac{3(\vec{\sigma}\cdot\vec{r}_j)(\vec{M}_j\cdot\vec{r}_j)}{r_j^5}+\frac{8\pi}{3}\vec{\sigma}\cdot\vec{M}_j\delta(\vec{r}_j) \\
&\qquad\qquad+2\,\epsilon_{\alpha\beta\gamma}M_j^{\alpha}r_j^{\beta}\frac{[\vec{p}+\hbar\vec{h}\times(\vec{r}-\vec{r}\,')]^{\gamma}}{\hbar r_j^3}\Bigg)\Bigg]\Bigg\} \\
&\quad\times e^{i\vec{k}''\cdot(\vec{r}-\vec{r}\,'')}U_{n'',\vec{k}'',\rho''}(\vec{r})U^{\dagger}_{n'',\vec{k}'',\rho''}(\vec{r}\,'')\widetilde{G}(\vec{r}\,'',\vec{r}\,',\vec{B},\vec{M},\zeta_l)U_{n',\vec{k}',\rho'}(\vec{r}\,')e^{i\vec{k}'\cdot\vec{r}\,'} \\
&\quad+\sum_{n'',\rho'',\vec{k}',\vec{k}''}\int d\vec{r}\,d\vec{r}\,'d\vec{r}\,''d\vec{r}\,'''e^{-i\vec{k}\cdot\vec{r}}U^{\dagger}_{n,\vec{k},\rho}(\vec{r}) \\
&\qquad\times e^{i\vec{h}\cdot(\vec{r}\,'\times\vec{r}+\vec{r}\times\vec{r}\,''+\vec{r}\,''\times\vec{r}\,')}\widetilde{\Sigma}(\vec{r},\vec{r}\,'',\vec{B},\vec{M},\zeta_l)e^{i\vec{k}''\cdot(\vec{r}\,''-\vec{r}\,''')}U_{n'',\vec{k}'',\rho''}(\vec{r}\,'')U^{\dagger}_{n'',\vec{k}'',\rho''}(\vec{r}\,''') \\
&\qquad\times\widetilde{G}(\vec{r}\,''',\vec{r}\,',\vec{B},\vec{M},\zeta_l)U_{n',\vec{k}',\rho'}(\vec{r}\,')e^{i\vec{k}'\cdot\vec{r}\,'}=\delta_{nn'}\delta_{\rho\rho'}\,.
\end{aligned}
\tag{2.11}
$$

By introducing change of variables $\vec{R}_1=\vec{r}\,''-\vec{r}\,'$, $\vec{R}_2=\frac{1}{2}(\vec{r}\,'+\vec{r}\,'')$ in the first integration, $\vec{R}_1=\vec{r}-\vec{r}\,''$, $\vec{R}_2=\frac{1}{2}(\vec{r}+\vec{r}\,'')$, $\vec{R}_3=\vec{r}\,'''-\vec{r}\,'$, and $\vec{R}_4=\frac{1}{2}(\vec{r}\,'+\vec{r}\,''')$ in the second integration, and by using partial integration of the type

$$
\begin{aligned}
&\sum_{\vec{k}''}(\vec{r}-\vec{r}\,')e^{i\vec{k}''\cdot(\vec{r}-\vec{r}\,')}e^{i\vec{k}''\cdot(\vec{r}\,'-\vec{r}\,'')}U_{n'',\vec{k}'',\rho''}(\vec{r})U^{\dagger}_{n'',\vec{k}'',\rho''}(\vec{r}\,'') \\
&\qquad=\sum_{\vec{k}''}e^{i\vec{k}''\cdot(\vec{r}-\vec{r}\,')}i\nabla_{\vec{k}''}e^{i\vec{k}''\cdot(\vec{r}\,'-\vec{r}\,'')}U_{n'',\vec{k}'',\rho''}(\vec{r})U^{\dagger}_{n'',\vec{k}'',\rho''}(\vec{r}\,'')\,,
\end{aligned}
\tag{2.12}
$$

Eq. (2.11) can be written in the form

$$
\sum_{n'',\rho''}[\zeta_l-H(\vec{\kappa}',\vec{B},\vec{M},\zeta_l)]_{n,\vec{k},\rho;n'',\vec{k},\rho''}\widetilde{G}_{n'',\vec{k},\rho'';n',\vec{k},\rho'}(\vec{k}\,',\vec{B},\vec{M},\zeta_l)\,|_{\vec{k}\,'=\vec{k}}=\delta_{nn'}\delta_{\rho\rho'}\,,
\tag{2.13}
$$

where

$$
\begin{aligned}
H(\vec{\kappa},\vec{B},\vec{M},\zeta_l)=&\frac{1}{2m}(\vec{p}+\hbar\vec{\kappa})^2+V(\vec{r})+\frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times(\vec{p}+\hbar\vec{\kappa})+\frac{\hbar^2}{8m^2c^2}\nabla^2V+\tfrac{1}{2}g_0\mu_0\vec{B}\cdot\vec{\sigma} \\
&+\sum_j\Bigg[-\frac{1}{N}\vec{M}_j\cdot\vec{B}+\mu_0\Bigg(-\frac{\vec{M}_j\cdot\vec{\sigma}}{r_j^3}+\frac{3(\vec{\sigma}\cdot\vec{r}_j)(\vec{M}_j\cdot\vec{r}_j)}{r_j^5}+\frac{8\pi}{3}\vec{\sigma}\cdot\vec{M}_j\delta(\vec{r}_j) \\
&\qquad+2\,\epsilon_{\alpha\beta\gamma}\frac{M_j^{\alpha}r_j^{\beta}(\vec{p}+\hbar\vec{\kappa})^{\gamma}}{\hbar r_j^3}\Bigg)\Bigg]+\widetilde{\Sigma}(\vec{\kappa},\vec{B},\vec{M},\zeta_l)\,,
\end{aligned}
\tag{2.14}
$$

$$
\vec{\kappa}=\vec{k}+i\vec{h}\times\nabla_{\vec{k}}\,,
\tag{2.15}
$$

$$
\widetilde{\Sigma}_{n,\vec{k},\rho,n'',\vec{k},\rho''}(\vec{\kappa}\,',\vec{B},\vec{M},\zeta_l)=\int d\vec{r}\,d\vec{r}\,'U^{\dagger}_{n,\vec{k},\rho}(\vec{r})e^{-i\vec{\kappa}\,'\cdot(\vec{r}-\vec{r}\,')}\widetilde{\Sigma}(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l)U_{n'',\vec{k},\rho''}(\vec{r}\,')\,,
\tag{2.16}
$$

and

$$
\widetilde{G}_{n'',\vec{k},\rho'',n',\vec{k},\rho'}(\vec{k}\,',\vec{B},\vec{M},\zeta_l)=\int d\vec{r}\,d\vec{r}\,'U^{\dagger}_{n'',\vec{k},\rho''}(\vec{r})\widetilde{G}(\vec{r},\vec{r}\,',\vec{B},\vec{M},\zeta_l)e^{-i\vec{k}\,'\cdot(\vec{r}-\vec{r}\,')}U_{n',\vec{k},\rho'}(\vec{r})\,.
\tag{2.17}
$$

It should be pointed out that $\widetilde{\Sigma}(\vec{\kappa},\vec{B},\vec{M},\zeta_l)$ is a (2×2) matrix, an operator in $\vec{k}$ space, and has both explicit (through $\vec{\kappa}$) and implicit $\vec{B}$ dependence. It also depends implicitly on the nuclear moment $\vec{M}$. Since the $U_{n,\vec{k},\rho}$'s form a complete set for periodic functions, Eq. (2.11) can be written in the alternate form

$$[\zeta_l - H(\vec{\kappa},\vec{B},\vec{M},\zeta_l)]\tilde{G}(\vec{k},\zeta_l) = I \ . \tag{2.18}$$

Equation (2.18) is the effective equation of motion of the Green's function in the magnetic field. This method of derivation of an effective equation of motion in the Bloch representation is a generalization of the procedure developed by us[32] for orbital motion of Bloch electrons in a magnetic field. We shall now use this equation of motion to obtain a general expression for the Knight shift of solids.

III. DERIVATION OF GENERAL FORMULA FOR KNIGHT SHIFT

A. Method of derivation

The Knight shift (K) at the nucleus j is calculated from the expression

$$K_j^{\nu\mu} = -\frac{1}{V} \lim_{\substack{\vec{B}\to 0 \\ \vec{M}\to 0}} \frac{\partial^2 \Omega}{\partial B_\mu \partial M_{j\nu}} \ , \tag{3.1}$$

where $\Omega(T,V,\mu,\vec{B},\vec{M})$ is the thermodynamic potential for an interacting electron system in the presence of a periodic potential $V(\vec{r})$, spin-orbit interaction, external magnetic field $\vec{B}$, and electron-nuclear hyperfine interaction. Using finite-temperature Green's-function formalism, Ω can be evaluated from Luttinger-Ward expression[33,34]

$$\Omega = \frac{1}{\beta}[\mathrm{Tr}\ln(-G_{\zeta_l}) - \mathrm{Tr}\Sigma(G_{\zeta_l})G_{\zeta_l} + \phi(G_{\zeta_l})] \ . \tag{3.2}$$

Here G_{ζ_l} and Σ_{ζ_l} are the abbreviated notations for the exact one-particle Green's function and proper self-energy defined earlier, Tr is defined as $\sum_l$ tr, where tr refers to summation over a complete one-particle set, and the functional $\phi(G_{\zeta_l})$ is defined as[33,34]

$$\phi(G_{\zeta_l}) = \lim_{\lambda\to 1} \mathrm{Tr} \sum_n \frac{\lambda^n}{2n} \Sigma^{(n)}(G_{\zeta_l})G_{\zeta_l} \ . \tag{3.3}$$

Here $\Sigma^{(n)}(G_{\zeta_l})$ is the nth-order self-energy part, where only the interaction parameter λ occurring explicitly in Eq. (3.3) is used to determine the order. In fact, $\phi(G_{\zeta_l})$ is defined through the decomposition of $\Sigma^{(n)}(G_{\zeta_l})$ into skeleton diagrams. There are $2n$ G_{ζ_l} lines for the nth-order diagrams in $\phi(G_{\zeta_l})$. Differentiating $\phi(G_{\zeta_l})$ with respect to G_{ζ_l} has the effect of "opening" any of the $2n$ lines of the nth-order diagram, and each will give the same contribution when Tr is taken.[33] From Eqs. (3.1)–(3.3), it can be easily shown that[34]

$$K_j^{\nu\mu} = \lim_{\substack{\vec{B}\to 0 \\ \vec{M}\to 0}} \frac{1}{V\beta} \left[-\frac{\partial^2}{\partial B_\mu \partial M_{j\nu}} \mathrm{Tr}\ln(-G_{\zeta_l}) + \mathrm{Tr}\frac{\partial^2 \tilde{\Sigma}_{\zeta_l}}{\partial B_\mu \partial M_{j\nu}} \tilde{G}_{\zeta_l} + \mathrm{Tr}\frac{\partial \tilde{\Sigma}_{\zeta_l}}{\partial M_{j\nu}} \frac{\partial \tilde{G}_{\zeta_l}}{\partial B_\mu} \right] . \tag{3.4}$$

Equation (3.4) can be written in the alternate form

$$K_j^{\nu\mu} = K_{j\,\mathrm{qp}}^{\nu\mu} + K_{j\,\mathrm{corr}}^{\nu\mu} \ , \tag{3.5}$$

where K_{qp} (qp denotes quasiparticle), the contribution due to the first term in the right-hand side in Eq. (3.4), has exactly the same form as that of noninteracting Fermi system, except for the replacement of the "noninteracting G_{ζ_l}" by the exact G_{ζ_l} for the interacting Bloch electrons. K_{corr}, the sum of the second and third terms in Eq. (3.4), is the contribution due to exchange and correlation effects. In order to evaluate K from Eq. (3.4), we expand

$$\tilde{\Sigma}(\vec{\kappa},\vec{B},\vec{M},\zeta_l) = \tilde{\Sigma}(\vec{k},\vec{B},\vec{M},\zeta_l) - ih_{\alpha\beta}\frac{\partial \tilde{\Sigma}(\vec{k},\vec{B},\vec{M},\zeta_l)}{\partial k^\alpha}\nabla_k^\beta + \cdots \tag{3.6}$$

and

$$\tilde{\Sigma}(\vec{k},\vec{B},\vec{M},\zeta_l) = \tilde{\Sigma}^0(\vec{k},\zeta_l) + B_\mu \tilde{\Sigma}^{1,\mu}(\vec{k},\zeta_l) + \sum_j M_{j\nu}\tilde{\Sigma}_j^{2,\nu}(\vec{k},\zeta_l) + \sum_j B_\mu M_{j\nu}\tilde{\Sigma}_j^{3,\mu\nu}(\vec{k},\zeta_l) + \cdots \ , \tag{3.7}$$

where

$$h_{\alpha\beta} = \epsilon_{\alpha\beta\gamma}h^\gamma \ , \tag{3.8}$$

$\epsilon_{\alpha\beta\gamma}$ is the antisymmetric tensor of the third rank, and we follow Einstein summation convention. From Eqs. (2.14), (3.6), and (3.7), we obtain

$$H(\vec{\kappa},\zeta_l) = H_0(\vec{k},\zeta_l) + H'(\vec{k},\zeta_l) \ , \tag{3.9}$$

where $H_0(\vec{k},\zeta_l)$ is the Hamiltonian in the absence of magnetic and hyperfine fields,

$$H_0(\vec{k},\zeta_l)=\frac{1}{2m}(\vec{p}+\hbar\vec{k})^2+V(\vec{r})+\frac{\hbar}{4m^2c^2}\vec{\sigma}\cdot\vec{\nabla}V\times(\vec{p}+\hbar\vec{k})+\frac{\hbar^2}{8m^2c^2}\nabla^2V+\widetilde{\Sigma}^0(\vec{k},\zeta_l)\ , \tag{3.10}$$

and $H'(\vec{k},\zeta_l)$ is the operator

$$\begin{aligned}H'(\vec{k},\zeta_l)=&-\frac{i\hbar}{m}h_{\alpha\beta}\Pi^\alpha(\vec{k},\zeta_l)\nabla_k^\beta+\tfrac{1}{2}g_0\mu_0B_\mu\sigma^\mu+B_\mu\widetilde{\Sigma}^{1,\mu}(\vec{k},\zeta_l)\\&+\sum_j\Bigg[M_{j\nu}\widetilde{\Sigma}_j^{2,\nu}(\vec{k},\zeta_l)+B_\mu M_{j\nu}\widetilde{\Sigma}_j^{3,\mu\nu}(\vec{k},\zeta_l)-ih_{\alpha\beta}M_{j\nu}\frac{\partial\widetilde{\Sigma}_j^{2,\nu}}{\partial k^\alpha}\nabla_k^\beta-\frac{1}{N}\vec{M}_j\cdot\vec{B}\\&+\mu_0\Bigg[-\frac{\vec{M}_j\cdot\vec{\sigma}}{r_j^3}+\frac{3(\sigma\cdot\vec{r}_j)(\vec{M}_j\cdot\vec{r}_j)}{r_j^5}+\frac{8\pi}{3}\vec{\sigma}\cdot\vec{M}_j\delta(\vec{r}_j)\\&+2\epsilon_{\alpha\beta\gamma}\frac{M_j^\alpha r_j^\beta(\vec{p}+\hbar\vec{k})^\gamma}{\hbar r_j^3}-2i\epsilon_{\alpha\beta\gamma}h_{\gamma\delta}\frac{M_j^\alpha r_j^\beta}{r_j^3}\nabla_k^\delta\Bigg]+\cdots\Bigg]\ ,\end{aligned} \tag{3.11}$$

where we have retained terms up to first order in both magnetic and hyperfine fields, and $\vec{\Pi}/m$ is the velocity operator in the absence of $\vec{B}$ and $\vec{M}$,

$$\vec{\Pi}(\vec{k},\zeta_l)=(\vec{p}+\hbar\vec{k})+\frac{\hbar}{4mc^2}\vec{\sigma}\times\vec{\nabla}V+\frac{m}{\hbar}\nabla_{\vec{k}}\widetilde{\Sigma}^0\ . \tag{3.12}$$

