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Theory of Hyperfine Properties of Liquid Metals – Application to Cadmium[†]

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A perturbation formulation is developed for the calculation of spin densities in liquid metals using nonlocal pseudopotentials. Specific application is made to liquid cadmium using experimental interference function data. The results explain the observed temperature independence of the Knight shift and nuclear-spin lattice relaxation time and provide empirical exchange-enhancement factors for these properties. A comparison is made with prediction of current exchange-enhancement theories and suggestions are made for improvement of the agreement between theoretical and experimental Knight shifts and relaxation times.

I. INTRODUCTION

A variety of experimental resonance data such as Knight shift K_s and nuclear-spin lattice relaxation time T_1 are becoming increasingly available for a number of liquid metals.[1-3] There appear to be three specific hyperfine effects associated with the data. Two of these, related to each other, are K_s and the relaxation rate $1/T_1$ due to the Korringa type of process, which is the only important one for spin-$\frac{1}{2}$ nuclei. The third property, namely, the nuclear quadrupole contribution to the relaxation rate,[3,4] requires a knowledge of the dynamics of the ionic motion in addition to the average ionic distribution and the electronic wave functions that the first two properties require. This paper will be concerned only with the Knight shift and Korringa type of relaxation process.[5]

The theoretical situation with respect to K_s and T_1 is currently becoming increasingly better understood in the solid state[6] from a quantitative point of view. One is now able to unravel from the data on K_s and T_1 such sophisticated effects as the conduction-conduction exchange contribution to the static and dynamic electronic susceptibilities.[7] This has become possible as a result of our improved understanding of the spin density in the solid due to two main developments. One of these is the availability of a practicable procedure for evaluating exchange-core-polarization (ECP) effects.[8,9] The second is the current possibility of carrying out detailed scanning of the spin density at the Fermi surface employing high-speed computers. The use of pseudopotential techniques[10] is particularly expeditious with respect to this latter step.

In the liquid a detailed scanning of the Fermi surface is not necessary because it is expected to be spherical on a time-averaged scale. There are, however, difficulties in developing theories for hyperfine effects in liquid metals, some of which are purely theoretical in nature and some due to lack of sufficient experimental information. Considering the latter features first, we need information in the liquid which is a convenient substitute for the known crystal structure in the solid. Such information is presently available from x-ray diffraction experiments in the liquid.[11,12] However, as will be shown later in the text of the paper, additional information pertaining to the ionic distribution is necessary for developing a complete theory for the spin density in the liquid.

From the theoretical point of view there are a number of questions to be answered. The first is connected with convergence effects in a perturbation approach involving continuum states of the electron gas. This question does not occur in the solid state in view of the periodicity of both the real and Fourier space lattices which avoids vanishing energy denominators in perturbation approaches to wave functions. A second and related question is the computational complexity associated with the use of nonlocal pseudopotentials which seem to be essential for a number of metals. A third question is the difference in nature of the exchange-enhancement effects for the static and dynamic susceptibility in the solid and liquid phases.

This paper addresses itself to these questions of theory with a particular application to liquid cadmium. This metal is of interest because of its unusual nuclear-magnetic-resonance (NMR) properties in the solid[1,13] and liquid phases.[1] The isotropic and anisotropic Knight shifts in the solid phase increase strongly with temperature. In the liquid K_s, however, is almost constant with temperature. The Korringa ratio is constant both in the solid and liquid states but changes discontinuously at the melting point. Additionally, the theoretical analysis of solid-state data[14] indicates that the exchange enhancements of the susceptibility and relaxation rates are substantially higher than those for the free-electron gas. It is interesting to investigate the corresponding situation in the liquid.

In Sec. II the problem of the spin density for the liquid state will be formulated by a perturbation approach using a nonlocal pseudopotential. Section III will be concerned with the technical details of the actual computation and discussion of the results as they pertain to cadmium in particular, and liquid metals in general. Section IV summarizes the main conclusions from this work.

II. THEORY

The Knight shift K_s in the liquid metal is given by the expression

$$K_s = \tfrac{8}{3}\pi \chi_s N \Omega_0 \zeta \, , \qquad (1)$$

analogous to the solid where ζ is the spin density and χ_s is the Pauli paramagnetic spin susceptibility per unit volume. N and Ω_0 are, respectively, the number of ions in the liquid and volume per atom parallel to the Wigner-Seitz volume in the solid state. The spin density ζ in the liquid is given by

$$\zeta = \langle \langle N^{-1} \textstyle\sum_i | \psi_{k_F}(\vec{\mathrm{R}}_i) |^2 \rangle \rangle_F , \qquad (2)$$

where $\psi_{k_F}(\vec{\mathrm{R}}_i)$ is the conduction-electron wave function at the R_ith nuclear site. The inner average with respect to N in Eq. (2) takes account of the fluctuations at the ionic sites due to the atomic motions in the liquid. In the solid, due to the ordered lattice structure, such an averaging is normally unnecessary unless one is interested in temperature variations of the Knight shift. The outer average sign with suffix F describes the Fermi-surface average and is of no consequence when the Fermi surface is assumed to be a sphere in the liquid state as we shall do here. Thus the spin density in the liquid is, in fact, taken in the form

$$\zeta = \langle N^{-1} \textstyle\sum_i | \psi_{k_F}(\vec{\mathrm{R}}_i) |^2 \rangle . \qquad (3)$$

In the orthogonalized-plane-wave (OPW) formalism, the value of the conduction-electron wave function at the nucleus at the Fermi surface is given by

$$\psi_{k_F}(\vec{\mathrm{R}}_i) = N_{k_F}^{-1} (N\Omega_0)^{-1/2} \textstyle\sum_{\vec{\mathrm{K}}} C(\vec{\mathrm{k}}_F + \vec{\mathrm{K}}) e^{i(\vec{\mathrm{k}}_F + \vec{\mathrm{K}}) \cdot \vec{\mathrm{R}}_i}$$

$$\times [1 - \textstyle\sum_t b_t(\vec{\mathrm{k}}_F + \vec{\mathrm{K}}) \Theta_t(0)] , \qquad (4)$$

where

$$N_{k_F} = [1 - (1/\Omega_0)\textstyle\sum_t b_t^2(\vec{k}_F)]^{1/2} \tag{5}$$

is the normalization constant. The quantities $C(\vec{k}_F+\vec{K})$ are the coefficients of linear combination of OPW which are obtained in the solid state by a variational procedure involving a discrete number of basis sets as a result of translational symmetry. Alternatively,[14,15] one can obtain a linear combination of plane waves using pseudopotentials and then orthogonalize them to the core states. In the liquid, however, due to the continuous nature of the mixing between plane waves belonging to adjacent values of k_F, a variational procedure is not applicable and one has to resort to a perturbation approach. The quantity $\Theta_t(0)$ is the value of the core-state wave function t at the origin. Since the non-s core states have zero density at the origin, the summation over t in Eq. (5) reduces only to summations over the core s states. $b_t(\vec{k}_F+\vec{K})$ is the orthogonalization parameter given by

$$b_t(\vec{k}_F+\vec{K}) = \langle \Theta_t(\vec{r}) | e^{i(\vec{k}_F+\vec{K})\cdot\vec{r}} \rangle . \tag{6}$$

