

Theory of Knight Shifts and Relaxation Times in Alkali Metals—Role of Exchange Core Polarization and Exchange-Enhancement Effects*

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The current situation with respect to theory as compared to experiment for Knight shifts and relaxation times in alkali metals is discussed. The roles of exchange core polarization effect and exchange enhancement of the susceptibility due to electron-electron interaction are discussed in detail. It is shown that through a consideration of these effects, combined with the relativistic corrections to the spin density for heavier alkali metals, one is able to obtain an over-all agreement with experiment. However, quantitative agreement with experiment is still lacking, and several additional contributing mechanisms are briefly discussed. The need for better treatments of exchange-enhancement effects on the susceptibility for Bloch electrons and more accurate wave functions, particularly for the lighter metals lithium, sodium, and potassium, is pointed out.

I. INTRODUCTION

Alkali metals, because of the simplicity of their crystalline and electronic structures, are most amenable for a detailed quantitative comparison between theory and experiment with respect to their observable properties. This is particularly true of their hyperfine properties which are manifested through Knight shifts, relaxation times, and indirect spin-spin interaction constants. Accurate experimental data¹⁻³ on all these quantities are available and calculations of the direct nonrelativistic⁴⁻⁶ and relativistic⁷ contributions to the spin density at the nuclei have already been reported. The present work deals with the role of exchange-core-polarization (ECP) effects on the hyperfine properties of these metals, in particular the Knight shifts (K_s) and relaxation time (T_1). A subsequent paper will be concerned with the influence of ECP effects on the indirect spin-spin interactions of the Ruderman-Kittel and pseudodipolar types.

The knowledge of all the major contributions to the wave-function density at the nucleus allows a critical evaluation of the effects of exchange and correlation among the conduction electrons on K_s and T_1 through the wave-number- and frequency-dependent susceptibility $\chi(\vec{q}, \omega)$. A previous analysis² of the importance of exchange and correlation effects on $\chi(\vec{q}, \omega)$, particularly with respect to the range of Coulomb interaction, was based on a comparison between experimental and theoretical Korringa constants $K_s^2 T_1 T$.

Section II will present the calculation of the ECP effect and its contribution to the wave-function density $|\psi(0)|^2$ at the nuclei using single-orthogonalized-plane-wave (OPW) functions for the conduction-

electron wave function. In Sec. III, we analyze the change in $|\psi(0)|^2$ by using a many-OPW (or equivalent) representation and present the direct, ECP, and relativistic contributions to $|\psi(0)|^2$. In Sec. IV, a brief review of the existing procedures to incorporate exchange and correlation effects on K_s and T_1 through $\chi(\vec{q}, \omega)$ is presented and the exchange-enhancement parameters for the different alkali metals are deduced from the experimental values of Pauli susceptibility. In Sec. V, we combine the various contributions to K_s , $T_1 T$, and the Korringa constant $K_s^2 T_1 T$, and compare our theoretical values with experiment.

II. ECP CONTRIBUTION TO $|\psi(0)|^2$ (ONE OPW RESULT)

The direct contribution⁸ to the Knight shift, K_s^d , is given by

$$K_s^d = \frac{8}{3} \pi \chi_p \Omega \langle |\psi(0)|_d^2 \rangle_{av}, \quad (1)$$

where $\langle |\psi(0)|_d^2 \rangle_{av}$ is the average density at the nucleus due to the conduction electrons at the Fermi surface, χ_p is the Pauli paramagnetic susceptibility, Ω is the Wigner-Seitz volume in which the conduction-electron wave function $\psi_{\vec{k}}$ is normalized. The ECP contribution to the Knight shift has been discussed earlier^{9,10} and for the convenience of notation we represent it by the equation

$$K_s^{cp} = \frac{8}{3} \pi \chi_p \Omega \sum_l \langle |\psi(0)|_{cp,l}^2 \rangle_{av}, \quad (2)$$

where $\langle |\psi(0)|_{cp,l}^2 \rangle_{av}$ symbolically defines the additional effective density at the nucleus arising from the ECP effect and associated with the l th angular component of the conduction electrons at the Fermi surface. The expression relating $|\psi(0)|_{cp,l}^2$ with the appropriate exchange integrals between $\psi_{\vec{k}}$ and

TABLE I. Direct and ECP contributions to $\langle |\psi(0)|^2 \rangle_{av}$ in units of a_0^{-3} (one-OPW result).

Metal	Direct	s part	Core polarization		Total
			p part	Rest	
Li	0.3944	0.0922	-0.0100	-0.0003	0.0819
Na	0.5817	0.1462	0.0031	-0.0006	0.1487
K	0.9069	0.1975	0.0193	-0.0022	0.2146
Rb	1.3866	0.3074	0.0414	-0.0075	0.3413
Cs	2.2390	0.4494	0.0761	-0.0096	0.5159

moment perturbed (MP) core- s functions is given in Ref. 10. In evaluating $|\psi(0)|_{cp,1}^2$, one may utilize either a single-OPW function or an appropriate linear combination of these for ψ_F . In the single-OPW approximation the averages in Eqs. (1) and (2) are replaced by their values at $k=k_F$, the Fermi wave vector.

Both for an understanding of the relative contribution to K_s^{cp} from single- and many-OPW functions, and also because many-OPW functions are unavailable for all the alkali metals, the ECP contributions were carried out in two stages, namely, with one-OPW and many-OPW functions. In this section, we shall be concerned with one-OPW functions only. The extension to many-OPW functions will be carried out in Sec. III. The core wave functions required for the purpose of orthogonalization were taken from Clementi's¹¹ Hartree-Fock calculations for lithium, sodium, and potassium. For rubidium and cesium, Hartree-Fock functions obtained by Froese¹¹ and Mann¹¹ were utilized. The MP functions were obtained by solving the MP equations using the same Hartree-Fock unperturbed core functions utilized in the construction of OPW's. The details of the calculation have been reported in Ref. 12.