We make a perturbation expansion

$$\widetilde{G}(\vec{k},\zeta_l)=\widetilde{G}_0(\vec{k},\zeta_l)+\widetilde{G}_0(\vec{k},\zeta_l)H'\widetilde{G}_0(\vec{k},\zeta_l)+\widetilde{G}_0(\vec{k},\zeta_l)H'\widetilde{G}_0(\vec{k},\zeta_l)H'\widetilde{G}_0(\vec{k},\zeta_l)+\cdots\ , \tag{3.13}$$

where

$$\widetilde{G}_0^{-1}(\vec{k},\zeta_l)=[\zeta_l-H_0(\vec{k},\zeta_l)] \tag{3.14}$$

and is diagonal in the basis $U_{n,\vec{k},\rho}$. Here we retain terms up to first order in both magnetic and hyperfine fields.

It can be easily shown that[31,35]

$$\nabla_k^\alpha\widetilde{G}_0(\vec{k},\zeta_l)=\frac{\hbar}{m}\widetilde{G}_0(\vec{k},\zeta_l)\Pi^\alpha\widetilde{G}_0(\vec{k},\zeta_l)\ . \tag{3.15}$$

From Eqs. (3.11) and (3.15), we obtain

$$\begin{aligned}\widetilde{G}(\vec{k},\zeta_l)=\widetilde{G}_0(\vec{k},\zeta_l)+\widetilde{G}_0\Bigg\{&-i\frac{\hbar^2}{m^2}h_{\alpha\beta}\Pi^\alpha\widetilde{G}_0\Pi^\beta+\tfrac{1}{2}g_0\mu_0B_\mu F^\mu\\&+\sum_j\Bigg[-\frac{1}{N}\vec{M}_j\cdot\vec{B}+B_\mu M_{j\nu}\widetilde{\Sigma}_j^{3,\mu\nu}+\mu_0M_{j\nu}D_j^\nu\\&+2i\frac{\hbar}{m}\mu_0\epsilon_{\nu\alpha\eta}h_{\alpha\beta}M_{j\nu}\frac{(r_j^\eta\widetilde{G}_0\Pi^\beta-\Pi^\beta\widetilde{G}_0r_j^\eta)}{r_j^3}\\&-i\frac{\hbar^2}{m^2}\mu_0h_{\alpha\beta}M_{j\nu}(D_j^\nu\widetilde{G}_0\Pi^\alpha\widetilde{G}_0\Pi^\beta+\Pi^\alpha\widetilde{G}_0D_j^\nu\widetilde{G}_0\Pi^\beta+\Pi^\alpha\widetilde{G}_0\Pi^\beta\widetilde{G}_0D_j^\nu)\\&+\tfrac{1}{2}g_0\mu_0^2B_\mu M_{j\nu}(D_j^\nu\widetilde{G}_0F^\mu+F^\mu\widetilde{G}_0D_j^\nu)\\&-\frac{i\hbar}{m}h_{\alpha\beta}M_{j\nu}\Bigg[\frac{\partial\widetilde{\Sigma}_j^{2,\nu}}{\partial k^\alpha}\widetilde{G}_0\Pi^\beta-\Pi^\beta\widetilde{G}_0\frac{\partial\widetilde{\Sigma}_j^{2,\nu}}{\partial k^\alpha}\Bigg]\Bigg]\Bigg\}\widetilde{G}_0+\cdots\ ,\end{aligned} \tag{3.16}$$

where

$$D_j^\nu = X_j^\nu + \frac{1}{\mu_0}\tilde{\Sigma}_j^{2,\nu} , \quad (3.17)$$

$$X_j^\nu = \left[\frac{8\pi}{3}\sigma^\nu \delta(\vec{r}_j) + \frac{3(\vec{\sigma}\cdot\hat{r}_j)\hat{r}_j^\nu - \sigma^\nu}{r_j^3} \right] + 2\epsilon_{\nu\mu\eta}\frac{\hat{r}_j^\mu(\vec{p}+\hbar\vec{k})}{\hbar r_j^2} \equiv X_j^{0\nu} + X_j^{1\nu} , \quad (3.18)$$

$$F^\mu = \sigma^\mu + \frac{2}{g_0\mu_0}\tilde{\Sigma}^{1,\mu} \quad (3.19)$$

and we have retained terms up to first order in both magnetic and hyperfine fields. We note that we have neglected all second- and higher-order terms in magnetic and hyperfine fields since we are interested in calculating the field-independent Knight shift.

B. Evaluation of $K_{\rm qp}$

We shall derive an expression for $K_{\rm qp}$ from Eqs. (3.4) and (3.16) by assuming that the self-energy is independent of frequency, which is valid in the statically screened exchange approximation.[36] In order to carry out the frequency sums appearing in $K_{\rm qp}^{\nu\mu}$, we use the identity[33]

$$\frac{1}{\beta}\sum_{\zeta_l} \ln\frac{1}{H-\zeta_l} = -\frac{1}{2\pi i}\int_c \frac{d\zeta}{e^{\beta(\zeta-\mu)}+1}\ln\frac{1}{H-\zeta} , \quad (3.20)$$

where the contour c encircles the imaginary axis in an anticlockwise direction. We define

$$\phi(\zeta) = -\frac{1}{\beta}\ln(1+e^{-\beta(\zeta-\mu)}) . \quad (3.21)$$

From Eqs. (3.2), (3.20), and (3.21), we obtain

$$\Omega_{\rm qp} = \frac{1}{2\pi i}\,{\rm tr}\int_c \frac{d\phi(\zeta)}{d\zeta}\ln(H-\zeta) , \quad (3.22)$$

where the trace is taken over one-particle states only. By partial integration, we obtain from Eq. (3.22)

$$\Omega_{\rm qp} = \frac{1}{2\pi i}\,{\rm tr}\left[\phi(\zeta)\ln(H-\zeta) - \int_c \phi(\zeta)\frac{1}{\zeta-H}d\zeta \right] . \quad (3.23)$$

Since the first term is zero, we have

$$\Omega_{\rm qp} = -\frac{1}{2\pi i}\,{\rm tr}\int_c \phi(\zeta)\tilde{G}(\zeta)d\zeta . \quad (3.24)$$

The advantage of using Eq. (3.24) is that after substituting the perturbation expansion for $\tilde{G}(\zeta)$ [Eq. (3.16)], the free energy can be easily evaluated. The results are the same as obtained by using the inverse Laplace transform technique,[31] but the present technique is simpler.

The one-particle trace is evaluated over the periodic part of $\psi_{n,\vec{k},\rho}$ which are eigenfunctions of $H_0(\vec{k})$. In this basis $\tilde{G}_0$ is diagonal and is given by

$$\tilde{G}_0^{-1} = (\zeta - E_{n\vec{k}}) . \quad (3.25)$$

After evaluating the trace, we perform the contour integration as prescribed in Eq. (3.24). We use the identity $\vec{\Pi}_{n\rho,n\bar{\rho}}=0$ where $\bar{\rho}$ is a spin state conjugate to ρ. We also adopt the convention that running index means that the sum over all the bands and all the spin indices shall be taken except that all band terms equal to n have been explicitly separated out. After considerable algebra, we obtain

$$\Omega_{\text{qp}}=\sum_{\vec{k}}\Bigg[\phi(E_n)+2i\frac{\hbar^2}{m^2}h_{\alpha\beta}\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}}{E^2_{mn}}\phi(E_n)+i\frac{\hbar^2}{m^2}h_{\alpha\beta}\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}}{E_{mn}}f(E_n)+\tfrac{1}{2}g_0\mu_0B_\mu F^\mu f(E_n)$$
$$+\sum_j\Bigg\{i\frac{\hbar^2}{m^2}h_{\alpha\beta}\mu_0M_{j\nu}\Bigg[D^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}\left[\frac{f'(E_n)}{E_{mn}}+\frac{3f(E_n)}{E^2_{mn}}+\frac{4\phi(E_n)}{E^3_{mn}}\right]$$
$$-\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}D^{\nu}_{jq\rho'',n\rho}\left[\frac{f(E_n)}{E_{qn}E_{mn}}+\frac{2\phi(E_n)}{E^2_{mn}E_{qn}}\right]$$
$$-\Pi^{\alpha}_{n\rho,m\rho'}D^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}\left[\frac{f(E_n)}{E_{qn}E_{mn}}+\frac{2\phi(E_n)}{E^2_{mn}E_{qn}}+\frac{2\phi(E_n)}{E^2_{qn}E_{mn}}\right]$$
$$-D^{\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}\left[\frac{f(E_n)}{E_{qn}E_{mn}}+\frac{2\phi(E_n)}{E^2_{qn}E_{mn}}\right]$$
$$+\Pi^{\alpha}_{n\rho,n\rho}D^{\nu}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}\left[\frac{f(E_n)}{E^2_{mn}}+\frac{2\phi(E_n)}{E^3_{mn}}\right]$$
$$-\Pi^{\alpha}_{n\rho,n\rho}\Pi^{\beta}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho}\left[\frac{f(E_n)}{E^2_{mn}}+\frac{2\phi(E_n)}{E^3_{mn}}\right]\Bigg]$$
$$+2A^{\eta\beta}_j\left[\frac{C^{\eta}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}C^{\eta}_{jm\rho',n\rho}}{E^2_{mn}}\right]\phi(E_n)$$
$$+A^{\eta\beta}_j\left[\frac{C^{\eta}_{nj\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}C^{\eta}_{jm\rho',n\rho}}{E_{mn}}\right]f(E_n)+\left[-\frac{1}{N}M_{j\nu}B_\mu+B_\mu M_{j\nu}\widetilde{\Sigma}^{3,\mu\nu}_{jn\rho,n\rho'}\right]f(E_n)$$
$$+\tfrac{1}{4}g_0\mu_0^2M_{j\nu}B_\mu(D^{\nu}_{jn\rho,n\rho'}F^{\mu}_{n\rho',n\rho}+F^{\mu}_{n\rho,n\rho'}D^{\nu}_{jn\rho',n\rho})f'(E_n)$$
$$-\tfrac{1}{2}\,g_0\mu_0^2M_{j\nu}B_\mu\frac{(D^{\nu}_{jn\rho,m\rho'}F^{\mu}_{m\rho',n\rho}+F^{\mu}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho})}{E_{mn}}f(E_n)\Bigg\}\Bigg]\,, \tag{3.26}$$

where

$$A^{\eta\beta}_jC^{\eta}_j=2i\frac{\hbar}{m}\mu_0M_{j\nu}\epsilon_{\nu\eta\alpha}h_{\alpha\beta}\frac{r^{\eta}_j}{r^3_j}+i\frac{\hbar}{m}h_{\alpha\beta}M_{j\nu}\frac{\partial\widetilde{\Sigma}^{2,\nu}_j}{\partial k^\alpha}\,. \tag{3.27}$$

As indicated earlier, sums will be taken over all indices n, m, q, ρ, and ρ', but $n\neq m,q$. In the above we have also used the notation

$$E_{mn}=E_m(\vec{k})-E_n(\vec{k})\,. \tag{3.28}$$

In Appendix A, we derive the following identities:

$$-i\frac{\hbar^2}{m^2}h_{\alpha\beta}M_{j\nu}\sum_{\vec{k}}\frac{D^{\nu}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}\Pi^{\alpha}_{n\rho,n\rho}}{E^2_{mn}}f(E_n)$$
$$=\sum_{\vec{k}}\Bigg[i\frac{\hbar^2}{m^2}h_{\alpha\beta}M_{j\nu}\Bigg[-\frac{\Pi^{\alpha}_{n\rho,m\rho'}D^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{mn}E^2_{qn}}+\frac{D^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}}{E^3_{mn}}$$
$$-\frac{D^{\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E^2_{qn}E_{mn}}+\frac{D^{\nu}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}\Pi^{\alpha}_{n\rho,n\rho}}{E^3_{mn}}\Bigg]+A^{\eta\beta}_j\frac{C^{\eta}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}}{E^2_{mn}}\Bigg]\phi(E_n) \tag{3.29}$$

and

$$
\begin{aligned}
&-i\frac{\hbar^2}{m^2}h_{\alpha\beta}M_{j\nu}\sum_{\vec{k}}\frac{\Pi^{\alpha}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho}\Pi^{\beta}_{n\rho,n\rho}}{E^2_{mn}}f(E_n)\\
&\quad=\sum_{\vec{k}}\left[i\frac{\hbar^2}{m^2}h_{\alpha\beta}M_{j\nu}\left(-\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}D^{\nu}_{jq\rho'',n\rho}}{E^2_{mn}E_{qn}}-\frac{\Pi^{\alpha}_{n\rho,n\rho}\Pi^{\beta}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho}}{E^3_{mn}}\right.\right.\\
&\qquad\left.\left.+\frac{D^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}}{E^3_{mn}}-\frac{\Pi^{\alpha}_{n\rho,m\rho'}D^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E^2_{mn}E_{qn}}\right)-A^{\eta\beta}_{j}\frac{\Pi^{\beta}_{n\rho,m\rho'}C^{\eta}_{jm\rho',n\rho}}{E^2_{mn}}\right]\phi(E_n)\ .
\end{aligned}
\tag{3.30}
$$