Since $b_t(\vec{k}_F+\vec{K})$ is a slowly varying function, we shall assume

$$b_t(\vec{k}_F+\vec{K}) \approx b_t(\vec{k}_F) . \tag{7}$$

Such an approximation was utilized recently in the calculation of the spin density in solid cadmium[14,16] and was found[14] to enhance the spin density by only 10% over the value obtained without this approximation. With this assumption, one obtains an enhancement factor

$$O_{k_F}^2 = \frac{1}{N_{k_F}^2}\left(1 - \sum_{ns} b_{ns}(\vec{k}_F)\Theta_{ns}(0)\right)^2 \tag{8}$$

to be multiplied to the spin density calculated from the linear combinations of plane-wave functions. Using Eq. (8), Eq. (3) takes the form

$$\zeta = O_{k_F}^2 \langle N^{-1}\textstyle\sum_i |\Phi_{k_F}(\vec{R}_i)|^2\rangle , \tag{9}$$

where the pseudofunction $\Phi_{k_F}(\vec{R}_i)$ is given by

$$\Phi_{k_F}(\vec{R}_i) = (N\Omega_0)^{-1/2}\textstyle\sum_{\vec{K}} C(\vec{k}_F+\vec{K}) e^{i(\vec{k}_F+\vec{K})\cdot\vec{R}_i} . \tag{10}$$

It is appropriate to refer to

$$P_F = \langle N^{-1}\textstyle\sum_i |\Phi_{k_F}(\vec{R}_i)|^2\rangle \tag{11}$$

as the pseudodensity. With these definitions, the Knight shift is given by

$$K_s = \tfrac{8}{3}\pi\chi_s N\Omega_0 O_{k_F}^2 P_F . \tag{12}$$

In perturbation theory, the pseudofunction in Eq. (1) can be expanded up to second order in the pseudopotential in the form

$$\Phi_{k_F}(\vec{R}_i) = \Phi_{k_F}^{(0)}(\vec{R}_i) + \Phi_{k_F}^{(1)}(\vec{R}_i) + \Phi_{k_F}^{(2)}(\vec{R}_i) , \tag{13}$$

where $\Phi_{k_F}^{(0)}(\vec{R}_i)$ is the zero-order function

$$\Phi_{k_F}^{(0)}(\vec{R}_i) = (N\Omega_0)^{-1/2} e^{i\vec{k}_F\cdot\vec{R}_i} . \tag{14}$$

The pseudopotential $W(\vec{r})$ can be expressed as a sum of equivalent terms centered at the various ion sites, namely,

$$W(\vec{r}) = \textstyle\sum_\nu w(\vec{r} - \vec{R}_\nu) . \tag{15}$$

The first- and second-order corrections $\Phi_{k_F}^{(1)}(\vec{R}_i)$ and $\Phi_{k_F}^{(2)}(\vec{R}_i)$ can be obtained using conventional perturbation theory,[17] with the summations over excited states replaced by integration due to their continuum nature. Thus

$$\Phi_{k_F}^{(1)}(\vec{R}_i) = \frac{1}{(N\Omega_0)^{1/2}} \frac{N\Omega_0}{(2\pi)^3} \frac{1}{N} \sum_\nu e^{i(\vec{k}_F-\vec{k}')\cdot\vec{R}_\nu} \times \mathcal{P}\int d^3k' \frac{\langle \vec{k}' | \omega | \vec{k}_F \rangle}{E_{k_F} - E_{k'}} e^{i\vec{k}'\cdot\vec{R}_i} , \tag{16}$$

where the symbol $\mathcal{P}$ stands for a principal-value integration and

$$\begin{aligned}\Phi_{k_F}^{(2)}(\vec{R}_i) = \frac{(N\Omega_0)^2}{(2\pi)^6}\Bigg[& \mathcal{P}\mathcal{P}\iint \frac{\langle \vec{k}'' | w | \vec{k}' \rangle \langle \vec{k}' | w | \vec{k}_F \rangle}{(E_{k_F} - E_{k'})(E_{k_F} - E_{k''})} \frac{e^{i\vec{k}''\cdot\vec{R}_i}}{(N\Omega_0)^{1/2}} d^3k' d^3k'' \frac{1}{N}\sum_\mu e^{i(\vec{k}'-\vec{k}'')\cdot\vec{R}_\mu} \frac{1}{N}\sum_\nu e^{i(\vec{k}_F-\vec{k}')\cdot\vec{R}_\nu} \\ & - \tfrac{1}{2}\mathcal{P}\int d^3k'' \frac{|\langle \vec{k}'' | w | \vec{k}_F \rangle|^2}{(E_{k_F} - E_{k''})^2} \frac{e^{i\vec{k}''\cdot\vec{R}_i}}{(N\Omega_0)^{1/2}} \frac{1}{N^2} \sum_{\mu,\nu} e^{i(\vec{k}_F-\vec{k}'')\cdot(\vec{R}_\mu-\vec{R}_\nu)} \\ & - \langle \vec{k}_F | w | \vec{k}_F \rangle \mathcal{P}\int d^3k'' \frac{\langle \vec{k}_F | w | \vec{k}'' \rangle}{(E_{k_F} - E_{k''})^2} \frac{e^{i\vec{k}''\cdot\vec{R}_i}}{(N\Omega_0)^{1/2}} \frac{1}{N}\sum_\nu e^{i(\vec{k}''-\vec{k}_F)\cdot\vec{R}_\nu}\Bigg] . \end{aligned} \tag{17}$$

In terms of the various perturbation components of Φ_{k_F}, the pseudodensity can be expressed as

$$P_F = P_F(00) + P_F(01) + P_F(11) + P_F(02), \tag{18}$$

where

$$P_F(00) = \langle N^{-1}\textstyle\sum_i |\Phi_{k_F}^{(0)}(\vec{R}_i)|^2\rangle , \tag{19}$$

$$P_F(01) = \langle 2\mathrm{Re}(1/N)\textstyle\sum_i \Phi_{k_F}^{(0)*}(\vec{R}_i)\Phi_{k_F}^{(1)}(\vec{R}_i)\rangle , \tag{20}$$

$$P_F(11) = \langle N^{-1}\textstyle\sum_i |\Phi_{k_F}^{(1)}(\vec{R}_i)|^2\rangle , \tag{21}$$

$$P_F(02)=\langle 2\mathrm{Re}(1/N)\textstyle\sum_i \Phi_{k_F}^{(0)*}(\vec{\mathrm{R}}_i)\Phi_{k_F}^{(2)}(\vec{\mathrm{R}}_i)\rangle, \qquad (22)$$

and Re in Eqs. (20) and (22) denotes the real part of the product and the suffixes m and n in $P_F(mn)$ refer to the combination of the pertinent orders of perturbation in the wave function that are involved.