The results for $|\psi(0)|_d^2$, $|\psi(0)|_{cp,1}^2$, and $|\psi(0)|_{total}^2$ are listed in Table I for all five metals. Atomic units (a_0^{-3}) are employed for the entries in this table and in the rest of the paper. The dominant contribution to $|\psi(0)|_{cp}^2$ comes from the s and p parts of the conduction electrons and will be denoted as $|\psi(0)|_{cp,s}^2$ and $|\psi(0)|_{cp,p}^2$, respectively. This is not true for the transition metals where the d contribution $|\psi(0)|_{cp,d}^2$ is quite important and often dominates over the s and p contributions. Certain qualitative features emerge from Table I. Generally speaking, $|\psi(0)|_{cp}^2$ is roughly 23% of the direct contribution $|\psi(0)|_d^2$, a feature quite similar to that found in alkali atoms.¹²

Also as in the case of alkali atoms,¹² the s component of the conduction-electron wave function was found to lead to positive ECP contributions from all the s cores. The p component on the other hand led to negative ECP effect from the innermost (1s in all cases and also 2s for cesium) cores and positive from the outer ones. The net p -type ECP

effect was thus *negative* for lithium but *positive* for the rest. This behavior for lithium metal is similar to that found for the 2P state of lithium atom, and can be understood as follows: The $2p$ and $1s$ charge distributions are well separated and so one can visualize that the p electrons by their exchange with the $1s$ electron of parallel spin draw out the latter towards themselves and away from the nucleus thereby leaving a surplus of antiparallel spin $1s$ electrons at the nucleus. A similar argument explains the negative p -type ECP effect from the inner cores in the rest of the metals, but does not hold for the outer cores since they are relatively diffuse compared to lithium $1s$ core and have nodes in their radial functions.¹³

From the Table I, we also notice that the ratio $|\psi(0)|_{cp,p}^2 / |\psi(0)|_{cp,s}^2$ goes from 0.17 (17%) for cesium to 0.024 (2.4%) for sodium and, of course, changes sign for lithium. This indicates a decrease in the p character of the conduction electrons in going from cesium to sodium. However, the net p character also depends on the nature of the linear combination of OPW functions in the many-OPW representation for the conduction-electron wave functions and will be considered in Sec. III. Further, the d and higher angular components of $|\psi(0)|_{cp}^2$ are seen to be negligible.

Before closing this section, it is worthwhile to comment on the importance of the p -type ECP contribution in influencing the relaxation time (T_1) and particularly the Korringa constant. For K_s , the important wave-function property is the total density at the nucleus which is just the sum of the direct and ECP contributions from all l components

$$|\psi(0)|_{total}^2 = |\psi(0)|_d^2 + |\psi(0)|_{cp,s}^2 + |\psi(0)|_{cp,p}^2 + \dots = A. \quad (3)$$

For T_1^{-1} , one requires the square of the matrix element $\langle \vec{k}' | \mathcal{H}' | \vec{k} \rangle$ that occurs in the nuclear spin transition probability. For the direct contact interaction, \mathcal{H}' is the usual Fermi contact hyperfine Hamiltonian and leads to the well-known expression

$$(T_1 T)^{-1} = c [\langle |\psi(0)|_d^2 \rangle]^2, \quad (4)$$

where

$$c = \frac{64}{9} \pi^3 \hbar^3 \gamma_e^2 \gamma_N^2 k_B g^2(E_F) \Omega^2 \quad (5)$$

and $g(E_F)$ is the density of states at the Fermi sur-

face per electron spin and per unit volume. For the ECP contribution to T_1^{-1} , \mathcal{K}' represents the combined effects of core-conduction exchange and Fermi contact interaction. Unlike the direct contribution, when one deals with the non- s ECP contribution to T_1^{-1} , a separation of the \vec{k} and \vec{k}' integrations in the transition-probability expression leading to the squared term $[\langle |\psi(0)|_d^2 \rangle]^2$ in Eq. (4) is no longer possible. Instead, one has to take account of the angular dependence in \vec{k} space in carrying out \vec{k} and \vec{k}' integration and gets¹⁴

$$(T_1 T)^{-1} = c \{ [|\psi(0)|_d^2 + |\psi(0)|_{cp,s}^2] + \frac{1}{3} [|\psi(0)|_{cp,p}^2 + \dots] \} = CB. \quad (6)$$

Equation (6) will be utilized to calculate the relaxation time T_1 . It can be seen from Eqs. (3) and (6) that if there is a finite but small amount of p character and a contribution to $|\psi(0)|_{\text{total}}^2$ through ECP effect, then it can influence K_s without affecting $(T_1 T)^{-1}$ appreciably.

The ratio A^2/B which occurs in the Korringa constant $K_s^2 T_1 T$ can be different from unity even if ECP contribution K_{cp} is small. For example, if, typically,

$$|\psi(0)|_{cp,s}^2 = 0.23 |\psi(0)|_d^2 \quad (7)$$

and

$$|\psi(0)|_{cp,p}^2 = 0.1 |\psi(0)|_d^2,$$

then the ratio $A^2/B = 1.17$ leads to a 17% increase in $K_s^2 T_1 T$ from its value in the absence of the p -type ECP effect.

III. SPIN DENSITIES INCLUDING MANY-OPW, ECP, AND RELATIVISTIC EFFECTS

Before analyzing the ECP contributions to spin densities for many-OPW functions, we would like to review briefly the current situation regarding the available conduction-electron wave functions for the alkali metals and the direct spin densities one ob-

tains from them. The many-OPW values of $|\psi(0)|^2$ and the source they were obtained from are given in the second column of Table II.

Detailed many-OPW wave functions are available only for cesium.⁴ For some of the other alkali metals, conduction-electron wave functions have been obtained by different procedures. For the sake of uniformity in terminology, we shall loosely refer to these latter wave functions as many OPW, since these procedures would ideally yield identical results as for the many-OPW procedure when carried to completion. It is observed both in these alkali metals and in other metals that single-OPW functions overemphasize the s character at the expense of other angular characters. Consequently, the direct wave-function density $|\psi(0)|_d^2$ decreases in going from a single- to many-OPW functions. For cesium,⁴ it was found that $|\psi(0)|_d^2$ changed from 2.24 to 1.83, a decrease by 18%. Callaway⁶ has calculated the energy bands of lithium, sodium, and potassium using empirical ionic potentials and the cellular method in combination with a $\vec{k} \cdot \vec{p}$ perturbation procedure to obtain the wave functions at the Fermi surface. The adequacy of retaining only k^2 -order terms in the $\vec{k} \cdot \vec{p}$ perturbation series is questionable as has been pointed out by Bienenstock and Brooks¹⁵ in the course of their calculation of the g shift in these metals. In addition, Moore and Vosko⁵ have emphasized that the inclusion of the Hartree term in the conduction-electron potential (which takes into account the Coulomb interaction among the conduction electrons) significantly changes $|\psi(0)|_d^2$ from its bare-ion potential value.

For lithium in particular, whose conduction electrons at the Fermi surface have large p character,¹⁶ the one-OPW approximation severely overestimates the density at the nucleus. For lithium, sodium, and potassium, we have used the results of Moore and Vosko.⁵ Comments on the accuracy of these wave functions obtained by using the cellular method will be postponed until Sec. V. It should be emphasized that the $|\psi(0)|_d^2$ obtained by

TABLE II. Direct, ECP, relativistic, and total contributions to $\langle |\psi(0)|^2 \rangle_{\text{av}}$ in units of a_0^{-3} (many-OPW result).