It can be easily shown from time reversal symmetry[37] that

$$\vec{\Pi}_{n\rho,m\rho'}(\vec{k})=\pm\vec{\Pi}_{m\bar{\rho}',n\bar{\rho}}(-\vec{k}) \tag{3.31}$$

and

$$\vec{F}_{n\rho,n\rho}(\vec{k})=-\vec{F}_{n\bar{\rho},n\bar{\rho}}(-\vec{k})\ . \tag{3.32}$$

Using $h_{\alpha\beta}=-h_{\beta\alpha}$ and the above, we have for nonferromagnetic crystals

$$\sum_{\substack{n,m,\rho,\rho',\vec{k}\\ n\neq m}} i\frac{\hbar^2}{m^2}h_{\alpha\beta}\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}\left[\frac{f(E_n)}{E_{mn}}+\frac{2\phi(E_n)}{E^2_{mn}}\right]+\sum_{n,\rho,\vec{k}}\tfrac{1}{2}g_0\mu_0B_{\mu}F^{\mu}_{n\rho,n\rho'}f(E_n)=0\ . \tag{3.33}$$

From Eqs. (3.1), (3.26), (3.29), (3.30) and (3.33), we obtain

$$
\begin{aligned}
K^{\nu\mu}_{j\,\mathrm{qp}}=\sum_{\vec{k}}\Bigg\{&\left[-\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\mu}\frac{D^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}}{E_{mn}}-\tfrac{1}{2}g_0\mu_0^2D^{\nu}_{jn\rho,n\rho'}F^{\mu}_{n\rho',n\rho}\right]f'(E_n)\\
&+\left[\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\mu}\left(-\frac{3D^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}}{E^2_{mn}}+\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}D^{\nu}_{jq\rho'',n\rho}}{E_{mn}E_{qn}}\right.\right.\\
&\qquad+\frac{\Pi^{\alpha}_{n\rho,m\rho'}D^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{qn}E_{mn}}+\frac{D^{\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{qn}E_{mn}}\\
&\qquad\left.+\frac{\Pi^{\alpha}_{n\rho,n\rho}D^{\nu}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}}{E^2_{mn}}-\frac{\Pi^{\alpha}_{n\rho,n\rho}\Pi^{\beta}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho}}{E^2_{mn}}\right)\\
&\quad+\tfrac{1}{2}g_0\mu_0^2\frac{D^{\nu}_{jn\rho,m\rho'}F^{\mu}_{m\rho',n\rho}+F^{\mu}_{n\rho,m\rho'}D^{\nu}_{jm\rho',n\rho}}{E_{mn}}-\widetilde{\Sigma}^{3,\mu\nu}_{jn\rho,n\rho'}\\
&\quad-\frac{2i}{\hbar}\mu_0^2(\delta_{\nu\beta}\delta_{\mu\eta}-\delta_{\nu\mu}\delta_{\beta\eta})\frac{(r_j^{\eta}/r_j^3)_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}(r_j^{\eta}/r_j^3)_{m\rho',n\rho}}{E_{mn}}\\
&\quad\left.-\frac{i\mu_0}{\hbar}\epsilon_{\alpha\beta\mu}\frac{\left[\dfrac{\partial\widetilde{\Sigma}^{2,\nu}_{j}}{\partial k^{\alpha}}\right]_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}\left[\dfrac{\partial\widetilde{\Sigma}^{2,\nu}_{j}}{\partial k^{\alpha}}\right]_{m\rho',n\rho}}{E_{mn}}\right]f(E_n)\Bigg\}\ ,
\end{aligned}
\tag{3.34}
$$

where we have used the identity

$$\sum_{\alpha}\epsilon_{\alpha\beta\mu}\epsilon_{\nu\alpha\eta}=\delta_{\nu\mu}\delta_{\beta\eta}-\delta_{\nu\beta}\delta_{\mu\eta} \tag{3.35}$$

and omitted the nuclear Zeeman term. We note that in the absence of electron-electron interactions, $\vec{F}=\vec{\sigma}, D^{\nu}=X^{\nu}$ and E_n and $\vec{\Pi}$ reduce to the corresponding values for noninteracting Bloch electrons.

C. Derivation of $K_{\rm corr}$

We shall now derive an expression for $K_{\rm corr}$. From Eqs. (3.4), (3.5), (3.7), and (3.16), we obtain

$$
\begin{aligned}
K^{\nu\mu}_{j\,\rm corr} &= \frac{1}{\beta}\mathrm{Tr}\left[\frac{\partial^2\widetilde{\Sigma}_{\zeta_l}}{\partial M_{j\nu}\partial B_\mu}\widetilde{G}_{\zeta_l}+\frac{\partial\widetilde{\Sigma}_{\zeta_l}}{\partial M_{j\nu}}\frac{\partial\widetilde{G}_{\zeta_l}}{\partial B_\mu}\right]_{\substack{\vec{B}\to 0\\ \vec{M}\to 0}}\\
&= \frac{1}{\beta}\mathrm{Tr}\Big[\widetilde{\Sigma}^{3,\mu\nu}_j(\vec{k},\zeta_l)\widetilde{G}_0(\vec{k},\zeta_l)+\tfrac{1}{2}g_0\mu_0\widetilde{\Sigma}^{2,\nu}_j(\vec{k},\zeta_l)\widetilde{G}_0(\vec{k},\zeta_l)F^\mu\widetilde{G}_0(\vec{k},\zeta_l)\\
&\quad -\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\widetilde{\Sigma}^{2,\nu}_j(\vec{k},\zeta_l)\widetilde{G}_0(\vec{k},\zeta_l)\Pi^\alpha\widetilde{G}_0(\vec{k},\zeta_l)\Pi^\beta\widetilde{G}_0(\vec{k},\zeta_l)\Big]\,.
\end{aligned}
\tag{3.36}
$$

As before, we assume the self-energy to be independent of frequency. We carry out the frequency sums as per prescription of Luttinger and Ward[33]:

$$
\frac{1}{\beta}\sum_l\frac{1}{(\zeta_l-E_n)^m}=\frac{1}{2\pi i}\int_{\Gamma_0}\frac{1}{(\zeta-E_n)^m}\frac{1}{e^{\beta(\zeta-\mu)}+1}d\zeta\,.
\tag{3.37}
$$

We obtain from Eqs. (3.36) and (3.37)

$$
\begin{aligned}
K^{\nu\mu}_{j\,\rm corr} = \sum_{\vec{k}}\Bigg\{&\Bigg[\tfrac{1}{2}g_0\mu_0\widetilde{\Sigma}^{2,\nu}_{jn\rho,n\rho'}F^\mu_{n\rho',n\rho}+\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\Bigg[\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,n\rho'}\Pi^\alpha_{n\rho',m\rho''}\Pi^\beta_{m\rho'',n\rho}}{E_{mn}}+\frac{\Pi^\beta_{n\rho,m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E_{mn}}\\
&\qquad+\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',n\rho}\Pi^\beta_{n\rho,n\rho}}{E_{mn}}\Bigg]\Bigg]f'(E_n)\\
&+\Bigg[-\tfrac{1}{2}g_0\mu_0\left[\frac{F^\mu_{n\rho,m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}+\widetilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}F^\mu_{m\rho',n\rho}}{E_{mn}}\right]\\
&\quad+\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\Bigg[\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,n\rho'}\Pi^\alpha_{n\rho',m\rho''}\Pi^\beta_{m\rho'',n\rho}}{E^2_{mn}}-\frac{\Pi^\beta_{n\rho,m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',m\rho''}\Pi^\alpha_{m\rho'',n\rho}}{E^2_{mn}}\\
&\quad-\frac{\Pi^\alpha_{n\rho,m\rho'}\Pi^\beta_{m\rho',m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}}{E^2_{mn}}+\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',n\rho}\Pi^\beta_{n\rho,n\rho}}{E^2_{mn}}\\
&\quad+\frac{\Pi^\beta_{n\rho,m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E^2_{mn}}-\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',m\rho'}\Pi^\beta_{m\rho',n\rho}}{E^2_{mn}}-\frac{\widetilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{mn}E_{qn}}\\
&\quad-\frac{\Pi^\alpha_{n\rho,m\rho'}\Pi^\beta_{m\rho',q\rho''}\widetilde{\Sigma}^{2,\nu}_{jq\rho'',n\rho}}{E_{mn}E_{qn}}-\frac{\Pi^\beta_{n\rho,m\rho'}\widetilde{\Sigma}^{2,\nu}_{jm\rho',q\rho''}\Pi^\alpha_{q\rho'',n\rho}}{E_{mn}E_{qn}}\Bigg]+\widetilde{\Sigma}^{3,\mu\nu}_{jn\rho,n\rho'}\Bigg]f(E_n)\Bigg\}\,.
\end{aligned}
\tag{3.38}
$$

We note that in the absence of electron-electron interaction, $K_{\rm corr}$ becomes zero as it should. However, as we shall see, in the presence of electron-electron interaction, there are significant cancellations between $K_{\rm qp}$ and $K_{\rm corr}$ terms.

D. General expression for the Knight shift

It has been shown in Appendix B that

$$\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\sum_{\vec{k}}\left[\frac{\Pi^{\beta}_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}\Pi^{\alpha}_{n\rho,n\rho}}{E_{mn}}+\frac{\tilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',n\rho}\Pi^{\beta}_{n\rho,n\rho}}{E_{mn}}\right]f'(E_n)$$

$$=\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\sum_{\vec{k}}\left[\frac{2\Pi^{\beta}_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',q\rho''}\Pi^{\alpha}_{q\rho'',n\rho}}{E_{mn}E_{qn}}-\frac{2\tilde{\Sigma}^{2,\nu}_{jn\rho,n\rho'}\Pi^{\beta}_{n\rho',m\rho''}\Pi^{\alpha}_{m\rho'',n\rho}}{E^2_{mn}}\right.$$

$$\left.+\frac{m}{\hbar}\frac{\left[\dfrac{\partial\tilde{\Sigma}^{2,\nu}_{j}}{\partial k^{\alpha}}\right]_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}\left[\dfrac{\partial\tilde{\Sigma}^{2,\nu}_{j}}{\partial k^{\alpha}}\right]_{m\rho',n\rho}}{E_{mn}}\right]f(E_n)\ . \quad (3.39)$$

We shall now obtain a general expression for the Knight shift of solids (K) in the presence of both many-body and spin-orbit effects. In order to simplify our results and present them in a familiar form, we use some partial integration results and make simplification of X terms as outlined in the appendixes.

In Appendix C, it has been shown that

$$\sum_{n,\vec{k},\rho}\left[\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\mu}\left[\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{\nu}_{jq\rho'',n\rho}}{E_{qn}E_{mn}}+\frac{\Pi^{\alpha}_{n\rho,m\rho'}X^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{qn}E_{mn}}+\frac{X^{\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{qn}E_{mn}}\right]\right.$$

$$\left.-\frac{2i}{\hbar}\mu_0^2(\delta_{\nu\beta}\delta_{\mu\eta}-\delta_{\nu\mu}\delta_{\beta\eta})\frac{(r^{\eta}_j/r^3_j)_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}-\Pi^{\beta}_{n\rho,m\rho'}(r^{\eta}_j/r^3_j)_{m\rho',n\rho}}{E_{mn}}\right]$$

$$=-\frac{e^2}{3mc^2}\sum_{n,\vec{k},\rho}\delta_{\nu\mu}(1/r_j)_{n\rho,n\rho}+\frac{2}{\hbar}\mu_0^2\epsilon_{\alpha\beta\mu}\sum_{n,\vec{k},\rho}\frac{(r^{\alpha}_j\Pi^{\beta})_{n\rho,m\rho'}(L^{\nu}_j/r^3_j)_{m\rho',n\rho}+(L^{\nu}_j/r^3_j)_{n\rho,m\rho'}(r^{\alpha}_j\Pi^{\beta})_{m\rho',n\rho}}{E_{mn}}$$

$$+\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\mu}\sum_{n,\vec{k},\rho}\left[\frac{\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{0\nu}_{jq\rho'',n\rho}}{E_{mn}E_{qn}}+\frac{\Pi^{\alpha}_{n\rho,m\rho'}X^{0\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{mn}E_{qn}}+\frac{X^{0\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{mn}E_{qn}}\right]\ . \quad (3.40)$$

From Eqs. (3.5), (3.34), (3.38), and (3.40), we obtain the general expression for the total Knight shift which we separate into three different contributions to K as was done in the case of magnetic susceptibility and write[37]

$$K^{\nu\mu}_j=K^{\nu\mu}_{js}+K^{\nu\mu}_{jo}+K^{\nu\mu}_{jso}\ , \quad (3.41)$$

where $K^{\nu\mu}_{js}$ is the spin-contribution to the Knight shift

$$K^{\nu\mu}_{js}=-\sum_{n,\vec{k},\rho,\rho'}\left[\tfrac{1}{2}g_0\mu_0^2X^{\nu}_{jn\rho,n\rho'}F^{\mu}_{n\rho',n\rho}+\frac{i}{m}\mu_0^2\epsilon_{\alpha\beta\mu}\sum_{\substack{m,\rho''\\ m\neq n}}\frac{X^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}}{E_{mn}}\right]f'(E_{n\vec{k}})\ , \quad (3.42)$$