The Knight shift can similarly be expressed as a summation over various orders of perturbation, namely,

$$K_s=K_s(00)+K_s(01)+K_s(11)+K_s(02). \qquad (23)$$

Expressions for $P_F(00)$, $P_F(01)$, $P_F(11)$, and $P_F(02)$ can be obtained by using Eqs. (14), (16), and (17). When this is done, we obtain a number of factors of the form

$$\left\langle \frac{1}{N}\sum_{i,\nu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_\nu)}\right\rangle$$

and

$$\left\langle \frac{1}{N}\sum_{i,\nu,\mu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{R}}_\nu-\vec{\mathrm{R}}_i)}\, e^{i(\vec{\mathrm{k}}'-\vec{\mathrm{k}}'')\cdot(\vec{\mathrm{R}}_\mu-\vec{\mathrm{R}}_i)}\right\rangle,$$

involving averages over ionic positions. In the solid such summations can be derived from a knowledge of the lattice positions, the averaging procedure producing a temperature-dependent Debye-Waller factor due to the effect of the lattice vibrations.[16] In the liquid one has to rely on interference data in order to obtain these averages. One of these averages, namely,

$$\left\langle \frac{1}{N}\sum_{i,\nu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{R}}_i-\vec{\mathrm{R}}_\nu)}\right\rangle = I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|), \qquad (24)$$

is directly available either from experiment[18] or the theory[19,20] and is referred to as the interference function. For the other average involving coordinates of three particles, no direct experimental data are available and we have made the plausible approximation

$$\left\langle \frac{1}{N}\sum_{i,\mu,\nu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{R}}_\nu-\vec{\mathrm{R}}_i)}e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}'')\cdot(\vec{\mathrm{R}}_\mu-\vec{\mathrm{R}}_i)}\right\rangle$$

$$\approx I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|)I(|\vec{\mathrm{k}}'_F-\vec{\mathrm{k}}''|) . \qquad (25)$$

This approximation corresponds to neglecting three-particle correlations[21,22] which are expected to contribute, in general, only a 10–15% error. An alternate approximation has been recently proposed,[23] namely,

$$\left\langle \frac{1}{N}\sum_{i,\mu,\nu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot(\vec{\mathrm{R}}_\nu-\vec{\mathrm{R}}_i)}e^{i(\vec{\mathrm{k}}'-\vec{\mathrm{k}}'')\cdot(\vec{\mathrm{R}}_\mu-\vec{\mathrm{R}}_i)}\right\rangle$$

$$=\left\langle \frac{1}{N}\sum_{i,\mu,\nu} e^{i(\vec{\mathrm{k}}_F-\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}_\nu}e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}'')\cdot\vec{\mathrm{R}}_\mu}e^{i(\vec{\mathrm{k}}''-\vec{\mathrm{k}}_F)\cdot\vec{\mathrm{R}}_i}\right\rangle$$

$$\approx I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|)I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}''|) . \qquad (26)$$

In the second form of the summations in Eq. (26), $\vec{\mathrm{k}}_F$, $\vec{\mathrm{k}}'$, and $\vec{\mathrm{k}}''$ appear symmetrically. However, it has been pointed out[23] that $\vec{\mathrm{k}}_F$ is physically more unique than $\vec{\mathrm{k}}'$ and $\vec{\mathrm{k}}''$ because excitations occur from the Fermi surface, the other two representing the virtual intermediate-state momenta. These features have been utilized to justify the unsymmetrical form on the right-hand side of Eq. (26). It is our feeling, however, that the approximation in (25) is no less justifiable than (26) and so we have utilized Eq. (25) for our spin-density calculations.

Using Eqs. (24) and (25), the expression for the various terms in P_F takes the form

$$P_F(00)=1/N\Omega_0 , \qquad (27)$$

$$P_F(01)=\left(\frac{1}{N\Omega_0}\right)\frac{\Omega_0}{(2\pi)^3}\, 2\mathrm{Re}\,\mathcal{P}\int d^3k' \times\frac{\langle\vec{\mathrm{k}}'|\omega|\vec{\mathrm{k}}_F\rangle}{k_F^2-k'^2}I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|) , \qquad (28)$$

$$P_F(11)=\left(\frac{1}{N\Omega_0}\right)\frac{\Omega_0^2}{(2\pi)^6}\left(\mathcal{P}\int d^3k' \times\frac{\langle\vec{\mathrm{k}}'|\omega|\vec{\mathrm{k}}_F\rangle}{k_F^2-k'^2}I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|)\right)^2 , \qquad (29)$$

and

$$P_F(02)=\frac{1}{N\Omega_0}\frac{\Omega_0^2}{(2\pi)^6}\,2\mathrm{Re}\left[\mathcal{P}\mathcal{P}\iint d^3k'd^3k''\frac{\langle\vec{\mathrm{k}}''|\omega|\vec{\mathrm{k}}'\rangle\langle\vec{\mathrm{k}}'|\omega|\vec{\mathrm{k}}_F\rangle}{(k_F^2-k'^2)(k_F^2-k''^2)}I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}'|)I(|\vec{\mathrm{k}}'-\vec{\mathrm{k}}''|)\right.$$
$$\left.-\frac{1}{2}\mathcal{P}\int\frac{|\langle\vec{\mathrm{k}}_F|\omega|\vec{\mathrm{k}}''\rangle|^2}{(k_F^2-k''^2)^2}I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}''|)d^3k''-\langle\vec{\mathrm{k}}_F|\omega|\vec{\mathrm{k}}_F\rangle\,\mathcal{P}\int\frac{\langle\vec{\mathrm{k}}_F|\omega|\vec{\mathrm{k}}''\rangle}{(k_F^2-k''^2)^2}I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}''|)d^3k''\right] . \qquad (30)$$

Note that in deriving Eqs. (28)–(30), we have replaced the energy denominator $E_{k_F}-E_{k'}$ by the corresponding kinetic-energy operator which in atomic units ($\hbar=1$, $e^2=2$, $m=\frac{1}{2}$) takes the form $k_F^2-k'^2$.