Metal	Direct		Core polarization			Total	Total
	Nonrel	Rel	s part	p part	Rest		
Li	0.0797	0.0797	0.0235 ^a	-0.0281 ^a	-0.0008 ^a	-0.0054 ^a	0.0743
Na	0.3644 ^b	0.3644	0.0916	0.0043	-0.0006	0.0953	0.4597
K	0.4830 ^b	0.4830	0.1047	0.0284	-0.0022	0.0953	0.6139
Rb	1.1370	1.2229	0.2467	0.0484	-0.0075	0.2876	1.5105
Cs	1.8340	2.4025	0.3685 ^c	0.0898 ^c	-0.0096 ^c	0.4487 ^c	2.8512 ^c
			0.3774 ^d	0.0690 ^d	-0.0283 ^d	0.4100 ^d	2.8125 ^d

^aTaken from Ref. 9.

^bObtained from Ref. 5.

^cThese results are estimated by applying the requisite weighting factors to the one-OPW results in Table I, as in the case of Na, K, Rb.

^dThese results were obtained through ECP calculations using calculated many-OPW functions.

the cellular method is extremely sensitive to the choice of the potential and this should be borne in mind while making comparisons with experiment. For the details of the calculation of $|\psi(0)|_d^2$, we refer the reader to the Ref. 5.

For rubidium, the only wave functions available were obtained¹⁷ with the OPW procedure using Hartree functions for the core states. To obtain a spin density for quantitative purposes, it would be necessary to repeat these calculations using Hartree-Fock core functions. In the absence of such calculations, we have scaled the one-OPW spin density in the Table I by 18%, the same factor that was found for cesium.⁴

We next turn our attention to the question of ECP contributions to the spin density in the many-OPW approximation. We have carried out actual calculations for cesium using many-OPW functions and the MP functions utilized for the one-OPW calculations in Sec. II. The results are presented in the last row of the Table II. Comparing with the one-OPW ECP results in the Table I, it is seen that the *s*-type ECP in the many-OPW approximation is about 16% less than the one-OPW result. This reduction factor compares favorably with the 18% found for the direct spin density. The *p*-type contribution is also found to decrease by about 20% compared to the one-OPW case. For lithium, ECP calculations are available⁹ using Kohn-Callaway¹⁸ wave functions which are substantially different from the one-OPW functions but give spin densities relatively close to those of Moore and Vosko.⁵ We have listed the ECP results of Ref. 9 in the Table II. These are not expected to be substantially different from what one would expect from ECP calculations with Moore-Vosko functions. A comparison with one-OPW ECP results in Table I indicates that in going from the one-OPW to the Kohn-Callaway functions, the *s*-type ECP does decrease by the same factor of nearly 4 as the direct spin density. For the *p*-type ECP, there is an increase by a factor of about 2.8 compared to the one-OPW case.

The analysis for the above two cases indicates that the *s*-type ECP does decrease by almost the same ratio as the direct density. We have therefore decreased the one-OPW *s*-type ECP results for sodium, potassium, and rubidium by the same ratio as the direct spin densities to arrive at the appropriate entries in the Table II. The *p*-type ECP situation is less certain. The lithium results indicate an increase from the one-OPW value while the cesium metal, with a number of *s* cores with opposing contributions as pointed out in Sec. II and as in the atomic case,¹² shows a decrease. It is thus difficult to anticipate the exact trend in the other three metals. However, we feel that the trend for the *p*-type ECP in these metals is likely to be closer to lithium than cesium because the cancelling effect

among cores is found to be less marked in these metals than in cesium in the one-OPW approximation. In the absence of any other compelling reasons for a better choice, we have up-graded the *p*-type ECP for the one-OPW case by the same ratio as the decrease for the *s*-type ECP. Departures from this approximation are not expected to be too crucial because the *p*-type ECP effect is itself rather small in magnitude relative to the direct and *s*-type ECP densities in these metals. The upper line under cesium in Table II gives the results of such an approximation for cesium. The total ECP density under this approximation is seen to be within about 10% (the total spin density agreeing within 2%) of the actual result with many-OPW functions.

In making use of the results for the spin density to obtain theoretical K_s and T_1T to compare with experiment, we have to include the influence of relativistic effects. Relativistic effects can influence K_s and T_1T in two ways, through the density of states at the Fermi surface and through the spin density at the nucleus. The former effect is not expected to be important for the following reason. In the alkali metals, the Fermi surface does not touch the Brillouin zone and therefore, there are no significant degeneracies or near degeneracies which could be influenced substantially by spin-orbit interaction in the relativistic formalism. The major relativistic effect is expected to arise from the change in the spin density at the nucleus.

In an earlier paper⁷ it was found that within a single-OPW framework $|\psi(0)|_d^2$ increased from its nonrelativistic value by 31.2% for cesium and 7.3% for rubidium. From the above trend and the fact that relativistic effects on the hyperfine constants in lithium, sodium, and potassium atoms were¹² rather small, it is reasonable to neglect such effects on the spin densities in corresponding alkali metals. Relativistic many-OPW calculations are not available for cesium and rubidium. However, since the major contribution to the relativistic effect arises from regions near the nucleus, it is reasonable to expect that the percentage-wise increase in $|\psi(0)|_d^2$ (in going from a nonrelativistic to a relativistic framework) will be unaltered if one carried out a complete many-OPW calculation. We have therefore applied corrections of 31.2 and 7.3% to the direct many-OPW nonrelativistic spin densities for cesium and rubidium, respectively, and these numbers are included in the column under direct relativistic contributions in the Table II.

The question of relativistic corrections to the ECP spin density is somewhat more complicated and can be answered quantitatively through relativistic MP calculations. Any estimate of their importance would be rather uncertain because $|\psi(0)|_d^2$ involves contributions from regions both near the nucleus (through densities of the core electrons) as well as

the rest of the Wigner-Seitz cell (through exchange interaction). We have therefore not included relativistic effects on $|\psi(0)|_{cp}^2$ in our analysis. The last column of the Table II gives the total spin density including both ECP and relativistic corrections.