$K^{\nu\mu}_{jo}$ is the orbital contribution to the Knight shift

$$K^{\nu\mu}_{jo}=-\frac{e^2}{3mc^2}\sum_{n,\vec{k},\rho}\left[\frac{1}{r_j}\right]_{n\rho,n\rho}\delta_{\nu\mu}f(E_{n\vec{k}})$$

$$+\frac{2\mu_0^2}{\hbar}\epsilon_{\alpha\beta\mu}\sum_{\substack{n,\vec{k},\rho,m,\rho'\\ n\neq m}}\left[\frac{(r^{\alpha}_j\Pi^{\beta})_{n\rho,m\rho'}(L^{\nu}_j/r^3_j)_{m\rho',n\rho}}{E_{mn}}+\frac{(L^{\nu}_j/r^3_j)_{n\rho,m\rho'}(r^{\alpha}_j\Pi^{\beta})_{m\rho',n\rho}}{E_{mn}}\right]f(E_{n\vec{k}})\ , \quad (3.43)$$

and $K^{\nu\mu}_{jso}$ is a new additional spin-orbit contribution to the Knight shift

$$K_{jso}^{\nu\mu}=\sum_{n,\vec{k},p}\left[\frac{i\mu_0^2}{m}\epsilon_{\alpha\beta\mu}\left[(-3X^{\nu}_{jnp,np'}\Pi^{\alpha}_{np',mp''}\Pi^{\beta}_{mp'',np}+\Pi^{\alpha}_{np,np}X^{\nu}_{jnp,mp'}\Pi^{\beta}_{mp',np}-\Pi^{\alpha}_{np,np}\Pi^{\beta}_{np,mp'}X^{\nu}_{jmp',np})\frac{1}{E_{mn}^2}\right.\right.$$

$$+(\Pi^{\alpha}_{np,mp'}\Pi^{\beta}_{mp'qp''}X^{0\nu}_{jqp'',np}+\Pi^{\alpha}_{np,mp'}X^{0\nu}_{jmp',qp''}\Pi^{\beta}_{qp'',np}$$

$$\left.+X^{0\nu}_{jnp,mp'}\Pi^{\alpha}_{mp',qp''}\Pi^{\beta}_{qp'',np})\frac{1}{E_{qn}E_{mn}}\right]$$

$$\left.+\tfrac{1}{2}g_0\mu_0^2\frac{(X^{\nu}_{jnp,mp'}F^{\mu}_{mp',np}+F^{\mu}_{np,mp'}X^{\nu}_{jmp',np})}{E_{mn}}\right]f(E_{n\vec{k}})\,. \tag{3.44}$$

We note that in Eq. (3.44), repeated indices imply summation. We can also write $K_{js}^{\nu\mu}$ in the alternate form

$$K_{js}^{\nu\mu}=-\tfrac{1}{2}\mu_0^2\sum_{n,\vec{k},p,p'}X^{\nu}_{jnp,np'}\left[g^{\mu}_{n,n}(\vec{k})\sigma^{\mu}_{np',np}+\frac{2}{\mu_0}\tilde{\Sigma}^{1,\mu}_{np',np}\right]f'(E_{n\vec{k}})\,, \tag{3.45}$$

where the effective g matrix $g^{\mu}_{n,n}(\vec{k})$ is defined through the equation

$$g^{\mu}_{n,n}(\vec{k})\sigma^{\mu}_{np,np'}(\vec{k})=g_0\sigma^{\mu}_{np,np'}(\vec{k})+\frac{2i}{m}\epsilon_{\alpha\beta\mu}\sum_{\substack{m,p''\\ m\neq n}}\frac{\Pi^{\alpha}_{np,mp''}\Pi^{\beta}_{mp'',np'}}{E_{mn}}\,. \tag{3.46}$$

From Eqs. (3.43) and (3.45), we note that K_s and K_o are the usual spin and orbital contributions[29] to K modified by the spin-orbit and many-body interactions. In fact, it has been hitherto thought that the entire effect of spin-orbit interaction on K can be incorporated through a modification of the g factor in the spin contribution (K_s) and through a change in the orbital contribution (K_o) via modification of the one-particle eigenstates. However, we have obtained new contributions (K_{so}) which vanish with spin-orbit interaction. K_{so} can be interpreted as the contribution to the Knight shift due to the effect of spin-orbit interaction on the orbital motion of Bloch electrons.

It is interesting to note that the effects of exchange and correlation (other than the usual effective-mass corrections) which comes through $\tilde{\Sigma}^{1,\mu}$ appear only in K_s and K_{so} and not in K_o, and also only certain terms in K_{so} get modified. In fact, the leading term of K_{so} [proportional to $-3X^{\nu}_{jnp,np'}$ in Eq. (3.44)], which is approximately proportional to the g factor, does not become modified by exchange and correlation (except via modification of the one-particle eigenstates). An important point is that had we considered the quasiparticle contributions only, we would have obtained exactly the same expression for K in Eqs. (3.42)–(3.44) with the modification $X^{\nu}\to D^{\nu}$, where $D^{\nu}=X^{\nu}+(1/\mu_0)\,\tilde{\Sigma}^{2,\nu}$ and $\tilde{\Sigma}^{2,\nu}$ has been defined in Eq. (3.7). Thus in the quasiparticle approximation, both spin vertex σ^{μ} and the hyperfine vertex X^{ν} become modified. The effect of $K_{\rm corr}$ is to cancel precisely all the corrections to the hyperfine vertex and keep the renormalization of the spin vertex. The source of the apparent asymmetry between the spin and hyperfine vertices is in Eq. (3.4), which depends upon the order of differentiation in obtaining K. But our final result is independent of this order of differentiation. This can be easily checked by obtaining a relationship between the two quantities $\tilde{\Sigma}^{1,\mu}$ and $\tilde{\Sigma}^{2,\nu}$.

We shall now show that in the absence of spin-orbit coupling and with inversion symmetry, every term in K_{so} vanishes. In the absence of spin-orbit coupling, every σ_{nm} and X^{0}_{nm} vanishes because of the orthogonality of the orbital functions. Hence the fourth up to the eighth terms vanish. If one chooses $\vec{B}$ to lie in the z direction, one has $\sum\sigma^{z}_{np,np'}=\sigma^{z}_{n\uparrow,n\uparrow}+\sigma^{z}_{n\downarrow,n\downarrow}=0$. This, coupled with the fact that in the absence of spin-orbit coupling

$$\vec{\Pi}_{n\uparrow,m\uparrow}=\vec{\Pi}_{n\downarrow,m\downarrow}$$

and

$$\vec{\Pi}_{n\uparrow,m\downarrow}=0 \tag{3.47}$$

and $h_{\alpha\beta}$ is antisymmetric, makes the first term vanish. If in addition to the absence of spin-orbit coupling, the crystal has inversion symmetry

$$\Pi^{\alpha}_{n\rho,m\rho}=\Pi^{\alpha}_{m\rho,n\rho} . \quad (3.48)$$

One can show from time-reversal property that

$$U^{*}_{n\uparrow}(-\vec{k})=-U_{n\downarrow}(\vec{k}) . \quad (3.49)$$

From Eqs. (3.47)–(3.49), we have

$$\Pi^{\alpha}_{n\uparrow,m\uparrow}(\vec{k})=-\Pi^{\alpha}_{m\uparrow,n\uparrow}(-\vec{k}) . \quad (3.50)$$

Similarly we can show that

$$[X^{1}_{j}(\vec{k})]_{n\uparrow,m\uparrow}=[X^{1}_{j}(-\vec{k})]_{m\uparrow,n\uparrow} . \quad (3.51)$$

From Eqs. (3.50) and (3.51), we have

$$\frac{\Pi^{\alpha}_{n\rho,n\rho}(\vec{k})\Pi^{\beta}_{n\rho,m\rho'}(\vec{k})X^{\nu}_{jm\rho',n\rho}(\vec{k})}{E^{2}_{mn}} = \frac{\Pi^{\alpha}_{n\rho,n\rho}(-\vec{k})X^{\nu}_{jn\rho,m\rho'}(-\vec{k})\Pi^{\beta}_{m\rho',n\rho}(-\vec{k})}{E^{2}_{mn}} . \quad (3.52)$$

Since the reduced Brillouin zone is invariant under reflection, when there is inversion symmetry, this term exactly cancels the $\Pi^{\alpha}_{n\rho,n\rho}(\vec{k})X^{\nu}_{jn\rho,m\rho'}(\vec{k}) \times\Pi^{\beta}_{m\rho',n\rho}(\vec{k})/E^{2}_{mn}$ term. Thus all the terms in K_{so} vanish in the absence of spin-orbit coupling if the crystal has inversion symmetry.

K_{so} should be considered as contribution due to spin-orbit effects on the orbital motion and distinguished from the spin-orbit contribution to the effective g factor for the following reason. There are two types of contributions of the magnetic and hyperfine energies of a one-electron eigenstate, terms linear in $\vec{B}$ which split the spin degeneracy and terms linear in $\vec{M}$ which do not. Both terms, of course, contribute quadratically (product of $\vec{B}$ and $\vec{M}$), to the thermodynamic potential. The linear terms in $\vec{B}$ are included in the g factor and are always independent of the sign of the g factor, i.e., independent of the sign of the splitting of the spin degeneracy. The quadratic terms which arise from a perturbation of the one-electron wave functions by both the magnetic and hyperfine fields are responsible for both K_o and K_{so}.

IV. MANY-BODY EFFECTS ON THE KNIGHT SHIFT

A. Exchange self-energy in the band model

We note that it has been generally thought[14,19,38] that the dominant effect of the electron-electron interaction is to enhance the Pauli spin susceptibility appearing in K_s. The complete effect of the electron-electron interaction on K for many-band systems including spin-orbit interaction has not been investigated. In order to calculate these many-body effects from Eqs. (3.42)–(3.44), we shall first consider the exchange self-energy in the band model. The exchange contribution to the self-energy is local in $\vec{r}$ space

$$\Sigma(\vec{r},\vec{r}\,',\zeta_l)=-\frac{1}{\beta}\sum_{\zeta_{l'}}v_{\text{eff}}(\vec{r},\vec{r}\,')G(\vec{r},\vec{r}\,',\zeta_l-\zeta_{l'}) , \quad (4.1)$$

where we have made a simple static screening approximation to obtain $v_{\text{eff}}(\vec{r},\vec{r}\,')$ from $v(\vec{r},\vec{r}\,')$. In this approximation the self-energy is independent of ζ_l and we have

$$\Sigma(\vec{r},\vec{r}\,')=-\frac{1}{\beta}\sum_{\zeta_l}v_{\text{eff}}(\vec{r},\vec{r}\,')G(\vec{r},\vec{r}\,',\zeta_l) . \quad (4.2)$$

We assume that $v_{\text{eff}}(\vec{r},\vec{r}\,')$ is field independent, i.e., neglecting the field dependence of screening, we obtain

$$\tilde{\Sigma}(\vec{r},\vec{r}\,')=-\frac{1}{\beta}\sum_{\zeta_l}v_{\text{eff}}(\vec{r},\vec{r}\,')\tilde{G}(\vec{r},\vec{r}\,',\zeta_l) . \quad (4.3)$$

$\tilde{\Sigma}$ and $\tilde{G}$ can be expanded in terms of Bloch states as follows:

$$\tilde{\Sigma}(\vec{r},\vec{r}\,')=\sum_{\substack{n,m\,\vec{k}\\ \rho,\rho'}}\tilde{\Sigma}_{n\rho,m\rho'}(\vec{k})\psi_{n,\vec{k},\rho}(\vec{r})\psi^{*}_{m,\vec{k},\rho'}(\vec{r}\,') \quad (4.4)$$

and

$$\tilde{G}(\vec{r},\vec{r}\,')=\sum_{\substack{n,m,\vec{k}\\ \rho,\rho'}}\tilde{G}_{n\rho,m\rho'}(\vec{k})\psi_{n,\vec{k},\rho}(\vec{r})\psi^{*}_{m,\vec{k},\rho'}(\vec{r}\,') . \quad (4.5)$$

Substituting Eqs. (4.4) and (4.5) in Eq. (4.3) we obtain

$$\sum_{\substack{n,m\\ \rho,\rho'}}\tilde{\Sigma}_{n\rho,m\rho'}(\vec{k})\psi_{n,\vec{k},\rho}(\vec{r})\psi^{*}_{m,\vec{k},\rho'}(\vec{r}\,') = -\frac{1}{\beta}\sum_{\zeta_l}\sum_{\substack{p,q,\vec{k}\,'\\ \bar{\rho},\bar{\rho}'}}v_{\text{eff}}(\vec{r},\vec{r}\,')\tilde{G}_{p\bar{\rho},q\bar{\rho}'}(\vec{k}\,') \times\psi_{p,\vec{k}\,',\bar{\rho}}(\vec{r})\psi^{*}_{q,\vec{k}\,',\bar{\rho}'}(\vec{r}\,') . \quad (4.6)$$

If the effective electron-electron interaction is spin-independent, then $\rho=\bar{\rho}$, $\rho'=\bar{\rho}'$ and we have

$$\tilde{\Sigma}_{n\rho,m\rho'}(\vec{k})=-\frac{1}{\beta}\sum_{\substack{\vec{k}',\zeta_l\\p,q}}\langle nm\,|\,v_{\text{eff}}(\vec{k},\vec{k}')\,|\,pq\,\rangle_{\rho\rho'}\times\tilde{G}_{p\rho,q\rho'}(\vec{k}',\zeta_l)\ , \tag{4.7}$$

where

$$\langle nm\,|\,v_{\text{eff}}(\vec{k},\vec{k}')\,|\,pq\,\rangle_{\rho\rho'}\equiv\int\psi^*_{n,\vec{k},\rho}(\vec{r})\psi_{m,\vec{k},\rho'}(\vec{r}')v_{\text{eff}}(\vec{r},\vec{r}')\times\psi_{p,\vec{k}',\rho}(\vec{r})\psi^*_{q,\vec{k}',\rho'}(\vec{r}')\ . \tag{4.8}$$

We shall now evaluate $\tilde{\Sigma}^1_{n\rho,n\rho'}$ and $\tilde{\Sigma}^1_{n\rho,m\rho'}$ which occur in the expressions for K_s and K_{so}. In order to evaluate $\tilde{\Sigma}^1_{n\rho,n\rho'}$, we make the further approximation

$$\langle nn\,|\,v_{\text{eff}}(\vec{k},\vec{k}')\,|\,pq\,\rangle_{\rho\rho'}\cong\langle nn\,|\,v_{\text{eff}}(\vec{k},\vec{k}')\,|\,pp\,\rangle\delta_{pq}\equiv v_{np}\delta_{pq}\ . \tag{4.9}$$

From Eqs. (4.7) and (4.9), we obtain

$$\tilde{\Sigma}_{n\rho,n\rho'}(\vec{k})=-\frac{1}{\beta}\sum_{\vec{k}',\zeta_l,p}v_{np}(\vec{k},\vec{k}')\tilde{G}_{p\rho,p\rho'}(\vec{k}',\zeta_l)\ . \tag{4.10}$$