So far we have not considered the form of the pseudopotential $W(\vec{\mathrm{r}})$. In general it can be split up into what are referred to in the literature as local and nonlocal components. While in some metals one can obtain empirical fits to the Fermi surface with only the local component, in some other metals, especially those with d cores such as cadmium and zinc, for example, the nonlocal component seems to be of crucial importance. We shall utilize a form for the nonlocal pseudopotential proposed and used by Stark and Falicov,[24] namely,

$$W(\vec{r}) = W_L(\vec{r}) + W_{NL}(\vec{r}) = \sum_\nu [\omega_L(\vec{r} - \vec{R}_\nu) + \omega_{NL}(\vec{r} - \vec{R}_\nu)] \ . \tag{31}$$

The $W_L(\vec{r})$ and $W_{NL}(\vec{r})$ refer to the local and nonlocal components where

$$\omega_{NL}(\vec{r}) = \sum_l v_l |l, \vec{r}\rangle\langle l, \vec{r}| \ , \tag{32}$$

the summation in l extending over the angular momenta of the three outermost core states of the Cd^{++} ion,[25] namely, $4s$, $4p$, and $4d$. The Fourier components of $\omega_L(\vec{r})$ and the parameters v_l are obtained by fitting Fermi-surface data in the solid state to values obtained from the pseudopotential. Local and nonlocal pseudopotential form factors for typical relative orientations of Fermi momentum $\vec{k}_F$ (assuming spherical Fermi surface) and $\vec{k}_F + \vec{q}$ for cadmium are shown in Fig. 1. Although in the solid state one considers only the matrix elements $\langle \vec{k} | W | \vec{k} + \vec{K} \rangle$, where the $\vec{K}$'s are discrete reciprocal-lattice vectors, the form of the nonlocal part of the pseudopotential allows one to obtain from it the matrix elements $\langle \vec{k} | W_{NL} | \vec{k} + \vec{q} \rangle$ for continuous $\vec{q}$. The Fourier components of the local potential, however, are only available for discrete $\vec{K}$ and had to be interpolated to get $\langle \vec{k} | W_L | \vec{k} + \vec{q} \rangle$ for continuous $\vec{q}$. Interpolated potentials of this type have been used earlier for study of electron-phonon enhancement effects[26] on the specific heat of cadmium.

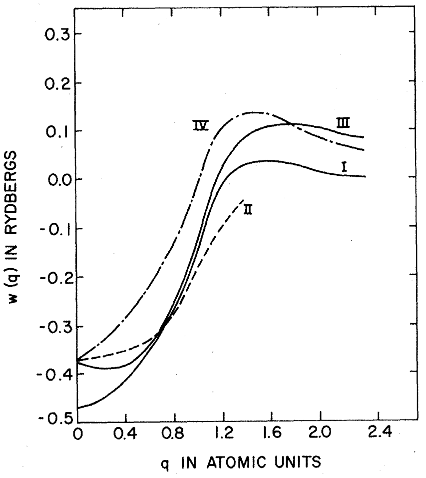

FIG. 1. Local and nonlocal pseudopotential form factors of cadmium: curve I, local pseudopotential; curve II, scattering on the Fermi surface, i.e., both $\vec{k}$ and $\vec{k} + \vec{q}$ are on the Fermi surface; curve III, backward scattering, i.e., $\vec{k}$ on the Fermi sphere and $\vec{k} + \vec{q}$ is smaller than and parallel to $\vec{k}$ or antiparallel to $\vec{k}$; curve IV, forward scattering i.e., $\vec{k}$ on the Fermi sphere and $\vec{k} + \vec{q}$ is larger than and parallel to $\vec{k}$.

To obtain first- and second-order contributions to P_F we have to evaluate the integrals in Eqs. (28)–(30) using the pseudopotential in Eq. (31). For the first-order shift it is convenient to define a quantity as

$$J = \mathcal{P} \int d^3k' I(|\vec{k}_F - \vec{k}'|)\langle \vec{k}' | \omega | \vec{k}_F \rangle / (k_F^2 - k'^2) \ , \tag{33}$$

which can be split up into parts arising from the local and nonlocal potentials, namely,

$$J = J_L + J_{NL} \ , \tag{34}$$

where

$$J_L = \mathcal{P} \int d^3k' I(|\vec{k}_F - \vec{k}'|)\omega_L(|\vec{k}_F - \vec{k}'|)/(k_F^2 - k'^2) \tag{35}$$

and

$$J_{NL} = \mathcal{P} \int d^3k' I(|\vec{k}_F - \vec{k}'|)\langle \vec{k}' | \omega_{NL} | \vec{k}_F \rangle / (k_F^2 - k'^2) \ . \tag{36}$$

Using Eq. (32) the nonlocal form factors have the form

$$\langle \vec{k}' | \omega_{NL} | \vec{k}_F \rangle = (4\pi/\Omega_0) \sum_l (2l+1) v_l T_l(|\vec{k}'|) \times T_l(|\vec{k}_F|) P_l(\cos\theta_{\vec{k}'\vec{k}_F}) \ , \tag{37}$$

where

$$T_l(|\vec{k}|) = \int_0^\infty j_l(|\vec{k}|r) U_l(r) r \, dr \ , \tag{38}$$

the $U_l(r)$ being the radial part of the appropriate atomic core functions. $P_l(\cos\theta_{\vec{k}'\vec{k}_F})$ in Eq. (37) are the Legendre polynomials of order l, and $\theta_{\vec{k}'\vec{k}_F}$ is the angle between $\vec{k}'$ and $\vec{k}_F$.