IV. INFLUENCE OF ELECTRON-ELECTRON INTERACTIONS ON K_s AND T_1

The spin densities, both direct and ECP, calculated in Sec. III can be utilized to obtain theoretical K_s and T_1T to compare with the experiment. However, one does need a quantitative knowledge of the spin susceptibility χ_p for K_s and $\chi(\vec{q}, \omega)$, the wave-number- and frequency-dependent susceptibility function for T_1 . In the analysis of relaxation time, a convenient form that has been utilized in the literature^{2,19} is

$$(T_1T)^{-1} = (4/\hbar^2)k_B(\gamma_e\hbar)^{-2}\sum_{\vec{q}}|A_{\vec{q}}|^2\omega_0^{-1}\chi_1''(\vec{q}, \omega_0), \quad (8)$$

where ω_0 is the nuclear Zeeman frequency $\gamma_N\hbar H$; k_B is the Boltzmann constant with $\gamma_e (=e/mc)$ and γ_N the gyromagnetic ratios for the electron and the nucleus, respectively;

$$A_{\vec{q}} = (\frac{2}{3}\pi)\gamma_e\gamma_N\hbar^2\psi_{\vec{k}+\vec{q}}^*(0)\psi_{\vec{k}}(0)\Omega. \quad (9)$$

In Eq. (8), $\chi_1''(\vec{q}, \omega_0)$ is the imaginary part of the transverse susceptibility (perpendicular to the z direction) $\chi_1(\vec{q}, \omega)$. For an isotropic system, $\chi_1(\vec{q}, \omega)$ is related to the longitudinal component $\chi_{||}(\vec{q}, \omega)$ through the relation

$$\chi_1(q) = \frac{1}{2}\chi_{||}(q),$$

where q stands for \vec{q} and ω . The Pauli susceptibility χ_p occurring in Eq. (1) is the $q=0$ limit of $\chi_{||}(q)$. The two basic aspects of the theoretical calculation of $\chi_{||}(q)$ are (a) the influence of crystal potential and (b) the incorporation of exchange and correlation effects. For nearly-free-electron-like metals, the effect of the former can be taken into account through an effective-mass approximation (through density-of-states effect). The adequacy of such an approximation even for the alkali metals is questionable and will be discussed while presenting the experimental values of χ_p . The latter represents the more complex aspect of the theoretical analysis. In the absence of electron-electron interaction, $\chi_{||}(q)$ is equal to its free-electron value $\chi_0(q)$ given by (per unit volume)

$$\chi_0(q) = \chi_0'(q) + i\chi_0''(q), \quad (10)$$

where

$$\chi_0'(q) = \frac{1}{2}(\gamma_e\hbar)^2 P \sum_{\vec{k}} \frac{n_{\vec{k}+\vec{q}} - n_{\vec{k}}}{\hbar\omega - E_{\vec{k}+\vec{q}} + E_{\vec{k}}} \quad (11)$$

and

$$\chi_0''(q) = \frac{\pi}{2}(\gamma_e\hbar)^2 \sum_{\vec{k}} (n_{\vec{k}+\vec{q}} - n_{\vec{k}}) \delta(\hbar\omega - E_{\vec{k}+\vec{q}} + E_{\vec{k}}). \quad (12)$$

In Eq. (11), P denotes the principal value. $n_{\vec{k}}$ is the usual Fermi function for a state of wave vector \vec{k} and energy $E_{\vec{k}}$.

The effect of electron-electron interaction on K_s and $(T_1T)^{-1}$ can be incorporated through its influence on the susceptibility function $\chi_{||}(q)$. In addition, correlation can influence K_s and T_1T through its effect on the spin density $|\psi(0)|^2$. However, band calculations in cesium⁴ incorporating this effect have shown this influence to be unimportant.

Although the importance of exchange and correlation in the study of $\chi_{||}(q)$ has been realized for a long time, there are no adequate theories for quantitative evaluations applicable to real systems. One of the earlier calculations of χ_p was that of Silverstein²⁰ who utilized an interpolation procedure between high- and low-momentum regimes to calculate the correlation energy in the presence of a magnetic field. The effect of the crystal potential was incorporated purely through an effective-mass approximation. The Silverstein expression for χ_p is

$$\chi_p = \chi_{||}(0, 0) = \chi_p^* \left[1 + \left(\frac{m}{m_t} - 1 \right) \frac{\chi_p^*}{\chi_p} \right]^{-1}, \quad (13)$$

where χ_p^* is the Pauli susceptibility for free non-interacting electrons, χ_p^* is that for interacting electrons without the influence of the lattice potential. The ratio m_t/m gives the enhancement of the density of states from its free-electron value, i. e.,

$$m_t/m = g(E_F)/g_0(E_F), \quad (14)$$

where $g(E_F)$ and $g_0(E_F)$ are the density of states at the Fermi surface with and without incorporating band-structure effects. There have been several improved calculations of χ_p^* after Silverstein. These are by Rice²¹ and Singwi *et al.*²² However, we will use the experimental values of χ_p in our calculation of theoretical K_s and T_1T .

Next, we briefly outline the situation regarding the exchange-enhancement effects on $\chi_{||}(q)$ for $q \neq 0$. Earlier calculations of Izuyama *et al.*²³ and Moriya¹⁹ assumed that the effect of screening was to make the effective interaction potential between the electrons of such a short range that one could replace it by a δ -function potential in the position space. This approximation leads to the following expression for $\chi_{||}(q)$:

$$\chi_{||}(q) = (\frac{1}{2}\gamma_e\hbar)^2 \tilde{\chi}_0(q) / [1 - \frac{1}{2}\bar{w}\tilde{\chi}_0(q)], \quad (15)$$

where $\tilde{\chi}_0(q)$ is related to $\chi_0(q)$ of Eq. (10) by the relation

$$\chi_0(q) = (\frac{1}{2}\gamma_e\hbar)^2 \tilde{\chi}_0(q) \quad (16)$$

and \bar{w} is the Fourier transform of the δ function potential. Recently, Narath and Weaver² have analyzed the applicability of such an approximation and have concluded that for the alkali metals the finite-range effects are quite important and should

be properly taken into account.

Although a simple expression for $\chi_{11}(q)$ given in Eq. (15) will no longer be valid when one takes proper account of the finite-range behavior, one can still define an effective interaction by the following equation:

$$\chi_{11}(q) = (\frac{1}{2}\gamma_e \hbar)^2 \tilde{\chi}_0(q) / \{1 - \frac{1}{2}[v_{\text{eff}}(q)]\tilde{\chi}_0(q)\}, \quad (17)$$

where $v_{\text{eff}}(q)$ is in general q and ω dependent and complex and can be obtained from an exact knowledge of $\chi_{11}(q)$ and $\tilde{\chi}_0(q)$. In the Appendix we have outlined a procedure for obtaining $v_{\text{eff}}(q)$ which takes into account the finite-range character in an approximate fashion. Using the Thomas-Fermi²⁴ model of the dielectric function to screen the bare Coulomb potential and making certain local approximations (see Appendix) we obtain

$$V_{\text{eff}}(q) = \frac{4\pi e^2}{2} \left[\frac{1}{k_F^2(1+\xi^2)} + \frac{1}{k_F^2(1+\xi^2) + |\vec{q}|^2} \right]. \quad (18)$$