Substituting the value of $\tilde{G}$ from Eq. (3.16) in Eq. (4.10), summing over ζ_l, expanding $\tilde{\Sigma}_1$ as in Eq. (3.7), and comparing the first-order terms in magnetic fields, we obtain

$$\tilde{\Sigma}^{1,\mu}_{n\rho,n\rho'}(\vec{k})=-\sum_{m,\vec{k}'}v_{nm}(\vec{k},\vec{k}')\tilde{\Sigma}^{1,\mu}_{m\rho,m\rho'}(\vec{k}')f'(E_{m\vec{k}'})-\tfrac{1}{2}\mu_0\sum_{m,\vec{k}'}v_{nm}(\vec{k},\vec{k}')g^{\mu}_{m,m}(\vec{k}')\sigma^{\mu}_{m\rho,m\rho'}f'(E_{m\vec{k}'})$$
$$-\frac{i\mu_0}{m}\epsilon_{\alpha\beta\mu}\sum_{\substack{m,\vec{k}',q,\rho''\\q\neq m}}v_{nm}(\vec{k},\vec{k}')\frac{\Pi^{\alpha}_{m\rho,q\rho''}\Pi^{\beta}_{q\rho'',m\rho'}}{E^2_{qm}}[f(E_{m\vec{k}'})-f(E_{q\vec{k}'})]\ , \tag{4.11}$$

where the effective diagonal g matrix g^{μ}_{mm} has been defined in Eq. (3.46). In order to calculate $\tilde{\Sigma}^1_{n\rho,m\rho'}(\vec{k})$, we assume

$$\langle nm\,|\,v_{\text{eff}}(\vec{k},\vec{k}')\,|\,pq\,\rangle_{\rho\rho'}\cong\bar{v}_{nm}(\vec{k},\vec{k}')\delta_{np}\delta_{mq}\ . \tag{4.12}$$

From Eqs. (4.7) and (4.12), we have

$$\tilde{\Sigma}_{n\rho,m\rho'}(\vec{k})=-\frac{1}{\beta}\sum_{\vec{k}',\zeta_l}\bar{v}_{nm}(\vec{k},\vec{k}')\tilde{G}_{n\rho,m\rho'}(\vec{k}',\zeta_l)\ . \tag{4.13}$$

Substituting the value of $\tilde{G}$ from Eq. (3.16) in Eq. (4.13), summing over ζ_l, and comparing first-order terms in magnetic field with such terms in Eq. (3.7), we obtain

$$\tilde{\Sigma}^{1,\mu}_{n\rho,m\rho'}(\vec{k})=-\sum_{\vec{k}'}\bar{v}_{nm}(\vec{k},\vec{k}')\tilde{\Sigma}^{1,\mu}_{n\rho,m\rho'}\left[\frac{f(E_{n\vec{k}'})-f(E_{m\vec{k}'})}{E_{nm}}\right]-\tfrac{1}{2}\mu_0\sum_{\vec{k}'}\bar{v}_{nm}(\vec{k},\vec{k}')g^{\mu}_{nm}\sigma^{\mu}_{n\rho,m\rho'}\left[\frac{f(E_{n\vec{k}'})-f(E_{m\vec{k}'})}{E_{nm}}\right]\ , \tag{4.14}$$

where we have defined the nondiagonal effective g matrix g^{μ}_{nm} as

$$g^{\mu}_{nm}(\vec{k})\sigma^{\mu}_{n\rho,m\rho'}(\vec{k})=g_0\sigma^{\mu}_{n\rho,m\rho'}(\vec{k})+\frac{2i}{m}\epsilon_{\alpha\beta\mu}\sum_{\substack{q,\rho''\\q\neq m}}\frac{\Pi^{\alpha}_{n\rho,q\rho''}\Pi^{\beta}_{q\rho'',n\rho'}}{E_{qm}}\ . \tag{4.15}$$

B. Exchange enhancement of K_{js}

We shall first investigate how $K^{\nu\mu}_{js}$ becomes exchange enhanced. We can write Eq. (3.45) in the alternate form

$$K^{\nu\mu}_{js}=K^{\nu\mu}_{j0s}+K^{\nu\mu}_{j1s}\ , \tag{4.16}$$

where

$$K^{\nu\mu}_{j0s}=-\tfrac{1}{2}\mu_0^2\sum_{n,\vec{k},\rho,\rho'}g^{\mu}_{n,n}(\vec{k})X^{\nu}_{jn\rho,n\rho'}\sigma^{\mu}_{n\rho',n\rho}f'(E_{n\vec{k}})=\sum_n K^{\nu\mu}_{j0s,n}\ , \tag{4.17}$$

is the spin contribution to the Knight shift for noninteracting Bloch electrons but with the free-electron g factor replaced by the effective g matrix,

$K^{\nu\mu}_{j0s,n}$ is the spin-contribution to K from the nth band, and

$$K^{\nu\mu}_{j1s} = -\mu_0 \sum_{n,\vec{k},\rho,\rho'} X^{\nu}_{jn\rho,n\rho'} \tilde{\Sigma}^{1,\mu}_{n\rho',n\rho} , \qquad (4.18)$$

is the contribution due to exchange and correlation. First, we consider individual band enhancement and neglect interband interactions. We make an average exchange enhancement ansatz, assume $v_{nm} \equiv \bar{v}_{nm}\,\delta_{nm}$ which is equivalent to the assumption that $\tilde{\Sigma}^{1,\mu}$ is independent of $\vec{k}$, and neglect terms proportional to f to obtain from Eq. (4.11)

$$\tilde{\Sigma}^{1,\mu}_{n\rho,n\rho'} \cong \frac{1}{2}\frac{\alpha_n}{1-\alpha_n}\mu_0 g^{\mu}_{nn}\sigma^{\mu}_{n\rho,n\rho'} , \qquad (4.19)$$

where

$$\alpha_n = -\sum_{\vec{k}',m} \bar{v}_{nm}(\vec{k},\vec{k}')f'(E_{m\vec{k}'}) \qquad (4.20)$$

is an average exchange enhancement parameter for the nth band electrons at the Fermi energy. From Eqs. (4.16)–(4.19), we obtain

$$K^{\nu\mu}_{js} = \sum_n \frac{K^{\nu\mu}_{j0s,n}}{1-\alpha_n} , \qquad (4.21)$$

which shows that the contribution from the nth bands gets enhanced by a factor $(1-\alpha_n)^{-1}$. We note that the intuitive result of Eq. (4.21), which gives rise to the well-known Stoner enhancement[39] of the effective Pauli spin susceptibility in the expression for Knight shift, is only valid if one makes drastic assumptions while solving the matrix integral equations for $\tilde{\Sigma}^{1,\mu}_{n\rho,n\rho'}$. However, the neglect of interband terms, i.e., coupling between the $\tilde{\Sigma}^{1,\mu}_{n\rho,n\rho'}$ for different occupied bands, might be too drastic for systems such as Be, Cd, etc. We now consider exchange enhancement of K_{js} in a two-band model. We define

$$\Sigma_m \equiv \tilde{\Sigma}^{1,\mu}_{m\rho,m\rho'} , \qquad (4.22)$$

$$a_m \equiv \tfrac{1}{2}\mu_0 g^{\mu}_{mm}\sigma^{\mu}_{m\rho,m\rho'} , \qquad (4.23)$$

and

$$N_m \equiv -\sum_{\vec{k}'} f'(E_{m\vec{k}'}) . \qquad (4.24)$$

From Eqs. (4.11) and (4.22)–(4.24), we obtain (neglecting f terms)

$$\Sigma_n = v_{nn}N_n\Sigma_n + v_{nm}N_m\Sigma_m + v_{nn}a_nN_n + v_{nm}a_mN_m \qquad (4.25)$$

and

$$\Sigma_m = v_{mm}N_m\Sigma_m + v_{nm}N_n\Sigma_n + v_{mn}a_nN_n + v_{mm}a_mN_m . \qquad (4.26)$$

Equations (4.25) and (4.26) can be solved self-consistently and we obtain

$$\Sigma_n = \frac{v_{nn}a_nN_n + v_{nm}a_mN_m - v_{nn}v_{mm}a_nN_nN_m + |V_{nm}|^2 a_nN_nN_m}{1 - v_{nn}N_n - v_{mm}N_m + (v_{nn}v_{mm} - |v_{nm}|^2)N_nN_m} \qquad (4.27)$$

and

$$\Sigma_m = \frac{v_{mm}a_mN_m + v_{mn}a_nN_n - v_{nn}v_{mm}a_mN_nN_m + |v_{nm}|^2 a_mN_nN_m}{1 - v_{nn}N_n - v_{mm}N_m + (v_{nn}v_{mm} - |v_{nm}|^2)N_nN_m} . \qquad (4.28)$$

From Eqs. (3.45), (4.17), (4.27), and (4.28), we obtain

$$K^{\nu\mu}_{js} = \frac{K^{\nu\mu}_{j0s,n}[1 - v_{mm}N_m + (a_m/a_n)v_{nm}N_m] + K^{\nu\mu}_{j0s,m}[1 - v_{nn}N_n + (a_n/a_m)v_{mn}N_n]}{1 - v_{nn}N_n - v_{mm}N_m + (v_{nn}v_{mm} - |v_{nm}|^2)N_nN_m} . \qquad (4.29)$$

We note that even in a simple two-band model, the exchange enhancement of K_{js} is different from the simple form obtained in Eq. (4.21).

C. Electron-electron interaction effects on K_{jo}

From Eq. (3.44), it may be noted that there are no exchange and correlation effects on K_{jo}. However, the effects of electron-electron interaction are incorporated through effective-mass corrections and through modification of the Bloch functions. These corrections are essentially small and can be neglected.

D. Exchange and correlation effects on K_{jso}

In order to calculate the exchange and correlation effects on the mixed spin-orbit contribution

K_{jso}, we write Eq. (4.14) in the form

$$\tilde{\Sigma}^{1,\mu}_{n\rho,m\rho'}(\vec{k})=\alpha_{nm}\tilde{\Sigma}^{1,\mu}_{n\rho,m\rho'}+\tfrac{1}{2}\mu_0\alpha_{nm}g^{\mu}_{nm}\sigma^{\mu}_{n\rho,m\rho'}\ , \tag{4.30}$$

where we have defined a new interband exchange enhancement parameter

$$\alpha_{nm}=-\sum_{\vec{k}'}\bar{v}_{nm}(\vec{k},\vec{k}')\frac{f(E_{n\vec{k}'})-f(E_{m\vec{k}'})}{E_{nm}}\ . \tag{4.31}$$

Equation (4.30) can be written in the alternate form

$$\tilde{\Sigma}^{1,\mu}_{n\rho,m\rho'}=\tfrac{1}{2}\mu_0\frac{\alpha_{nm}}{1-\alpha_{nm}}g^{\mu}_{nm}\sigma^{\mu}_{n\rho,m\rho'}\ . \tag{4.32}$$

From Eqs. (3.19) and (4.32), we obtain

$$F^{\mu}_{n\rho,m\rho'}=\sigma^{\mu}_{n\rho,m\rho'}+\frac{\alpha_{nm}}{g_0(1-\alpha_{nm})}g^{\mu}_{nm}\sigma^{\mu}_{n\rho,m\rho'}\ . \tag{4.33}$$

Using Eq. (4.33), we have, considering only two bands n and m,

$$-\frac{i\mu_0^2}{m}\epsilon_{\alpha\beta\mu}\left[\frac{\Pi^{\alpha}_{n\rho,n\rho}\Pi^{\beta}_{n\rho,m\rho'}X^{\nu}_{jm\rho',n\rho}}{E^2_{mn}}-\frac{X^{0\nu}_{jn\rho,m\rho''}\Pi^{\alpha}_{m\rho'',q\rho'''}\Pi^{\beta}_{q\rho''',n\rho}}{E_{mn}E_{qn}}\right]+\tfrac{1}{2}g_0\mu_0^2\left[\frac{X^{\nu}_{jn\rho,m\rho'}F^{\mu}_{m\rho',n\rho}+F^{\mu}_{n\rho,m\rho'}X^{\nu}_{jm\rho',n\rho}}{E_{mn}}\right]$$
$$=\frac{1}{2(1-\alpha_{nm})}\mu_0^2\frac{[g^{\mu}_{nm}(\vec{k})\sigma^{\mu}_{n\rho,m\rho'}X^{\nu}_{jm\rho',n\rho}+g^{\mu}_{mn}(\vec{k})X^{\nu}_{jn\rho,m\rho'}\sigma^{\mu}_{m\rho',n\rho}]}{E_{mn}}$$
$$-\frac{2i\mu_0^2}{m}\epsilon_{\alpha\beta\mu}\epsilon_{\gamma\delta\nu}\frac{[(\hat{r}^{\gamma}_j/r_j^2)(\vec{p}+\hbar\vec{k})^{\delta}]_{n\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E^2_{mn}} \tag{4.34}$$

where we have taken $\alpha_{nm}=\alpha_{mn}$. From Eqs. (3.44) and (4.34), we have

$$K^{\nu\mu}_{jso}=K^{\nu\mu}_{jso,1}+K^{\nu\mu}_{jso,2}\ , \tag{4.35}$$

where

$$K^{\nu\mu}_{jso,1}=\sum_{n,\vec{k},\rho}\frac{\mu_0^2}{2(1-\alpha_{nm})}\left[\frac{g^{\mu}_{nm}(\vec{k})\sigma^{\mu}_{n\rho,m\rho'}X^{\nu}_{jm\rho',n\rho}}{E_{mn}}+\frac{g^{\mu}_{nm}(\vec{k})X^{\nu}_{jn\rho,m\rho'}\sigma^{\mu}_{m\rho',n\rho}}{E_{mn}}\right]f(E_n) \tag{4.36}$$

and

$$K^{\nu\mu}_{jso,2}=\sum_{m,\vec{k},\rho}\left\{\frac{i\mu_0^2}{m}\epsilon_{\alpha\beta\mu}[-3X^{\nu}_{jn\rho,n\rho'}\Pi^{\alpha}_{n\rho',m\rho''}\Pi^{\beta}_{m\rho'',n\rho}+\Pi^{\alpha}_{n\rho,n\rho}X^{\nu}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',n\rho}]\frac{1}{E^2_{mn}}\right.$$
$$+(\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{0\nu}_{jq\rho'',n\rho}+\Pi^{\alpha}_{n\rho,m\rho'}X^{0\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho})\frac{1}{E_{qn}E_{mn}}$$
$$\left.-\frac{2i\mu_0^2}{m}\epsilon_{\alpha\beta\mu}\epsilon_{\gamma\delta\nu}\frac{[(\hat{r}^{\gamma}_j/r_j^2)(\vec{p}+\hbar\vec{k})^{\delta}]_{n\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E^2_{mn}}\right\}f(E_n)\ . \tag{4.37}$$

Thus we note that the effect of electron-electron interaction is different for the different terms of $K^{\nu\mu}_{jso}$ and involves the calculation of interband matrix elements of $\tilde{\Sigma}^{1,\mu}$. $K^{\nu\mu}_{jso,1}$ becomes exchange enhanced through the interband enhancement term α_{nm}. In a sense, this exchange enhancement is similar to $K^{\nu\mu}_{js}$ although the enhancement parameters are different. However, $K^{\nu\mu}_{jso,2}$ does not become modified by exchange and correlation. The effect of electron-electron interactions on these terms is incorporated through an effective mass and through the modification of the Bloch functions.