The angular integration (35) can be carried out analytically by changing the variable of integration to $\vec{q} = \vec{k}_F - \vec{k}'$ and integrating first over the angular components of $\vec{q}$. The form of J_L after this simplification procedure is

$$J_L = \frac{\pi}{k_F} \mathcal{P} \int_0^\infty I(q) \omega_L(q) \ln \left| \frac{q - 2k_F}{q + 2k_F} \right| q \, dq \ . \tag{39}$$

However, such a procedure is not helpful in evaluating the integral in Eq. (36) since the form factors in the numerator depend on $\theta_{\vec{q}\vec{k}_F}$ while the denominator involves $\theta_{\vec{k}'\vec{k}_F}$. The principal value integrations were carried out numerically. The procedure we have employed is given in the Appendix. For purposes of computation, it is convenient to reexpress J_{NL} in the form

$$J_{NL} = \frac{8\pi^2}{\Omega_0} \sum_l (2l+1) v_l T_l(|\vec{k}_F|) \mathcal{P} \int_0^\infty k'^2 dk' \frac{T_l(|\vec{k}'|)}{k_F^2 - k'^2} \times \int_{-1}^{1} P_l(\kappa) I(|\vec{k}_F - \vec{k}'|) d\kappa \ , \tag{40}$$

where

$$|\vec{k}_F-\vec{k}'| = (k_F^2+k'^2-2k_Fk'\kappa)^{1/2} ,$$

the κ being the cosine of the angle between $\vec{k}'$ and $\vec{k}_F$. The first-order spin-density expression in (28) thus reduces to

$$P_F(01)=(N\Omega_0)^{-1}[\Omega_0/(2\pi)^3]2\,\mathrm{Re}(J_{\mathrm{L}}+J_{\mathrm{NL}}) . \qquad (41)$$

The (11) term in the second-order contribution can also be shown similarly to have the form

$$P_F(11)=(N\Omega_0)^{-1}[\Omega_0^2/(2\pi)^6](J_{\mathrm{L}}+J_{\mathrm{NL}})^2 . \qquad (42)$$

The other three second-order terms classified as (02) are somewhat more complex in form than (11) and cannot be expressed in terms of J_{L} and J_{NL}. Considering the first of these three terms first, we see that it involves the double integral

$$J'(1)=\mathcal{P}\int d^3k'\,I(|\vec{k}_F-\vec{k}'|)\langle\vec{k}'|\omega|\vec{k}_F\rangle/(k_F^2-k'^2)$$
$$\times[\mathcal{P}\int d^3k''\,I(|\vec{k}'-\vec{k}''|)\langle\vec{k}''|\omega|\vec{k}'\rangle/(k_F^2-k''^2)] . \qquad (43)$$

In attempting to simplify this expression let us denote the principal value integral over the variable $\vec{k}''$ by

$$F(\vec{k}')=\mathcal{P}\int d^3k''\,I(|\vec{k}'-\vec{k}''|)\langle\vec{k}''|\omega|\vec{k}'\rangle/(k_F^2-k''^2) . \qquad (44)$$

The contribution to this integral from the local part of ω is given by

$$F_{\mathrm{L}}(|\vec{k}'|)$$
$$=\mathcal{P}\int d^3k''\,I(|\vec{k}'-\vec{k}''|)\omega_{\mathrm{L}}(|\vec{k}'-\vec{k}''|)/(k_F^2-k''^2) ,$$

which by change of variables and integration over the angles in the denominator as in the case of $P_F(01)$ can be reexpressed in the form

$$F_{\mathrm{L}}(|\vec{k}'|)=\frac{\pi}{k'}\,\mathcal{P}\int q\,dq\,I(q)\omega_{\mathrm{L}}(q)$$
$$\times\ln\left|\frac{k_F^2-q^2-k'^2-2k'q}{k_F^2-q^2-k'^2+2k'q}\right| . \qquad (45)$$

Similarly, from the nonlocal part of ω ,

$$F_{\mathrm{NL}}(|\vec{k}'|)=\frac{8\pi^2}{\Omega_0}\sum_l(2l+1)v_lT_l(|\vec{k}'|)$$
$$\times\mathcal{P}\int_0^\infty k''^2dk''\frac{T_l(|\vec{k}''|)}{k_F^2-k''^2}$$
$$\times\int_{-1}^1P_l(\kappa)I(|\vec{k}'-\vec{k}''|)d\kappa . \qquad (46)$$

On substituting Eqs. (45) and (46) in Eq. (43) we get a set of four terms corresponding to pairing between the local and nonlocal terms of the first integral with those of the second integral, namely,

$$J'(1)=J'_{\mathrm{L\text{-}L}}(1)+J'_{\mathrm{NL\text{-}NL}}(1)+J'_{\mathrm{L\text{-}NL}}(1)+J'_{\mathrm{NL\text{-}L}}(1) \qquad (47)$$

with

$$J^{1}_{L\text{-}L}(1)=\mathcal{P}\int_0^\infty k'^2\,dk'\frac{F_L(|\vec{k}'|)}{k_F^2-k'^2}$$
$$\times2\pi\int_{-1}^1I(|\vec{k}_F-\vec{k}'|)\omega_{\mathrm{L}}(|\vec{k}_F-\vec{k}'|)d\kappa , \qquad (48)$$

$$J'_{\mathrm{NL\text{-}NL}}(1)=\frac{4\pi}{\Omega_0}\sum_l(2l+1)v_lT_l(|\vec{k}_F|)$$
$$\times\mathcal{P}\int_0^\infty k'^2dk'\,F_{\mathrm{NL}}(|\vec{k}'|)$$
$$\times\frac{T_l(|\vec{k}'|)}{k_F^2-k'^2}$$
$$\times2\pi\int_{-1}^1P_l(\kappa)I(|\vec{k}_F-\vec{k}'|)d\kappa , \qquad (49)$$

$$J'_{\mathrm{L\text{-}NL}}(1)=\frac{4\pi}{\Omega_0}\sum_l(2l+1)v_lT_l(|\vec{k}_F|)$$
$$\times\mathcal{P}\int_0^\infty k'^2dk'\,F_{\mathrm{L}}(|\vec{k}'|)T_l(|\vec{k}|)$$
$$\times\frac{2\pi}{k_F^2-k'^2}\int_{-1}^1P_l(\kappa)I(|\vec{k}_F-\vec{k}'|)d\kappa , \qquad (50)$$

and

$$J'_{\mathrm{NL\text{-}L}}(1)=\mathcal{P}\int_0^\infty k'^2dk'\frac{F_{\mathrm{NL}}(|\vec{k}'|)}{k_F^2-k'^2}$$
$$\times2\pi\int_{-1}^1I(|\vec{k}_F-\vec{k}'|)\omega_{\mathrm{L}}(|\vec{k}_F-\vec{k}'|)d\kappa . \qquad (51)$$