Although the Thomas-Fermi model gives a value of the screening parameter ξ as a function of r_s (the electron sphere radius), we will keep ξ as an open parameter to be determined from the experimental value of χ_p . Since $v_{\text{eff}}(q)$ is frequency independent and real it can be treated precisely in the same manner as \bar{w} (excepting for the \vec{q} integration) while calculating the exchange enhancement of $(T_1 T)^{-1}$. In this case, the Korringa ratio $R [= K_s^2 T_1 T / (K_s^2 T_1 T)_0]$ can be calculated by the usual procedure using Eqs. (8), (12), and (17). We distinguish two cases:

(a) δ -function interaction:

$$R^{-1} = [(1-\alpha)^2 \langle [1 - \alpha W(q/2k_F)]^{-2} \rangle], \quad (19)$$

where

$$\alpha = \frac{1}{2} \frac{\bar{w}}{(\frac{1}{2}\gamma_e \hbar)^2} \chi_p^f; \quad (20)$$

(b) finite-range approximation,

$$R^{-1} = \{[1 - \alpha(0)]^2 \langle [1 - \alpha(q) W(q/2k_F)]^{-2} \rangle\}, \quad (21)$$

$$\alpha(q) = \frac{1}{2} \frac{V_{\text{eff}}(q)}{(\frac{1}{2}\gamma_e \hbar)^2} \chi_p^f. \quad (22)$$

The function $W(x)$ is the usual dielectric response function² for a free-electron gas. The effect of band structure on R will be discussed while analyzing the experimental values of χ_p .

Before proceeding to the numerical calculations, let us analyze what happens to R when $v_{\text{eff}}(q)$ is ω dependent and complex. Denoting $v_{\text{eff}}(q)$ as

$$v_{\text{eff}}(q) = V'_{\text{eff}}(q) + i v''_{\text{eff}}(q), \quad (23)$$

we find that

$$R^{-1} = \{[1 - \alpha(0)]^2 \langle [1 - \alpha(q) W(q/2k_F)]^{-2} [1 + \gamma(q)] \rangle\}, \quad (24)$$

where

$$\alpha(q) = \frac{1}{2} \frac{V'_{\text{eff}}(q, 0)}{(\frac{1}{2}\gamma_e \hbar)^2} \chi_p^f, \quad \gamma(q) = \frac{1}{2} [\tilde{\chi}'_0(q, 0)]^2 \frac{v''_{\text{eff}}(q, \omega)}{\chi''_0(q, \omega)} \Big|_{\omega=0}. \quad (25)$$

In deriving the above expression for R^{-1} , we have made use of the fact that $v''_{\text{eff}}(q, \omega) \rightarrow 0$ with ω . Thus we see that if $\gamma(q)$ is negative, then R increases from its value when $\gamma(q)=0$. The amount of increase is larger for systems with large $\tilde{\chi}'_0(q)$, for example, lithium. In order to calculate $\gamma(q)$ one has to obtain $\chi_{11}(q, \omega)$ for small but nonzero values of ω . This requires the solution of a complex integral equation and is beyond the scope of the present work.

Since we use the experimental values of χ_p to calculate K_s and derive an effective exchange-enhancement parameter $\alpha(0)$, we would like to discuss the situation regarding χ_p^{expt} for all the alkali metals. Electron-spin-resonance (ESR) measurements which directly give χ_p^{expt} have been made for lithium²⁵ and sodium²⁶ (both in the solid state). Spin-wave (SW) experiments²⁷ furnish the Fermi-liquid (FL) parameters from which one can calculate χ_p^{expt} . Shultz and Dunnifer have measured the FL parameters for both sodium²⁷ and potassium.²⁸ The ESR and SW measurements do not yield identical results for sodium. Neither of these two measurements is available for rubidium and cesium. We have used the values of χ_p^{expt} obtained by Kaeck²⁹ from the Knight-shift measurements in the liquid alkali-metal alloys. There are some uncertainties in these values due to the approximations made regarding the variations of the spin density as a function of alloy concentration. However, it is interesting that the value of $\chi_p^{\text{expt}}/\chi_p^f$ for potassium obtained by Kaeck agrees well with that obtained by Shultz and Dunnifer from SW measurements in the solid.

The question one would like to answer is if one can use the measurements of χ_p^{expt} in the liquid state to calculate K_s and $\alpha(0)$ for the solid. The answer to this question is important since the effective mass and the density of states at the Fermi surface alter appreciably during melting, at least for lithium, rubidium, and cesium. For sodium and potassium, the question is unimportant since their effective masses are nearly equal to the free-electron values in the solid and more so in the liquid. Kaeck²⁹ did not make any measurements with the lithium metal for obvious experimental difficulties. It would have been interesting to compare the values of χ_p^{expt} for liquid lithium (scaled to χ_p for liquid sodium) with χ_p obtained from ESR measurements in solid lithium.²⁵

Returning to the question of extracting χ_p for

TABLE III. Theoretical and experimental values of the spin susceptibility $\chi_p = \chi_H(0, 0)$ (in cgs Volume units).

Metal	r_s	m_t/m	$10^6 \chi_p^f$	$10^6 \chi_p^{\text{ext}}$
Li	3.22	1.66	0.85	2.09
Na	4.00	1.00	0.67	1.13 ± 0.05
K	4.87	1.09	0.55	0.84 ± 0.08
Rb	5.20	1.21	0.50	0.80 ± 0.08
Cs	5.64	1.30	0.47	0.80 ± 0.08

solids from the liquid-state measurements for the alkali metals, let us discuss the case of cesium. Naively speaking, one would assume that m_t/m for the liquid is nearly equal to unity. Knowing m_t/m for the solid and substituting χ_p^{11q}/χ_p^f for χ_p^*/χ_p^f in Silverstein's expression [Eq. (13)], one can calculate χ_p for the solid. Using 1.30^4 for m_t/m one finds $\chi_p = 1.32 \times 10^{-6}$. If this value of χ_p is utilized to calculate K_s , the Knight shift is much too high compared to the experiment. It appears that the simple effective-mass approximation leading to the Eq. (13) needs a more critical evaluation. If we ignore the effect of electron-electron interaction for the time being, the effective-mass approximation gives

$$\beta = \chi_p^{\text{band}}/\chi_p^f = m_t/m. \quad (26)$$

In deriving the above equation, only the change in the electronic energy spectrum due to the lattice potential has been considered. However, one should also incorporate the effects of change in the wave function and the chemical potential. Recently, Timbie and White³⁰ have used a pseudopotential procedure and second-order perturbation theory to obtain β incorporating the effects mentioned above. They find that, excepting for lithium, the ratio β differs from unity by less than 1%. In other words, including the effect of changes in the wave function and the chemical potential reduces β from its value given by Eq. (26) to nearly unity. (This is not true in general as in some cases m_t/m is itself less than unity and both effects add to reduce χ_p^{band} appreciably from χ_p^f .) This is easily seen from the

expression for $\chi(q)$ given in the Appendix in terms of single-particle Green's function (GF). The GF that one has to use not only has pole at an energy different from the free-electron value, but is also multiplied by the quasiparticle amplitude renormalization factor³¹ Z_k which is less than unity. The amount of reduction of Z_k from unity depends upon the strength of the crystal potential. Thus it appears that the simple model of Silverstein which includes only the effect of density-of-states enhancement is not adequate to incorporate all the effects of the lattice potential.