In this sense $K^{\nu\mu}_{jso,2}$ is similar to $K^{\nu\mu}_{jo}$. We note that the leading term of $K^{\nu\mu}_{jso,2}$ [proportional to $-3X^{\nu}_{jn\rho,n\rho'}$ in Eq. (4.37)] is the dominant term in $K^{\nu\mu}_{jso}$. We also note that exchange and correlation effects on $K^{\nu\mu}_{jso}$ could not be incorporated in an intuitive way because of the mixed character of these terms.

V. KNIGHT SHIFT IN p-TYPE PbTe

As an example of the importance of the new contribution K_{so} to Knight shift of solids with large effective g factors, we have calculated the isotropic Knight shift of ^{207}Pb in p-type PbTe which has large spin-orbit coupling and small energy gaps. The wave functions used in the calculation have been obtained by using $\vec{k}\cdot\vec{p}$ perturbation theory on the twelve double-group basis functions for the six levels at the L point obtained by Mitchell and Wallis.[40] The double-group basis functions in the notation of Mitchell and Wallis[40] are

$$L_{61}^{+}\beta = i\cos\theta^{+}R\downarrow + \sin\theta^{+}S_{-}\uparrow ,$$
$$L_{61}^{-}\beta = \cos\theta^{-}Z\downarrow + \sin\theta^{-}X_{-}\uparrow ,$$
$$L_{62}^{+}\beta = i\sin\theta^{+}R\downarrow - \cos\theta^{+}S_{-}\uparrow ,$$
$$L_{62}^{-}\beta = \sin\theta^{-}Z\downarrow - \cos\theta^{-}X_{-}\uparrow , \qquad (5.1)$$
$$L_{4}^{+}\beta = \frac{1}{\sqrt{2}}(S_{+}\uparrow - iS_{-}\downarrow) ,$$

and

$$L_{4}^{-}\beta = \frac{1}{\sqrt{2}}(X_{+}\uparrow - iX_{-}\downarrow) .$$

Here the α and β indices denote the partners of a Kramers pair, the spin functions $\uparrow$ and $\downarrow$ refer to eigenstates of S_z in a coordinate system with x along the $[\bar{1}\bar{1}2]$, y along $[1\bar{1}0]$, and z along $[111]$ axes of a valley. R is an atomic s state, $X_{\pm}$ and Z transform like atomic p functions with $m_z = \pm 1$ and $m_z = 0$, respectively, and $S_{\pm}$ transform like atomic d functions with $m_z = \pm 1$. $\sin\theta^{\pm}$, $\cos\theta^{\pm}$ are the amplitudes of the single groups in the double-group basis functions. We note that there is some controversy about band ordering at the L point.[41,42] We have chosen the Lin-Kleinman ordering[41] since, using this ordering, Bernick and Kleinman[43] have obtained good agreement for energy gaps, effective masses, and g values.

We have first diagonalized exactly the conduction-band ($L_{62}^{-}\alpha$, $L_{62}^{-}\beta$) and valence-band wave functions ($L_{61}^{+}\alpha$, $L_{61}^{+}\beta$) to obtain

$$\psi_1 = \left[\frac{1+W}{2W}\right]^{1/2} L_{62}^{-}\alpha - \frac{\sqrt{2}(\hbar/m)sk_z}{E_G\sqrt{W(1+W)}}L_{61}^{+}\alpha + \frac{\sqrt{2}(\hbar/m)tk_{+}}{E_G\sqrt{W(1+W)}}L_{61}^{+}\beta ,$$
$$\psi_2 = \left[\frac{1+W}{2W}\right]^{1/2} L_{62}^{-}\beta + \frac{\sqrt{2}(\hbar/m)sk_z}{E_G\sqrt{W(1+W)}}L_{61}^{+}\beta + \frac{\sqrt{2}(\hbar/m)tk_{-}}{E_G\sqrt{W(1+W)}}L_{61}^{+}\alpha ,$$
$$\psi_3 = \left[\frac{1+W}{2W}\right]^{1/2} L_{61}^{+}\alpha + \frac{\sqrt{2}(\hbar/m)sk_z}{E_G\sqrt{W(1+W)}}L_{62}^{-}\alpha - \frac{\sqrt{2}(\hbar/m)tk_{+}}{E_G\sqrt{W(1+W)}}L_{62}^{-}\beta , \qquad (5.2)$$

and

$$\psi_4 = \left[\frac{1+W}{2W}\right]^{1/2} L_{61}^{+}\beta - \frac{\sqrt{2}(\hbar/m)sk_z}{E_G\sqrt{W(1+W)}}L_{62}^{-}\beta - \frac{\sqrt{2}(\hbar/m)tk_{-}}{E_G\sqrt{W(1+W)}}L_{62}^{-}\alpha .$$

Here E_G is the energy gap,

$$W = \left[1 + \frac{2\hbar^2 t^2}{m^2 E_G^2}(k_x^2 + k_y^2) + \frac{4\hbar^2 s^2}{m^2 E_G^2}k_z^2\right]^{1/2} , \qquad (5.3)$$

$$t = -\sin\theta^{+}\sin\theta^{-}P_{31} - \cos\theta^{+}\cos\theta^{-}P_{13} , \qquad (5.4)$$

$$s = -\sin\theta^{-}\cos\theta^{+}P_{11} + \cos\theta^{-}\sin\theta^{+}P_{21} , \qquad (5.5)$$

$$k_{\pm} = \frac{1}{\sqrt{2}}(k_x \pm ik_y) , \qquad (5.6)$$

and P_{11}, P_{21}, P_{31}, and P_{13} are the nonzero momentum matrix elements between single-group states defined in Ref. 40. The interaction of the ψ's with the far bands $L_{61}^{-}\alpha$, $L_{61}^{-}\beta$, $L_{62}^{+}\alpha$, $L_{62}^{+}\beta$, $L_{4}^{\pm}\beta$, and $L_{5}^{\pm}\alpha$ have been obtained by using $\vec{k}\cdot\vec{p}$ perturbation theory. The new valence-band energy $E_v(\vec{k})$ is obtained as

$$E_v(\vec{k}) = \epsilon_1^{+} + \frac{\hbar^2 k^2}{2m} - \tfrac{1}{2}E_G(W-1) + M_1(k_x^2+k_y^2) + M_2 k_z^2 + \left[\frac{M_3}{W(1+W)} + \frac{M_4}{W}\right](k_x^2+k_y^2)^2$$
$$+ \left[\frac{M_5}{W(1+W)} + \frac{M_6}{W}\right]k_z^4 + \left[\frac{M_7}{W(1+W)} + \frac{M_8}{W}\right](k_x^2+k_y^2)k_z^2 , \qquad (5.7)$$

where M_1, M_2, etc., are functions of momentum matrix elements, energy gaps, etc. Similarly, the matrix elements of $\vec{\Pi}$, $\vec{\sigma}$, and $\vec{X}$ have been expanded in powers of $\vec{k}$ and obtained in terms of the corresponding values at the band edges. The amplitudes of the single group in the double-group basis functions ($\sin\theta^{\pm}, \cos\theta^{\pm}$) and the momentum matrix elements and the energy gaps at the band edges were obtained from Bernick and Kleinman.[43] However, we have taken $\sin\theta^{\pm}$ to be positive instead of negative since otherwise the longitudinal (K_l) and transverse (K_t) Knight shifts have opposite signs. We note from the following argument that this change of sign neither alters the numerical results nor the band ordering. The energy expressions of Mitchell and Wallis[40] are

$$\epsilon_1^{\pm} = \epsilon_0^{\pm}\cos^2\theta^{\pm} - \Delta_1^{\pm}\sin^2\theta^{\pm} + 2\sqrt{2}\Delta_2^{\pm}\sin\theta^{\pm}\cos\theta^{\pm} \tag{5.8}$$

and

$$\epsilon_2^{\pm} = \epsilon_0^{\pm}\sin^2\theta^{\pm} - \Delta_1^{\pm}\cos^2\theta^{\pm} - 2\sqrt{2}\Delta_2^{\pm}\sin\theta^{\pm}\cos\theta^{\pm} , \tag{5.9}$$

where $\epsilon_0^{\pm}$, $\Delta_1^{\pm}$, and $\Delta_2^{\pm}$ are energy parameters. Furthermore,

$$\tan 2\theta^{\pm} = \frac{2\sqrt{2}\Delta_2^{\pm}}{\epsilon_0^{\pm} + \Delta_1^{\pm}} . \tag{5.10}$$

From Eqs. (5.8)–(5.10), it can be easily seen that $\epsilon_1^{\pm}$ and $\epsilon_2^{\pm}$ do not change if the signs of both $\sin\theta^{+}$ and $\sin\theta^{-}$ are changed simultaneously.

The matrix elements of $\vec{\Pi}$, $\vec{\sigma}$, and $\vec{X}$ and new energy gaps were substituted in the general expression for Knight shift [Eqs. (3.41)–(3.44)] to obtain the Knight shift $K(\vec{k})$ at an arbitrary $\vec{k}$. The result was then summed over all $\vec{k}$ states. In an arbitrarily oriented external magnetic field $\vec{B}$, neither the matrix elements of $\vec{\sigma}$ nor the Fermi population factors are identical in the four valleys at the $\langle 111 \rangle$ zone edges. Thus the sum over the four valleys in PbTe must be carried out, valley by valley, for the assumed direction of $\vec{B}$. However, since the cubic symmetry of the lead salts requires that the final result of isotropic Knight shift be independent of the orientation of $\vec{B}$, one may choose $\vec{B}$ in any direction. Therefore, we have simplified the problem by taking $\vec{B}$ along [001], in which case the four valleys are fully equivalent. For convenience, K was calculated for the valley around the point L with coordinates $(2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. Since there are four inequivalent L points, the total Knight shift is obtained from the formula

$$K = 4(\tfrac{1}{3}K^{l} + \tfrac{2}{3}K^{t}) , \tag{5.11}$$

where K^l is the longitudinal and K^t is the transverse Knight shift for any valley. For numerical calculations in p-type PbTe we have ignored exchange effects, which is justified in view of the low density of carriers.

Before presenting our numerical results we would like to point out that the negative (positive) sign of K in p (n)-type PbTe has been attributed to negative (positive) g factors in corresponding systems. However, it is well known[28] that whereas the sign of g factor is not uniquely determined, the sign of K is. Thus a calculation of K provides a stringent test of the accuracy of electronic wave functions in the solid.

The results of our calculation of the contributions from each valley to the longitudinal and transverse components of Knight shift in p-type PbTe for two different hole concentrations are given in Table I. The spin, orbital, and mixed spin-orbit contributions to the Knight shift have been calculated from these results using Eq. (5.11) and have been tabulated in Table II along with the experimental results. From Table II it can be seen that the orbital contribution to the Knight shift is about 3 orders of magnitude smaller than the spin and mixed spin-orbit contributions. It may be noted that the new contribution K_{so}, which has been missed in the earlier theories, has the same sign as

TABLE I. Longitudinal and transverse contributions to components of the Knight shift of ^{207}Pb in p-type PbTe for each valley (for two different hole concentrations).

Hole concentration (cm^{-3})	K_s^l	K_s^t	K_o^l	K_o^t	K_{so}^l	K_{so}^t
7.1×10^{17}	-1.98×10^{-3}	-4.13×10^{-4}	-1.74×10^{-9}	-1.06×10^{-9}	-4.2×10^{-4}	-1.21×10^{-4}
1.8×10^{18}	-2.15×10^{-3}	-4.37×10^{-4}	-6.19×10^{-9}	-3.78×10^{-9}	-7.6×10^{-4}	-2.46×10^{-4}

TABLE II. Spin, orbital, and spin-orbit contributions to the Knight shift of ^{207}Pb in p-type PbTe and comparison with experimental results.

Hole concentration (cm^{-3})	K_s	K_o	K_{so}	K_o/K_s	K_{so}/K_s	K_{tot}	K_{expt} (Ref. 44)
7.1×10^{17}	-3.74×10^{-3}	-5.12×10^{-9}	$-8.9\ \times10^{-4}$	1.37×10^{-6}	0.23	-4.63×10^{-3}	-4.7×10^{-3}
1.8×10^{18}	-4.03×10^{-3}	-1.81×10^{-8}	-1.68×10^{-3}	$4.5\ \times10^{-6}$	0.41	-5.71×10^{-3}	-6.1×10^{-3}

K_s and contributes a significant fraction of the total Knight shift. It is also interesting to note that ratio K_{so}/K_s increases with the hole concentration. The physical reason for this is the increase in the strength of the spin-orbit interaction as one goes away from the L point in the Brillouin zone. The quantitative agreement of our result with the experiment is quite encouraging if we note that exchange enhancement effects will increase with hole concentration, bringing theory and experiment into better quantitative agreement.

VI. SUMMARY AND CONCLUSION

In this paper we have presented what we believe is a reasonably complete theory of the Knight shift in solids, which includes the effect of electron-electron interaction on the Knight shift for many-band systems including spin-orbit interaction. We have analyzed all contributions carefully and obtained new contributions to the Knight shift (K_{so}) which have been missed in all the earlier theories. We have also calculated the effects of exchange and correlations on K_{so} which are important for solids with large effective g factors.

In order to calculate the relative importance of K_{so} we have applied our theory to calculate the Knight shift of ^{207}Pb in p-type PbTe with small hole concentrations. Our results indicate that K_{so} contributes a significant fraction of the total Knight shift and this contribution increases with the hole concentration, as it should, since the strength of the spin-orbit interaction is increased as one goes away from the L point in the Brillouin zone. Our results agree quite well with experimental results.