The other two terms in the $P_F(02)$ expression in Eq. (30) can also each be expressed as a sum of four terms as in Eq. (47). However, the evaluation of these component terms does pose some problems. Thus from an inspection of the denominators of the integrals in the second and third terms in Eq. (30) one might get the impression that these integrals would give infinite answers since the integrands diverge in the positive direction at the singularity $\vec{k}'=\vec{k}_F$. This impression is, however, incorrect as will be demonstrated directly now by carrying out the angular integrations for the integrals involving W_L. On making the substitution $\vec{q}=\vec{k}_F-\vec{k}'$ in the integral

$$\mathcal{P}\int d^3k'\ |\omega_{\mathrm{L}}(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}''|)|^2 I(|\vec{\mathrm{k}}_F-\vec{\mathrm{k}}''|)/(k_F^2-k''^2)^2\ ,$$

it follows that

$$\mathcal{P}\int_0^\infty q^2\,dq\ |\omega_{\mathrm{L}}(q)|^2 I(q)2\pi\int_{-1}^{1}d\kappa/(q^2+2k_F q\kappa)^2$$

$$=4\pi\,\mathcal{P}\int_0^\infty dq\,I(q)|\omega_L(q)|^2/(q^2-4k_F^2)\,. \tag{52}$$

The result in Eq. (52) is similar to the principal-value integral in Eq. (40) and does not diverge. The only difference from Eq. (40) is that the singularity now occurs at $q=2k_F$ instead of $q=k_F$. The angular integration over the direction of the q variable cannot, however, be carried out analytically for the partners of (52) involving $|\omega_{\mathrm{L}}(\vec{q})\omega_{\mathrm{NL}}(\vec{q})|$, $|\omega_{\mathrm{NL}}(\vec{q})\omega_{\mathrm{L}}(\vec{q})|$, and $|\omega_{\mathrm{NL}}(\vec{q})|^2$. These integrals have been estimated by a numerical comparison of the pertinent integrands with those of Eq. (52). The (02) term in P_F can thus be expressed in concise form

$$P_F(02)=(N\Omega_0)^{-1}\,2\,\mathrm{Re}(J')\,, \tag{53}$$

where

$$J'=J'(1)+J'(2)+J'(3), \tag{54}$$

$J'(2)$ and $J'(3)$ representing the second and third terms within the square brackets of Eq. (30). These integrals can be evaluated in a similar manner as $J'(1)$.

Thus combining the (00), (01), (11), and (02) terms in P_F and using Eq. (12), one can express the total Knight shift in the form

$$K_s=\frac{8\pi}{3}\chi_s O_{k_F}^2\left(1+\frac{\Omega_0}{(2\pi)^3}\,2\mathrm{Re}\,J+\frac{\Omega_0^2}{(2\pi)^6}J^2+\frac{\Omega_0}{(2\pi)^6}\,2\mathrm{Re}\,J'\right)\ . \tag{55}$$

For the numerical evaluation of K_s in the above equation, one needs to have a knowledge of Ω_0, $O_{k_F}^2$, and χ_s, in addition to J and J'. The ionic volume Ω_0 was taken to be the same as the Wigner-Seitz volume in the solid state. For the spin susceptibility χ_s as will be discussed in Sec. III, we have considered the free-electron value, namely, $\chi_s=0.95\times10^{-6}$ cgs volume units. The quantity $O_{k_F}^2$ was calculated using the Hartree-Fock atomic core functions tabulated by Mann[27]; thus, $O_{k_F}^2=534.9$. For the evaluation of J and J' we have used the nonlocal pseudopotential parameters of Stark and Falicov[24] and the experimental interference functions of North and Wagner.[18]

If there were no complications due to exchange-enhancement, ECP, and orbital effects, as in solid state, we could obtain T_1 using the calculated K_s and the Korringa relation

$$(K_s^2T_1T)_{\mathrm{ideal}}=(\hbar/4\pi k_B)(\gamma_e/\gamma_n)^2\ , \tag{56}$$

where k_B is the Boltzmann constant. The ratio between T_1T calculated by this process and the experimental value can be utilized to analyze the importance of the above effect.

TABLE I. Various terms contributing to the first- and second-order spin densities in liquid cadmium at 350 °C. Note that these quantities are related to the spin densities through Eqs. (41), (42), and (53).

First order		Second order				
			(02) terms			(11) terms
J_{L}	J_{NL}	Term type	1	2	3	
0.386	−0.606	$J'_{\mathrm{L}\text{-}\mathrm{L}}$	−0.056	0.030	0.065	0.048
		$J'_{\mathrm{L}\text{-}\mathrm{NL}}$	0.082	−0.044	−0.021	
		$J'_{\mathrm{NL}\text{-}\mathrm{L}}$	0.053	−0.028	−0.013	
		$J'_{\mathrm{NL}\text{-}\mathrm{NL}}$	0.137	−0.073	−0.035	

III. RESULTS AND DISCUSSION

The various terms in Eqs. (39), (40), (48)–(51), and (54) that constitute the contributions from the first- and second-order spin-density terms are presented in Table I for the temperature 350 °C. It is interesting to compare the contributions from terms involving local and nonlocal parts of the pseudopotential and their various combinations. Examination of the first-order results indicate that the nonlocal pseudopotential contribution is substantially larger and of opposite sign to that of its local counterpart. One, therefore, should be particularly careful to include the effects of the nonlocal terms, even if they lead to computational difficulties. The breakdown of the contributions from various terms in second order also exhibit similar trends, the nonlocal-nonlocal component being generally the leading term in the series for each of the three terms that enter into the expression of P_F (02). One also observes from Table I that the signs of various combinations of local and nonlocal contributions vary among the three component terms in P_F (02) and that there is a substantial cancellation between terms of comparable magnitude but opposite sign. As a result of these cancellations, although the sum of the individual (02) terms are larger than the (11) term, the net P_F (02) is comparable to $P_F(11)$. However, the (11) and (02) terms (both total and individual terms) are smaller than (00) and (01) terms, showing a definite trend towards convergence of the total P_F.

This demonstration of convergence of the perturbation expansion is important because, at a first glance, one might expect problems connected with singularities in the denominator of the various terms in the spin-density expression. The second-order terms tend to infinity at the singularity substantially faster than do the first order. If the numerators of the integrands in both orders had been symmetric about the singularities, it is clear that the associated spin densities would vanish. In fact, the integrands in both cases are asymmetric about the singularities and lead to nonvanishing spin densities. The relative contributions of the two orders depend sensitively on the region in $\vec{k}'$ and $\vec{k}''$ from which the maximum contribution is derived, regions near k_F being more favorable to second-order terms due to the stronger singularity they have in the neighborhood of $\vec{k}_F$. However, a numerical analysis of the first- and second-order terms indicates that the major contributions to them arise from admixtures of states with momenta higher ($\frac{3}{2}\vec{k}_F$ to $\frac{7}{2}\vec{k}_F$) than k_F. The energy denominators are therefore sizable and one expects that their higher powers in higher-order terms will effectively reduce the contributions from the latter. The sum of the first- and second-order contributions to the spin densities [in units of $(1/N\Omega_0)$] obtained by using results in Table I and Eqs. (41) and (42) is seen to be 0.83 at 350 °C. However, one can attempt to include the effects of higher-order terms through a geometric-series approximation, assuming the ratio of alternate orders to be equal to that between the second and first orders. With this approximation the spin density at 350 °C is found to be 0.80, in close agreement with our value 0.83.