The calculation of Timbie and White³⁰ both for the solid and the liquid show that for Na, K, Rb, and Cs, the cancellation mentioned in the last paragraph is nearly exact (within 1%) whereas for Li, the density-of-state effect still remains, its effect being reduced from 1.66 to 1.30. This point is quite important in determining an experimental value of $\alpha(0) \{ \chi_p^{\text{ext}}/\chi_p^{\text{band}} = 1/[1 - \alpha(0)] \}$ which is the appropriate parameter to use in the study of Korringa constant.

We have used the experimental values of χ_p given in Table III to calculate K_s . For all the alkali metals excepting lithium, $\alpha(0)$ has been obtained by putting $\beta=1$, whereas for lithium $\beta=1.3$. Simple second-order perturbation-theory result of Timbie and White³⁰ for lithium whose Fermi surface is considerably distorted and nearly touches the Brillouin zone is doubtful. However, it is likely that β is considerably smaller than 1.66 which the simple density-of-states enhancement model predicts. For the sake of analysis we shall quote the results using both the values of β (1.3 and 1.66) to obtain $\alpha(0)$.

Next we discuss the results of our calculation of $R^{-1}(\alpha)$ using Eqs. (19) and (21). The effect of ECP (which is large only for lithium) will be postponed until Sec. V. The values of $\alpha(0)$, $1 + \xi^2$, $R^{-1}(\alpha)$ using finite-range and δ -function models are given in the Table IV along with the experimental values of Narath and Weaver.² For lithium, two values of $\alpha(0)$ which were mentioned in the last paragraph are used. For a particular metal (definite r_s), $\alpha(0)$

TABLE IV. Exchange and correlation effects on inverse Korringa constant [$R^{-1}(\alpha)$], the parameters $\alpha(0)$ and $1 + \xi^2$ for the alkali metals.

Metal	$\alpha(0)$	$1 + \xi^2$	$R^{-1}(\alpha)^a$	$R^{-1}(\alpha)^b$	$R^{-1}(\alpha)^c$	$R^{-1}(\alpha)^d$
Li	0.47 (0.325)	2.27 (3.28)	0.582 (0.754)	0.738 (0.837)	0.637	
Na	0.402	3.30	0.687	0.787	0.625	0.623
K	0.345	4.68	0.754	0.825	0.614	
Rb	0.375	4.60	0.728	0.805	0.617	
Cs	0.412	4.54	0.696	0.780	0.578	

^aFinite range.

^b δ function.

^cExperiment.

^dHamann and Overhauser (see text).

TABLE V. Theoretical and experimental results for K_s , T_1T , and R .

Metal result	Li	Na	K	Rb	Cs
$K_{s,Th}$	0.018	0.115	0.216	0.614	1.419
$K_{s,expt}$	0.025	0.108(5)	0.270	0.648	1.570
$(T_1T)_{Th}$	44.80 (34.60) ^a	4.09	34.27	1.03	0.108
$(T_1T)_{expt}$	42 ± 1	5.1 ± 0.2	26.88	1.09	0.106
R_{Th}	0.869 (0.671) ^a	1.46	1.33	1.37	1.44
R_{expt}	1.57	1.60	1.63	1.62	1.73

^aRefers to the values of $\alpha(0)$ given inside parenthesis in Table IV.

uniquely determines the screening parameter ξ of Eq. (18). It is seen from the Table IV that the finite-range model improves the values of $R^{-1}(\alpha)$ by 10–15% over the δ -function model. However, it is still 10–18% off from the experimental value, the agreement being better for smaller r_s values.

For the sake of comparison, we have used Hamann and Overhauser's³² results for $\chi'(q)/\chi_p^f$ to calculate $R^{-1}(\alpha)$ for sodium. This is equivalent to neglecting the imaginary part of $v_{eff}(q)$ of Eq. (23). For this metal, HW obtain $\alpha(0)$ to be nearly 0.40, same as that obtained from the experiment. Thus a direct comparison of this result with those of finite-range and δ -function models is possible. For the rest of the alkali metals HW's values of χ_p/χ_p^f [equivalently $\alpha(0)$] do not agree with those obtained from experiment. Therefore a comparison for these metals is not meaningful. For sodium, a better treatment of the screening (not making small q approximation for the dielectric function) and the solution of the integral equation (A2) explicitly gives $R^{-1}(\alpha)$ (0.623), in exact agreement with the experiment (0.625). However, the screened exchange model for $\chi(q)/\chi_p^f$ within the random-phase-approximation (RPA) framework becomes increasingly worse for larger r_s values, and a better treatment of exchange and correlation in the presence of a magnetic field is necessary. Furthermore, additional contributions to K_s that may not alter T_1T appreciably, thereby affecting $R^{-1}(\alpha)$, will be considered in Sec. V.

For lithium, using $\alpha(0) = 0.47$, we see that $R^{-1}(\alpha)$ is in good agreement with experiment. For this metal whose r_s value is small, our model for calculating $R^{-1}(\alpha)$ is expected to be quite good. However, as we have mentioned earlier, there is some uncertainty regarding the value of $\alpha(0)$. If the cancellation between the density-of-states enhancement and the quasiparticle amplitude reduction factor is also exact for this metal, then $\alpha(0) = 0.61$. Using this value of $\alpha(0)$, $R(\alpha)$ is found to be 2.32

which is considerably larger than experiment. We shall refer to this point in Sec. V while discussing the results for lithium including the ECP effect.

V. RESULTS FOR KNIGHT SHIFTS, RELAXATION TIMES, KORRINGA RATIO AND DISCUSSION

The analysis of ECP effects in this paper is part of a continuing effort at understanding the hyperfine properties of alkali metals. Earlier efforts have concentrated on the direct nonrelativistic contributions and relativistic corrections to K_s and T_1T . It is therefore helpful at this point to take stock of the theoretical *vis-a-vis* experimental values of K_s , T_1T , and R including ECP effects as well. This is done in the Table V for all the five alkali metals. $K_{s,Th}$, $(T_1T)_{Th}$, and R_{Th} have been obtained by using $|\psi(0)|^2$ of Table II, experimental χ_p and the parameter $\alpha(0)$ derived therefrom.