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APPENDIX A

In order to prove the partial integrations in Eqs. (3.29) and (3.30) we first wish to obtain expressions for $\nabla_k^\alpha \Pi_{np,mp'}^\beta$ and $\nabla_k^\alpha D_{jnp,mp'}^\nu$. We have

$$\nabla_k^\alpha \Pi_{np,mp'}^\beta = \frac{m}{\hbar}\nabla_k^\alpha \int d\vec{r}\, U^*_{n,\vec{k},\rho}(\nabla_k^\beta H_0)U_{m,\vec{k},\rho'}$$

$$= \frac{m}{\hbar}\left[\int d\vec{r}(\nabla_k^\alpha U^*_{n,\vec{k},\rho})(\nabla_k^\beta H_0)U_{m,\vec{k},\rho'} + \int d\vec{r}\, U^*_{n,\vec{k},\rho}(\nabla_k^\alpha\nabla_k^\beta H_0)U_{m,\vec{k},\rho'} \right.$$

$$\left. + \int d\vec{r}\, U^*_{n,\vec{k},\rho}(\nabla_k^\beta H_0)\nabla_k^\alpha U_{m,\vec{k},\rho'}\right]. \tag{A1}$$

Since $U_{n,\vec{k},\rho}$ are a complete set for periodic functions, we can insert the identity $|U_{q,\vec{k},\rho''}\rangle\langle U_{q,\vec{k},\rho''}|$ in the first and third terms. Therefore, we have

$$\nabla_k^\alpha \Pi_{n\rho,m\rho'}^\beta = \frac{m}{\hbar}\Bigg[\sum_{\substack{q,\rho''\\ q\neq n}} \int d\vec{r}(\nabla_k^\alpha U_{n,\vec{k},\rho}^*)U_{q,\vec{k},\rho''}\int d\vec{r}\,' U_{q,\vec{k},\rho''}^*(\nabla_k^\beta H_0)U_{m,\vec{k},\rho'}$$
$$+\sum_{\rho''}\int d\vec{r}(\nabla_k^\alpha U_{n,\vec{k},\rho}^*)U_{n,\vec{k},\rho''}\int d\vec{r}\,' U_{n,\vec{k},\rho''}^*(\nabla_k^\beta H_0)U_{m,\vec{k},\rho'}$$
$$+\sum_{\substack{q,\rho''\\ q\neq m}}\int d\vec{r}\,U_{n,\vec{k},\rho}^*(\nabla_k^\beta H_0)U_{q,\vec{k},\rho''}\int d\vec{r}\,' U_{q,\vec{k},\rho''}^*\nabla_k^\alpha U_{m,\vec{k},\rho'}$$
$$+\sum_{\rho''}\int d\vec{r}\,U_{n,\vec{k},\rho}^*(\nabla_k^\beta H_0)U_{m,\vec{k},\rho''}\int d\vec{r}\,' U_{m,\vec{k},\rho''}^*\nabla_k^\alpha U_{m,\vec{k},\rho'}+\frac{\hbar^2}{m}\delta_{\alpha\beta}\delta_{n\rho,m\rho'}+Y_{n\rho,m\rho'}^{\alpha\beta}\Bigg], \tag{A2}$$

where

$$Y^{\alpha\beta}=\nabla_k^\alpha\nabla_k^\beta\tilde{\Sigma}^0 . \tag{A3}$$

We also have

$$\nabla_k^\alpha\int d\vec{r}\,U_{n,\vec{k},\rho}^* H_0 U_{q,\vec{k},\rho'}=0 , \tag{A4}$$

from which we obtain

$$E_q\int d\vec{r}(\nabla_k^\alpha U_{n,\vec{k},\rho}^*)U_{q,\vec{k},\rho'}+E_n\int d\vec{r}\,U_{n,\vec{k},\rho}^*\nabla_k^\alpha U_{q,\vec{k},\rho'}+\frac{\hbar}{m}\Pi_{n\rho,q\rho'}^\alpha=0 \tag{A5}$$

and

$$\nabla_k^\alpha\int d\vec{r}\,U_{n,\vec{k},\rho}^* U_{q,\vec{k},\rho'}=0 , \tag{A6}$$

from which we obtain

$$\int d\vec{r}(\nabla_k^\alpha U_{n,\vec{k},\rho}^*)U_{q,\vec{k},\rho'}=-\int d\vec{r}\,U_{n,\vec{k},\rho}^*\nabla_k^\alpha U_{q,\vec{k},\rho'} . \tag{A7}$$

From Eqs. (A5) and (A7) we have for $q\neq n$

$$\int d\vec{r}\,U_{n,\vec{k},\rho}^*\nabla_k^\alpha U_{q,\vec{k},\rho'}=\frac{\hbar}{m}\frac{\Pi_{n\rho,q\rho'}^\alpha}{E_{qn}} . \tag{A8}$$

We define

$$\vec{Q}_{n\rho,n\rho'}\equiv\int d\vec{r}\,U_{n,\vec{k},\rho}^*\nabla_k U_{n,\vec{k},\rho'} . \tag{A9}$$

From Eqs. (A2), (A8), and (A9) we obtain

$$\nabla_k^\alpha\Pi_{n\rho,m\rho'}^\beta=\sum_{\substack{q,\rho''\\ q\neq n}}\frac{\hbar}{m}\frac{\Pi_{n\rho,q\rho''}^\alpha\Pi_{q\rho'',m\rho'}^\beta}{E_{nq}}+\sum_{\substack{q,\rho''\\ q\neq m}}\frac{\hbar}{m}\frac{\Pi_{n\rho,q\rho''}^\beta\Pi_{q\rho'',m\rho'}^\alpha}{E_{mq}}$$
$$-\sum_{\rho''}(Q_{n\rho,n\rho''}^\alpha\Pi_{n\rho'',m\rho'}^\beta-\Pi_{n\rho,m\rho''}^\beta Q_{m\rho'',m\rho'}^\alpha)+\hbar\delta_{\alpha\beta}\delta_{n\rho,m\rho'}+\frac{m}{\hbar}Y_{n\rho,m\rho'}^{\alpha\beta} . \tag{A10}$$

In a similar fashion we can prove

$$\nabla_k^\alpha D_{jn\rho,m\rho'}^\nu=\sum_{\substack{q,\rho''\\ q\neq n}}\frac{\hbar}{m}\frac{\Pi_{n\rho,q\rho''}^\alpha D_{jq\rho'',m\rho'}^\nu}{E_{nq}}+\sum_{\substack{q,\rho''\\ q\neq m}}\frac{\hbar}{m}\frac{D_{jn\rho,q\rho''}^\nu\Pi_{q\rho'',m\rho'}^\alpha}{E_{mq}}$$
$$-\sum_{\rho''}(Q_{n\rho,n\rho''}^\alpha D_{jn\rho'',m\rho'}^\nu-D_{jn\rho,m\rho''}^\nu Q_{m\rho'',m\rho'}^\alpha)+2\epsilon_{\nu\eta\alpha}\left[\frac{r_j^\eta}{r_j^3}\right]_{n\rho,m\rho'}+\frac{1}{\mu_0}\left[\frac{\partial\tilde{\Sigma}_j^{2,\nu}}{\partial k^\alpha}\right]_{n\rho,m\rho'} \tag{A11}$$

and

$$\nabla_k^\alpha \Pi^\beta_{m\rho',n\rho} = \sum_{\substack{q,\rho'' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{mq}} + \sum_{\substack{q,\rho'' \\ q\neq n}} \frac{\hbar}{m} \frac{\Pi^\beta_{m\rho',q\rho''}\Pi^\alpha_{q,\rho'',n\rho}}{E_{nq}} - \sum_{\rho''} (Q^\alpha_{m\rho',m\rho''}\Pi^\beta_{m\rho'',n\rho} - \Pi^\beta_{m\rho',n\rho''}Q^\alpha_{n\rho'',n\rho}) + \hbar\delta_{\alpha\beta}\delta_{m\rho',n\rho} + \frac{m}{\hbar} Y^{\alpha\beta}_{m\rho',n\rho} . \tag{A12}$$

The partial integration can be done in the following way. We consider the following differentiation:

$$h_{\alpha\beta}M_{j\nu}\nabla_k^\alpha \left[\frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}}{E^2_{mn}} \phi(E_n) \right]$$

$$= h_{\alpha\beta}M_{j\nu} \Bigg\{ \Bigg[\Bigg[\sum_{\substack{q,\rho'' \\ q\neq n}} \frac{\hbar}{m} \frac{\Pi^\alpha_{n\rho,q\rho''}D^\nu_{jq\rho'',m\rho'}}{E_{nq}} + \sum_{\substack{q,\rho'' \\ q\neq m}} \frac{\hbar}{m} \frac{D^\nu_{jn\rho,q\rho''}\Pi^\alpha_{q\rho'',m\rho'}}{E_{mq}} - \sum_{\rho''} (Q^\alpha_{n\rho,n\rho''}D^\nu_{jn\rho'',m\rho'} - D^\nu_{jn\rho,m\rho''}Q^\alpha_{m\rho'',m\rho'})$$

$$+ 2\epsilon_{\nu\eta\alpha} \left[\frac{r_j^\eta}{r_j^3} \right]_{n\rho,m\rho'} + \frac{1}{\mu_0} \left[\frac{\partial \tilde{\Sigma}_j^{2,\nu}}{\partial k^\alpha} \right]_{n\rho,m\rho'} \Bigg] \frac{\Pi^\beta_{m\rho',n\rho}}{E^2_{mn}} \phi(E_n)$$

$$+ \frac{D^\nu_{jn\rho,m\rho'}}{E^2_{mn}} \Bigg[\sum_{\substack{q,\rho'' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{mq}} + \sum_{\substack{q,\rho'' \\ q\neq n}} \frac{\hbar}{m} \frac{\Pi^\beta_{m\rho',q\rho''}\Pi^\alpha_{q\rho'',n\rho}}{E_{nq}}$$

$$- \sum_{\rho''} (Q^\alpha_{m\rho',m\rho''}\Pi^\beta_{m\rho'',n\rho} - \Pi^\beta_{m\rho',n\rho''}Q^\alpha_{n\rho'',n\rho}) + \hbar\delta_{\alpha\beta}\delta_{m\rho',n\rho} \Bigg] \phi(E_n)$$

$$-2\frac{\hbar}{m} \Bigg[\frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}\Pi^\alpha_{m\rho',m\rho'}}{E^3_{mn}} - \frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E^3_{mn}} \Bigg] \phi(E_n) + \frac{\hbar}{m} \frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}\Pi^\alpha_{n\rho',n\rho}}{E^2_{mn}} f(E_n) \Bigg\} , \tag{A13}$$

where we sum over all the band indices but $n\neq m\neq q$. We note that the sum $h_{\alpha\beta}Y^{\alpha\beta}$ is zero because of the antisymmetric nature of $h_{\alpha\beta}$. We simplify the sum by interchanging band indices (except n) wherever necessary and then group together the diagonal terms in the band indices q and m with the nondiagonal terms. Since we have a summation over $\vec{k}$, which can be changed to an integration, the volume integral over the $\vec{k}$ space can be changed to a surface intergral, and since the integrand is periodic in $\vec{k}$, the surface integral vanishes. Thus the sum is zero and so the term proportional to $f(E_n)$ will be equal and opposite in sign to all the terms proportional to $\phi(E_n)$. Finally we obtain

$$-i\frac{\hbar^2}{m^2} h_{\alpha\beta}M_{j\nu} \sum_{\vec{k}} \frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E^2_{mn}} f(E_n)$$

$$= \sum_{\vec{k}} \Bigg[i\frac{\hbar^2}{m^2} h_{\alpha\beta}M_{j\nu} \Bigg(-\frac{\Pi^\alpha_{n\rho,m\rho'}D^\nu_{jm\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{mn}E^2_{qn}} + \frac{D^\nu_{jn\rho,n\rho'}\Pi^\alpha_{n\rho',m\rho''}\Pi^\beta_{m\rho'',n\rho}}{E^3_{mn}} - \frac{D^\nu_{jn\rho,m\rho'}\Pi^\alpha_{m\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E^2_{qn}E_{mn}}$$

$$+ \frac{D^\nu_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E^3_{mn}} \Bigg] + A_j^{\eta\beta} \frac{C^\eta_{jn\rho,m\rho'}\Pi^\beta_{m\rho',n\rho}}{E^2_{mn}} \Bigg] \phi(E_n) , \tag{A14}$$

where the sums are over m,ρ',q,ρ'', but $m,q\neq n$. Following a similar procedure we can prove Eq. (3.30).

APPENDIX B

We shall now prove Eq. (3.39). We write, interchanging α and β in Eq. (A10),

$$\nabla_k^\beta \Pi^\alpha_{n\rho,m\rho'} = \sum_{\substack{q,\rho'' \\ q\neq n}} \frac{\hbar}{m} \frac{\Pi^\beta_{n\rho,q\rho''}\Pi^\alpha_{q\rho'',m\rho'}}{E_{nq}} + \sum_{\substack{q,\rho'' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\alpha_{n\rho,q\rho''}\Pi^\beta_{q\rho'',m\rho'}}{E_{mq}}$$

$$- \sum_{\rho''} (Q^\beta_{n\rho,n\rho''}\Pi^\alpha_{n\rho'',m\rho'} - \Pi^\alpha_{n\rho,m\rho''}Q^\beta_{m\rho'',m\rho'}) + \hbar\delta_{\alpha\beta}\delta_{n\rho,m\rho'} + \frac{m}{\hbar} Y^{\alpha\beta}_{n\rho,m\rho'} \tag{B1}$$

and, in a similar fashion as Eq. (A11), we can prove

$$\nabla_k^\beta \tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho''} = \sum_{\substack{q,\rho''' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\beta_{m\rho',q\rho'''}\tilde{\Sigma}^{2,\nu}_{jq\rho''',n\rho''}}{E_{mq}} + \sum_{\substack{q,\rho''' \\ q\neq n}} \frac{\hbar}{m} \frac{\tilde{\Sigma}^{2,\nu}_{jm\rho',q\rho'''}\Pi^\beta_{q\rho''',n\rho''}}{E_{nq}}$$

$$- \sum_{\rho'''} (Q^\beta_{m\rho',m\rho'''}\tilde{\Sigma}^{2,\nu}_{jm\rho''',n\rho''} - \tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho'''}Q^\beta_{n\rho''',n\rho''}) + \left[\frac{\partial}{\partial k^\beta}\tilde{\Sigma}^{2,\nu}_j\right]_{m\rho',n\rho''} . \tag{B2}$$