In evaluating the Knight shifts one needs, in addition to the direct spin density discussed above, the Pauli-spin susceptibility χ_s and also the ECP contribution to the spin density. Considering the latter first, we refer to our recent solid-state calculation[14] for this effect. There, it was found that the ECP contribution from the s part of the conduction-electron wave function was about 10% of the direct spin density while that from the higher angular momentum components was negligibly small. This smallness in the ECP contribution, compared to that in solid beryllium and magnesium,[6] was not primarily a consequence of the shape of the Fermi surface, but a result of cancellation among the various core states. One thus expects the ECP contribution in the liquid to be no more than 10% of the direct effect. As regards χ_s, there is unfortunately no experimental measurement available, neither in the liquid nor the solid state of cadmium. Offhand, one would expect that the electrons in the liquid resemble a free-electron gas due to the disappearance of Brillouin-zone-boundary effects that occur in the solid state. We have, therefore, used the value of χ_s determined by the free-electron density of states, namely,

$$\chi_s^{\text{free}} = 0.95 \times 10^{-6} \text{ cgs volume units,} \tag{57}$$

and then have attempted to obtain the empirical enhancement factor due to the conduction-conduction exchange effect by comparing theoretical and experimental K_s. In Table II we have listed the spin densities, Knight shift, and relaxation times at four temperatures. From our results of K_s in the fourth row of Table II, it appears that one can fit the experimental data over the range of temperatures that are available, by a single enhancement factor $\eta_s^{\text{liquid}}(\text{emp})$ listed[28] in Table III. It is interesting to compare $\eta_s^{\text{liquid}}(\text{emp})$ with the theoretical value[29] obtained from a free-electron effective-mass approximation. Assuming $m^*/m = 1$ for the liquid, one obtains the theoretical value $\eta_s^{\text{liquid}}(\text{theoret})$ listed in Table III. Corresponding empirical and theoretical enhancement factors in the solid are also listed in Table III for comparison.

TABLE II. Spin density (in units of $1/N\Omega_0$), Knight shift (in %), and relaxation time (in deg sec) of liquid cadmium at various temperatures.

Spin density order	Temp 350 °C	450 °C	550 °C	650 °C
Zero order	1.0	1.0	1.0	1.0
First order	−0.25	−0.25	−0.23	−0.23
Second order	0.079	0.073	0.069	0.048
Total	0.83	0.82	0.84	0.82
K_s^{direct} (%)	0.35	0.35	0.36	0.35
K_s^{ECP} (%)	0.04	0.04	0.04	0.04
K_s^{total} (%)	0.39	0.39	0.40	0.39
T_1T (deg sec)	0.38	0.38	0.36	0.38

TABLE III. Theoretical and empirical exchange-enhancement parameters η_s (for uniform susceptibility) and η_M (for nonuniform susceptibility) for liquid and solid cadmium.

Quantities	Solid		Liquid	
	Theoretical	Empirical	Theoretical	Empirical
η_s	1.17	1.89	1.32	2.05
η_M	1.27	3.10	1.55	2.92
η_s^2/η_M	1.08	1.15	1.12	1.44

We consider next the relaxation time T_1. In keeping with the Knight-shift analysis, we have used the free-electron density of states in the standard Korringa expression[5] as a reference to study exchange-enhancement effects empirically. As regards ECP effects, these are known to influence T_1T differently[6] for the contributions from the s and non-s components of the conduction-electron contribution. The influence of the latter is expected to be insignificant since it has been demonstrated that ECP effects from non-s components of cadmium are small. Consequently, the influence of the ECP effect on the Korringa ratio is expected to be unimportant.

On comparing our calculated T_1T using the free-electron density of states with the available experimental data, it appears that the latter can be fitted over the range of temperature studied by a nearly constant enhancement factor shown in Table III. The corresponding enhancement factor for the solid state is also included for reference. The theoretical value[29] for η_M listed in Table III is obtained from Moriya's theory[30] for the enhancement of $\chi_s(q)$, again using an effective mass corresponding to the free electron for the liquid.

The important feature one notices from Table III is that in both the solid and liquid there is a substantial difference between empirical enhancement factors and those from currently available theory. The factor η_s^2/η_M gives the departure from the ideal Korringa constant and is larger than unity as expected from theory. The reason for the latter is that $\chi_s(\vec{q})$ is enhanced less effectively than $\chi_s(0)$ through exchange effects. The difference between enhancement effects in the solid and the liquid does show up a little more effectively in the ratio η_s^2/η_M. This is expected because this ratio is a reflection of the difference between comparable enhancement effects.

In drawing conclusions from Table III, it should be pointed out that the empirical values of η_s and η_M were obtained by using wave functions obtained in the pseudopotential scheme. However, there is no no exact evidence that pseudopotentials give numerically correct wave functions. A recent pseudopotential calculation of K_s in solid magnesium, using the exchange-enhanced χ_s in the framework of Silverstein's[29] theory, has shown good agreement with experiment. Kasowski and Falicov[16] have also been able to explain the temperature dependence of isotropic and anisotropic Knight shifts using wave functions derived from pseudopotential model. A careful comparison between the actual (OPW) and pseudopotential calculations is needed to settle this issue. The following comments on the nature of exchange enhancement, therefore, should be taken with this qualification in mind.

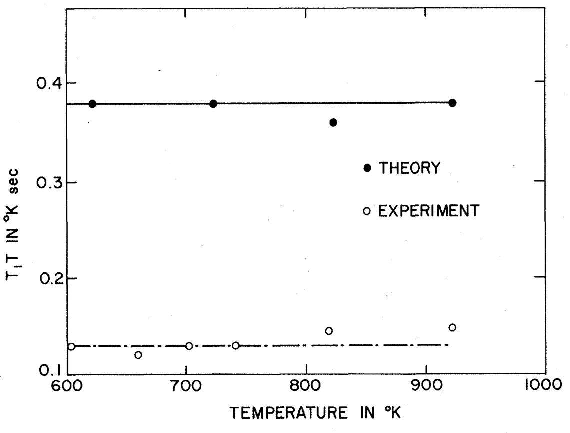

FIG. 2. Temperature dependence of relaxation time. The solid and the dotted curves are theoretical predictions without and with exchange-enhancement effects, respectively.