An inspection of the entries in the Table V indicates that for rubidium and cesium, the nature of agreement between theory and experiment is similar. Thus for both metals, the theoretical K_s are about 10 to 12% smaller than experiment, while the agreement between theoretical and experimental T_1T is near exact for cesium and within 5% for rubidium. The smaller theoretical values of K_s lead to smaller values of R compared to the experiment, although theoretical and experimental values of R agree in nature, both being substantially larger than unity.

For potassium, both K_s and $(T_1T)^{-1}$ are found to be smaller than experiment, while for sodium, K_s is in near exact agreement but T_1T is about 20% smaller than experiment. The theoretical value of R for sodium is in better agreement with experiment whereas that for potassium, the nature of agreement is similar to that for rubidium and cesium. For lithium, the over-all situation is rather intriguing in that the theoretical K_s appears to be substantially smaller than experiment while the relaxation rate represented by the value of $(T_1T)^{-1}$

is stronger than experiment if one uses $\alpha(0) = 0.325$ whereas the value of $(T_1T)^{-1}$ obtained by using $\alpha(0) = 0.47$ agrees with the experiment. Consequently, the theoretical value of R including the ECP effect is rather small, about a factor of 0.5 (between 0.55 and 0.45) compared to experiment and less than unity while the experimental R is more than unity.

Before drawing any general conclusions from these results, we would like to speculate on some of the possible mechanisms and improvements in the theory that could lead to better agreement with experiment.

We shall consider the situation in cesium first, primarily because band calculations in this metal were carried out⁴ with specific attention towards obtaining wave functions of sufficient accuracy. If we do not want to ascribe remaining discrepancies between theory and experiment to inaccuracies in the wave functions employed, some additional mechanisms are needed that will have the feature of retaining the good agreement of T_1T with experiment, but improve upon the 10% remaining disagreement for K_s with experiment.

Let us consider the various possible mechanisms that we have not included one by one. First, there is the exchange polarization of the conduction electrons^{10,33} below the Fermi surface by those on the Fermi surface. This is the analog of the ECP mechanism except that now the conduction electrons below the Fermi surface are exchange polarized rather than the cores. It is difficult to assess the quantitative importance of this mechanism without actual calculations because while the density of the paired conduction electrons at the nucleus is much smaller than that of the core electrons, their exchange interaction with the Fermi-surface electrons is much stronger. It is possible for this mechanism to contribute differently to K_s and T_1T , but again, no definite statement can be made without an actual calculation. A second possibility is the orbital contribution^{34,35} to K_s . Again, the importance of this mechanism is difficult to assess without actual calculations. Since there is appreciable p character⁴ in the wave function at the Fermi surface, the orbital mechanism can make significant contribution to K_s . The orbital hyperfine interaction can also contribute to the relaxation rate, and it is possible that the effectiveness of the orbital mechanism is qualitatively different³⁶ for K_s and $(T_1T)^{-1}$. Two related mechanisms that can contribute to $(T_1T)^{-1}$ are the nuclear spin dipolar and electric quadrupolar mechanisms which are often referred to as Mitchell³⁷ mechanisms. Preliminary estimates of their contributions indicate⁴ that they are, respectively, two and five orders of magnitude weaker than the Korringa (contact hyperfine) mechanism. A third possible mechanism³⁸ that has not been considered for K_s is one arising out of one or

der each in electron nuclear contact hyperfine interaction, spin-orbit effect, and electron-orbit magnetic field interaction. While the relativistic treatment⁷ of hyperfine effects does include spin-orbit effect implicitly, this particular mechanism is not included because it requires the inclusion of orbit magnetic field interaction. This mechanism is expected to be sensitively dependent on the strength of the spin-orbit interaction and thus be significant only for the heaviest of the alkali metals, namely, cesium.

The important remaining sources for difference between theory and experiment are possible errors in χ_p [hence in $\alpha(0)$], treatment of the exchange enhancement of $\chi_0(q)$, and the neglect of core-conduction correlation effects on both the conduction and core wave functions. As regards the former two, we have already pointed out in Sec. IV the limitations of current exchange-enhancement treatments in their applicability to Bloch electrons and systems with large r_s . Both an improved theory and direct measurement of χ_p will be helpful in clearing up this point. As regards the role of core-conduction correlation effects, no quantitative treatments are currently available. However, the comparable phenomenon in atoms is the valence-core correlation effect and recent treatments using Brueckner-Goldstone many-body perturbation theory on several atoms including the alkali atoms lithium and sodium³⁹ indicate that such effects can be quite significant.

All these observations for cesium apply equally well for rubidium where the agreement between theory and experiment is of similar nature as in cesium. There is some uncertainty in rubidium, however, due to the lack of wave functions of comparable accuracy to cesium.

In the case of potassium, the results in Table V indicate that both K_s and $(T_1T)^{-1}$ are underestimated. Thus, mechanisms that have been neglected or the inaccuracies in the present calculation must be such as to enhance both K_s and $(T_1T)^{-1}$. Any of the additional sources of contribution listed for cesium would be important in this respect, except the one³⁸ involving the spin-orbit effect, since the potassium is much lighter. In particular, the core-conduction correlation effect may be the most important one, in keeping with the trend observed^{11,39} from the study of hyperfine constants in alkali atoms. However, it is also possible that the experimental χ_p used is inaccurate and the treatment of exchange enhancement of $\chi_0(q)$ is not adequate. Additionally, there could be some inaccuracy in the conduction-electron wave function used. The latter was obtained using the spherical cellular approximation and some of the uncertainties discussed a little later for lithium could well apply to potassium.

For sodium, the theoretical situation appears to

be rather satisfactory with respect to K_s when one makes use of the experimental χ_p . The good agreement between theory and experiment could be taken as an indication that (a) the wave functions utilized are accurate and (b) that the other mechanisms contributing to K_s which have been neglected make either individually small or mutually cancelling contributions. However, definite conclusions on these points would require actual calculations. In particular, core-valence correlation effects have been studied in sodium atom and lead to about 10% contribution to the hyperfine constant. If one assumes a similar effect in the metal, this would spoil the apparent good agreement with experiment for K_s . As regards the discrepancy between theoretical T_1T and R and experiment, it appears that an improved treatment of $\chi(\vec{q}, 0)$ can remove the discrepancy. If the additional effects do in fact turn out to be important, one would have to withhold making conclusions from the good agreement for K_s about the accuracy of the wave functions utilized. Calculation of these wave functions by other methods would therefore be helpful, also in view of the surprisingly large change in the spin density in going from one-OPW to the cellular wave functions as also in the case of potassium (Tables I and II).