Using Eqs. (B1) and (B2), we have

$$\epsilon_{\alpha\beta\mu}\nabla_k^\beta \left[\frac{\Pi^\alpha_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho''}}{E_{mn}} f(E_n)\right]$$

$$= \epsilon_{\alpha\beta\mu} \Bigg\{ \Bigg[\sum_{\substack{q,\rho'' \\ q\neq n}} \frac{\hbar}{m} \frac{\Pi^\beta_{n\rho,q\rho''}\Pi^\alpha_{q\rho'',m\rho'}}{E_{nq}} + \sum_{\substack{q,\rho'' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\alpha_{n\rho,q\rho''}\Pi^\beta_{q\rho'',m\rho'}}{E_{mq}}$$

$$- \sum_{\rho''} (Q^\beta_{n\rho,n\rho''}\Pi^\alpha_{n\rho'',m\rho'} - \Pi^\alpha_{n\rho,m\rho''}Q^\beta_{m\rho'',m\rho'}) + \hbar\delta_{\alpha\beta}\delta_{n\rho,m\rho'} \Bigg] \frac{\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho''}}{E_{mn}} f(E_n)$$

$$+ \frac{\Pi^\alpha_{n\rho,m\rho'}}{E_{mn}} \Bigg[\sum_{\substack{q,\rho''' \\ q\neq m}} \frac{\hbar}{m} \frac{\Pi^\beta_{m\rho',q\rho'''}\tilde{\Sigma}^{2,\nu}_{jq\rho''',n\rho''}}{E_{mq}} + \sum_{\substack{q,\rho''' \\ q\neq n}} \frac{\hbar}{m} \frac{\tilde{\Sigma}^{2,\nu}_{jm\rho',q\rho'''}\Pi^\beta_{q\rho''',n\rho''}}{E_{nq}} - \sum_{\rho'''} (Q^\beta_{m\rho',m\rho'''}\tilde{\Sigma}^{2,\nu}_{jm\rho''',n\rho''}$$

$$- \tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho'''}Q^\beta_{n\rho''',n\rho''}) + \left[\frac{\partial}{\partial k^\beta}\tilde{\Sigma}^{2,\nu}_j\right]_{m\rho',n\rho''} \Bigg] f(E_n)$$

$$+ \frac{\hbar}{m} \left[\frac{\Pi^\alpha_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho''}\Pi^\beta_{n\rho'',n\rho''}}{E^2_{mn}} - \frac{\Pi^\alpha_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho''}\Pi^\beta_{m\rho',m\rho'}}{E^2_{mn}} \right] f(E_n)$$

$$+ \frac{\hbar}{m} \frac{\Pi^\alpha_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}\Pi^\beta_{n\rho,n\rho}}{E_{mn}} f'(E_n) \Bigg\} . \tag{B3}$$

By a procedure similar to that followed in Eq. (A14), we obtain from Eq. (B3)

$$\epsilon_{\alpha\beta\mu} \sum_{\vec{k}} \frac{\Pi^\beta_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',n\rho}\Pi^\alpha_{n\rho,n\rho}}{E_{mn}} f'(E_n) = \epsilon_{\alpha\beta\mu} \sum_{\vec{k}} \Bigg[- \frac{\Pi^\alpha_{n\rho,m\rho'}\tilde{\Sigma}^{2,\nu}_{jm\rho',q\rho''}\Pi^\beta_{q\rho'',n\rho}}{E_{mn}E_{qn}} + \frac{\Pi^\alpha_{n\rho,m\rho'}\Pi^\beta_{m\rho',n\rho''}\tilde{\Sigma}^{2,\nu}_{jn\rho'',n\rho}}{E^2_{mn}}$$

$$+ \frac{m}{\hbar} \frac{\Pi^\alpha_{n\rho,m\rho'}\left[\dfrac{\partial\tilde{\Sigma}^{2,\nu}_j}{\partial k^\beta}\right]_{m\rho',n\rho}}{E_{mn}} \Bigg] f(E_n) . \tag{B4}$$

Similarly, we have

$$\epsilon_{\alpha\beta\mu}\sum_{\vec{k}}\frac{\tilde{\Sigma}^{2,\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',n\rho}\Pi^{\beta}_{n\rho,n\rho}}{E_{mn}}f'(E_n)=\epsilon_{\alpha\beta\mu}\sum_{\vec{k}}\left\{\frac{\Pi^{\beta}_{n\rho,m\rho''}\tilde{\Sigma}^{2,\nu}_{jm\rho'',q\rho'}\Pi^{\alpha}_{q\rho',n\rho}}{E_{mn}E_{qn}}-\frac{\tilde{\Sigma}^{2,\nu}_{jn\rho,n\rho'}\Pi^{\beta}_{n\rho',m\rho''}\Pi^{\alpha}_{m\rho'',n\rho}}{E^2_{mn}}-\frac{m}{\hbar}\frac{\left[\frac{\partial\tilde{\Sigma}^{2,\nu}_{j}}{\partial k^{\beta}}\right]_{n\rho,m\rho'}\Pi^{\alpha}_{m\rho',n\rho}}{E_{mn}}\right\}f(E_n)\ . \tag{B5}$$

By summing Eqs. (B4) and (B5), we obtain Eq. (3.39).

APPENDIX C

We shall now prove Eq. (3.40). Using Eq. (3.18), we write

$$\begin{aligned}\sum_{\substack{n,\vec{k},\rho\\ m,q,\rho',\rho''}}&(\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{\nu}_{jq\rho'',n\rho}+\Pi^{\alpha}_{n\rho,m\rho'}X^{\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}+X^{\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho})\frac{1}{E_{qn}E_{mn}}\\
=\sum_{\substack{n,\vec{k},\rho\\ m,q,\rho',\rho''}}&\Bigg[(\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{0\nu}_{jq\rho'',n\rho}+\Pi^{\alpha}_{n\rho,m\rho'}X^{0\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}+X^{0\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho})\frac{1}{E_{qn}E_{mn}}\\
&+(\Pi^{\alpha}_{n\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{1\nu}_{jq\rho'',n\rho}+\Pi^{\alpha}_{n\rho,m\rho'}X^{1\nu}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}+X^{1\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho})\frac{1}{E_{qn}E_{mn}}\Bigg]\ .\end{aligned} \tag{C1}$$

Denoting the second term in Eq. (C1) as T_l, we can write it in the alternate form

$$T_l=\sum_{\substack{n,\vec{k},\rho\\ m,q,\rho',\rho''}}\left[\frac{im}{\hbar}\left[-\frac{r^{\alpha}_{jn\rho,m\rho'}\Pi^{\beta}_{m\rho',q\rho''}X^{1\nu}_{jq\rho'',n\rho}}{E_{qn}}+\frac{X^{1\nu}_{jn\rho,m\rho'}\Pi^{\alpha}_{m\rho',q\rho''}r^{\beta}_{jq\rho'',n\rho}}{E_{mn}}\right]+\frac{m^2}{\hbar^2}(r^{\alpha}_{jn\rho,m\rho'}X^{1\nu}_{jm\rho',q\rho''}r^{\beta}_{jq\rho'',n\rho})\right]\ , \tag{C2}$$

where we have used the well-known relation

$$\frac{\vec{\Pi}_{n\rho,m\rho'}}{E_{nm}}=\frac{im}{\hbar}\vec{r}_{n\rho,m\rho'}\ . \tag{C3}$$

Using the completeness of the periodic functions, we write

$$\frac{(r^{\alpha}_j\Pi^{\beta})_{n\rho,m\rho'}X^{1\nu}_{jm\rho',n\rho}}{E_{mn}}=\sum_{q,\rho''}\frac{r^{\alpha}_{jn\rho,q\rho''}\Pi^{\beta}_{q\rho'',m\rho'}X^{1\nu}_{jm\rho',n\rho}}{E_{mn}}+\sum_{\rho''}\frac{r^{\alpha}_{jn\rho,n\rho''}\Pi^{\beta}_{n\rho'',m\rho'}X^{1\nu}_{jm\rho',n\rho}}{E_{mn}}\ , \tag{C4}$$

$$\frac{X^{1\nu}_{jn\rho,m\rho'}(r^{\alpha}_j\Pi^{\beta})_{m\rho',n\rho}}{E_{mn}}=\sum_{q,\rho''}\frac{X^{1\nu}_{jn\rho,m\rho'}r^{\alpha}_{jm\rho',q\rho''}\Pi^{\beta}_{q\rho'',n\rho}}{E_{mn}}+\sum_{\rho''}\frac{X^{1\nu}_{jn\rho,m\rho'}r^{\alpha}_{jm\rho',n\rho''}\Pi^{\beta}_{n\rho'',n\rho}}{E_{mn}}\ , \tag{C5}$$

and

$$(r^{\alpha}_jX^{1\nu}_jr^{\beta}_j)_{n\rho,n\rho}=\sum_{m,\rho'}(r^{\alpha}_jX^{1\nu}_j)_{n\rho,m\rho'}r^{\beta}_{jm\rho',n\rho}+\sum_{\rho'}(r^{\alpha}_jX^{1\nu}_j)_{n\rho,n\rho'}r^{\beta}_{jn\rho',n\rho}\ . \tag{C6}$$

From Eqs. (C2) and (C4)–(C6), we have

$$T_l = -\sum_{\substack{n,\vec{k},\rho \\ m,\rho',\rho''}} \left[\frac{im}{\hbar} \left[\frac{(r_j^\alpha \Pi^\beta)_{n\rho,m\rho'} X^{1\nu}_{jm\rho',n\rho} + X^{1\nu}_{jn\rho,m\rho'} (r_j^\alpha \Pi^\beta)_{m\rho',n\rho}}{E_{mn}} \right] \right.$$

$$+ \frac{m^2}{\hbar^2} [r^\alpha_{jn\rho,n\rho'} r^\beta_{jn\rho',m\rho''} X^{1\nu}_{jm\rho'',n\rho} + X^{1\nu}_{jn\rho,m\rho'} r^\alpha_{jm\rho',n\rho''} r^\beta_{jn\rho'',n\rho} + (r_j^\alpha X_j^{1\nu} r_j^\beta)_{n\rho,n\rho} - (r_j^\alpha X_j^{1\nu})_{n\rho,n\rho'} r^\beta_{jn\rho',n\rho}$$

$$\left. - r^\alpha_{jn\rho,n\rho'} X^{1\nu}_{jn\rho',m\rho''} r^\beta_{jm\rho'',n\rho}] \right] . \tag{C7}$$

We can also write

$$r^\alpha_{jn\rho,n\rho'} (r_j^\beta X_j^{1\nu})_{n\rho',n\rho} = \sum_{m,\rho''} r^\alpha_{jn\rho,n\rho'} r^\beta_{jn\rho',m\rho''} X^{1\nu}_{jm\rho'',n\rho} + \sum_{\rho''} r^\alpha_{jn\rho,n\rho'} r^\beta_{jn\rho',n\rho''} X^{1\nu}_{jn\rho'',n\rho} \tag{C8}$$

and

$$(X_j^{1\nu} r_j^\alpha)_{n\rho,n\rho''} r^\beta_{jn\rho'',n\rho} = \sum_{m,\rho'} X^{1\nu}_{jn\rho,m\rho'} r^\alpha_{jm\rho',n\rho''} r^\beta_{jn\rho'',n\rho} + \sum_{\rho'} X^{1\nu}_{jn\rho,n\rho'} r^\alpha_{jn\rho',n\rho''} r^\beta_{jn\rho'',n\rho} . \tag{C9}$$

From Eqs. (C7)–(C9), and using the commutation relation

$$[r_j^\beta, X_j^{1\nu}] = 2i\epsilon_{\nu\eta\beta} \left[\frac{r_j^\eta}{r_j^3} \right] , \tag{C10}$$

and the identity equation (3.35), we obtain

$$\frac{i}{m}\mu_0^2 \epsilon_{\alpha\beta\mu} T_l = \frac{2}{\hbar}\mu_0^2 \epsilon_{\alpha\beta\mu} \sum_{\substack{n,\vec{k},\rho \\ m,\rho'}} \left[(r_j^\alpha \Pi^\beta)_{n\rho,m\rho'} \left[\frac{L_j^\nu}{r_j^3} \right]_{m\rho',n\rho} + \left[\frac{L_j^\nu}{r_j^3} \right]_{n\rho,m\rho'} (r_j^\alpha \Pi^\beta)_{m\rho',n\rho} \right] \frac{1}{E_{mn}}$$

$$+ \frac{2m}{\hbar^2}\mu_0^2 (\delta_{\nu\beta}\delta_{\mu\eta} - \delta_{\nu\mu}\delta_{\beta\eta}) \sum_{n,\vec{k},\rho,\rho'} \left[\left[\frac{r_j^\eta}{r_j^3} \right]_{n\rho,n\rho'} r^\beta_{jn\rho',n\rho} - \left[\frac{r_j^\beta r_j^\eta}{r_j^3} \right]_{n\rho,n\rho} + r^\beta_{jn\rho,n\rho'} \left[\frac{r_j^\eta}{r_j^3} \right]_{n\rho',n\rho} \right] . \tag{C11}$$

We also have, using Eq. (C3),

$$-\frac{2i\mu_0^2}{\hbar} (\delta_{\nu\beta}\delta_{\mu\eta} - \delta_{\nu\mu}\delta_{\beta\eta}) \sum_{\substack{n,\vec{k},\rho \\ m,\rho'}} \frac{(r_j^\eta / r_j^3)_{n\rho,m\rho'} \Pi^\beta_{m\rho',n\rho} - \Pi^\beta_{n\rho,m\rho'} (r_j^\eta / r_j^3)_{m\rho',n\rho}}{E_{mn}}$$

$$= \frac{2m}{\hbar^2}\mu_0^2 (\delta_{\nu\beta}\delta_{\mu\eta} - \delta_{\nu\mu}\delta_{\beta\eta}) \sum_{n,\vec{k},\rho,\rho'} \left[\left[\frac{r_j^\eta r_j^\beta}{r_j^3} \right]_{n\rho,n\rho} + \left[\frac{r_j^\beta r_j^\eta}{r_j^3} \right]_{n\rho,n\rho} - \left[\frac{r_j^\eta}{r_j^3} \right]_{n\rho,n\rho'} r^\beta_{jn\rho',n\rho} - r^\beta_{jn\rho,n\rho'} \left[\frac{r_j^\eta}{r_j^3} \right]_{n\rho',n\rho} \right] . \tag{C12}$$

From Eqs. (C1), (C11), and (C12) and using the identity $(r_j^\eta r_j^\beta)_{n\rho,n\rho} = 0$ for $\eta \neq \beta$, we obtain the desired result in Eq. (3.40).

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