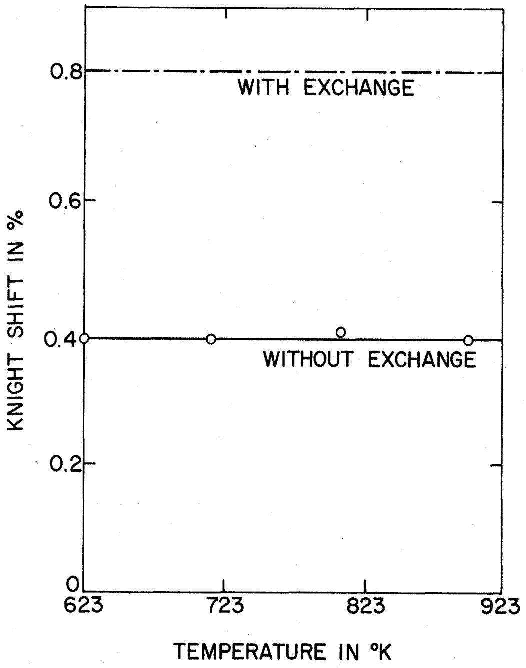

FIG. 3. Temperature dependence of Knight shift. The solid and the dotted curves are theoretical predictions without and with exchange-enhancement effects, respectively.

It is worthwhile to remark that there are two types of corrections to the free-electron theory of exchange enhancement. The first one is due to the presence of the potential around the ions which is the relevant state of affairs in the liquid. In the solid state one has, in addition, to consider the anisotropy effects imposed by the lattice structure. The fact that η_s and η_M in both the liquid and solid differ substantially from free-electron values indicates that the former effect is perhaps the major source of correction.

Our calculated values of T_1T are presented in the last row of Table II. In Figs. 2 and 3 the temperature dependence of calculated K_s and T_1T are compared with experiment. For K_s experimental data are available only for a limited range of temperatures near the melting point. For T_1T, data are, however, available for a wider range of temperatures. The most important feature of these results is the near constancy of both the experimental and theoretical value of K_s and $T_1 T$. This is in marked contrast to the observed behavior of K_s and $T_1 T$ in liquid indium. The interference functions $I(q)$ which enter into the calculations also show a similar trend with a much weaker temperature dependence for cadium than for indium. These trends may be regarded as indicative of the temperature independence of χ_s and the exchange enhancement factors η_s and η_M in the liquid.

IV. CONCLUSION

A first-principles analysis of the hyperfine spin density in liquid metals has been developed up to second order in perturbation theory using a pseudopotential formalism. Specific application has been made to liquid cadmium. The results give evidence for rapid convergence of higher-order terms and strongly suggest that first-order perturbation in the wave functions are sufficient for a reasonably quantitative (to better than 10% understanding) of K_s and T_1T. The results also indicate that the nonlocal pseudopotential terms make dominant contributions to the spin density. From our analysis of Knight shift and relaxation time, it has been possible to extract the pertinent exchange-enhancement contributions to the q-dependent and q-independent susceptibilities in the liquid from experimental data. A comparison of these empirical enhancement factors with the predictions from current free-electron theories indicates the need for a better understanding of electron-electron interactions in the presence of the potential field of the ions.

The observed independence of K_s and T_1T as well as the interference function data $I(q)$ on temperature indicates that the other factors involved, namely, χ_s, η_s, and η_M, are temperature independent. This conclusion appears to be supported by earlier semiquantitative studies of the temperature dependence of K_s in other metals.[31] The interference function $I(q)$ thus turns out to be of crucial importance for temperature dependence of resonance properties.

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APPENDIX: TECHNIQUE FOR NUMERICAL EVALUATION OF PRINCIPAL-VALUE INTEGRAL

The problem is to evaluate the prinicpal-value integral of the form

$$\mathcal{P}\int_0^\infty \frac{f(x)\,dx}{x^2-x_0^2}\ , \tag{A1}$$

where $f(x)$ is not symmetric about $x=x_0$, in which case the integral would have vanished. We rewrite the integral as

$$\mathcal{P}\int_0^\infty \frac{f(x)\,dx}{x^2-x_0^2} = \lim_{\delta\to 0}\int_0^{x_0-\delta}\frac{f(x)\,dx}{x^2-x_0^2} + \lim_{\delta\to 0}\int_{x_0+\delta}^{\infty}\frac{f(x)\,dx}{x^2-x_0^2}\ . \tag{A2}$$

The right-hand side of Eq. (A2) can be reexpressed as

$$\lim_{\delta\to 0}\int_0^{x_0-\delta}\frac{f(x)-g(x)}{x^2-x_0^2}\,dx + \lim_{\delta\to 0}\int_{x_0+\delta}^{\infty}\frac{f(x)-g(x)}{x^2-x_0^2}\,dx + \lim_{\delta\to 0}\int_0^{x_0-\delta}\frac{g(x)\,dx}{x^2-x_0^2} + \lim_{\delta\to 0}\int_{x_0+\delta}^{\infty}\frac{g(x)\,dx}{x^2-x_0^2}\ , \tag{A3}$$

where the reference function $g(x)$ is chosen in such a way that it satisfies the following two conditions:

$$\lim_{\delta\to 0}\ ,\ \text{i.e.},\ \lim_{x\to x_0}[f(x)-g(x)]\to 0 \tag{A4}$$

and

$$\lim_{\delta\to 0}\int_0^{x_0-\delta}\frac{g(x)\,dx}{x^2-x_0^2} + \int_{x_0+\delta}^{\infty}\frac{g(x)\,dx}{x^2-x_0^2}\to 0\ . \tag{A5}$$

Substituting expression (A3) in Eq. (A2) and using the conditions in Eqs. (A4) and (A5), we have

$$\mathcal{P}\int_0^\infty \frac{f(x)\,dx}{x^2-x_0^2} = \int_0^\infty \frac{f(x)-g(x)}{x^2-x_0^2}\,dx\ . \tag{A6}$$

The expression for $g(x)$ in Eq. (A7) was found to satisfy the conditions (A4) and (A5) and was thus suitable for our evaluation of principal-value integral as expressed in Eq. (A6)

$$g(x) = (x+x_0)\,[f(x_0)/2x_0](x_0/x)^{1/2}\ . \tag{A7}$$

The Gauss-Laguerre integration was utilized in the numerical integration of (A6).

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