The situation in lithium is somewhat intriguing because the theoretical K_s is smaller than experiment while the relaxation rate is stronger than or nearly same as the experiment. If one attempts to explain these discrepancies through alteration in the spin density, one faces the contradictory situation that the explanation of K_s requires an increase in the spin density while the relaxation rate requires a decrease. One also arrives at this enigma in trying to explain the situation through a change in the ECP effect by alterations in the p character. A possible explanation out of this ambiguous situation is to assume that the changes in the p character are compensated by corresponding changes in the d and higher angular components. To be more definitive about the situation regarding the spin density, it would be helpful to have revised calculations of the wave functions in lithium, preferably by the OPW technique and coupled with a careful scanning of the Fermi surface. The latter is important to take proper account of the variation of the angular character of the wave functions with the direction of \vec{k} . The cellular calculations performed on this metal do not allow for this variation of the spin density with the direction of \vec{k} , while the OPW calculation in cesium⁴ which includes directional effects in \vec{k} space, both through the wave functions and the local density of states, indicates that such effects are of substantial importance.

In addition, one should study the following in greater detail: (i) the appropriate $\alpha(0)$ for the solid which includes the effect of the lattice poten-

tial; (ii) since the Fermi surface of lithium nearly touches the Brillouin-zone boundary, Umklapp corrections to $\chi(q)$ can be quite significant. These will alter the simple form of $\chi_0(\vec{q}, 0)$ utilized in the calculation of R , T_1T ; (iii) the frequency dependence of $v_{eff}(q)$ in Eq. (17) should be analyzed properly. Evidence for the important role of Bloch effects is available from beryllium metal¹⁰ where the free-electron-type (effective-mass approximation) exchange-enhancement theories^{4,19,20} indicate an enhancement of K_s and $(T_1T)^{-1}$, while the analysis of the experimental data suggest deenhancement. In summary, it appears that the theoretical situation for K_s and T_1T for lithium is the least well understood of all the alkali metals, and that efforts are needed to obtain better wave functions and exchange-enhancement factors. In addition, attempts to estimate the importance of other contributing mechanisms, particularly the orbital contribution to K_s , should be made. Although lithium is a light metal, it has very large p character and since the direct K_s is itself small, the orbital contribution may be of comparable magnitude.

VI. CONCLUSION

It appears from the work in the present paper that ECP effects are of substantial importance in explaining observed K_s and $(T_1T)^{-1}$ in all the alkali metals. For lithium, ECP effects have determining influence on the Korringa ratio R through the p character of the wave functions. Exchange-enhancement effects on the q -dependent susceptibility also have substantial influence on R , both in lithium and other metals. For the latter, exchange-enhancement effects are more important for R than the ECP effects. A consideration of these mechanisms as well as relativistic effects for rubidium and cesium leads to a reasonable over-all quantitative understanding of K_s and T_1T for all the metals. However, since the alkali metals are expected to be the simplest of all metallic systems, one would like to resolve the remaining quantitative disagreements between the experiment and theory. The leading problems to be tackled are more accurate wave functions for the rest of these metals comparable to those for cesium,⁴ a quantitative treatment of exchange-enhancement effects appropriate for Bloch electrons, and the inclusion of core-conduction correlation effects.

APPENDIX

For the sake of brevity we shall denote (\vec{q}, ω) by a four vector q . In the presence of electron-electron interaction, $\chi_{||}(q)$ is given by⁴⁰ [in units of $(\frac{1}{2}\gamma_e\hbar)^2$]

$$\chi_{||}(q) = \frac{i}{(2\pi)^4} \int \text{tr} [\tau_3 G(q+q') \Lambda_3(q'; q) G(q')] d^4q', \quad (\text{A1})$$

where $G(q)$ is the single-particle Green's function³¹ and τ_3 , τ_+ , and τ_- are the three components of the Pauli spin matrix ($\tau_{\pm} = \tau_x \pm i\tau_y$, $\tau_3 = \tau_z$). The vertex function $\Lambda_3(q'; q)$ in Eq. (A1) satisfies an integral equation of the form

$$\Lambda_3(k; q) = -\tau_3 - \frac{i}{(2\pi)^4} \int \frac{v(k-\bar{q})}{\epsilon(\bar{q}-k)} G(q+\bar{q}) \times \Lambda_3(\bar{q}; q) G(\bar{q}) \Lambda_0(k; \bar{q}-k) d^4\bar{q}, \quad (\text{A2})$$

where $v(q)$ is the Fourier transform of the Coulomb interaction and is equal to $4\pi e^2/q^2$. $\epsilon(q)$ is the wave-vector- and frequency-dependent dielectric function and $\Lambda_0(k; q)$ on the right-hand side of Eq. (A2) accounts for the effects of density fluctuations on the susceptibility. This will be ignored in the present analysis which amounts to replacing Λ_0 by $-\tau_0$, where τ_0 is the identity operator in the (2×2) spin space.

If one approximates $v(k)/\epsilon(k)$ by \bar{w} , one recovers the result of Moriya¹⁹ [see also Eq. (20)]. If instead of \bar{w} , one uses $v(q)$, then the infinite-range model of Narath and Weaver² is obtained.

We approximate $\epsilon(\bar{q}, \omega)$ by its long-wavelength and static value $\epsilon_{TF}(\bar{q}, 0)$ in the Thomas-Fermi approximation. This makes the effective interaction (screened exchange) frequency independent and amounts to replacing $v_{sc}(\bar{q}) [= v(\bar{q})/\epsilon(\bar{q}, 0)]$ by

$$v_{sc}(\bar{q}) = \frac{4\pi e^2}{|\bar{q}|^2 + \xi^2 k_F^2}, \quad (\text{A3})$$

where ξ is a screening parameter and k_F is the Fermi wave vector. In addition, making the following local approximations⁴¹:

$$|\bar{k} - \bar{q}'|^2 + \xi^2 k_F^2 \rightarrow k_F^2 + \xi^2 k_F^2, \quad (\text{A4})$$

$$|\bar{k} - \bar{q}' + \bar{q}|^2 + \xi^2 k_F^2 \rightarrow k_F^2 + q^2 + \xi^2 k_F^2, \quad (\text{A5})$$

one obtains

$$\Lambda_3(\bar{q}, \omega) = -\tau_3 \left[1 - \frac{2v_{eff}(q)}{(2\pi)^3} \int \frac{n_{\bar{q}'}}{\hbar\omega - E_{\bar{q}+\bar{q}'} + E_{\bar{q}'}} d^3q' \right]^{-1}, \quad (\text{A6})$$

where

$$v_{eff}(q) = \frac{4\pi e^2}{2} \left[\frac{1}{k_F^2(1+\xi^2)} + \frac{1}{k_F^2(1+\xi^2)+q^2} \right]. \quad (\text{A7})$$

The effective interaction given by Eq. (A7) incorporates screening effects while retaining the feature of decreasing strength of the interaction with increasing q as in the case of $v(q)$. This formally completes the solution of $\chi_1''(\bar{q}, \omega)$ which occurs in the expression for $(T_1 T)^{-1}$ in Eq. (8) within the framework of the approximation that we have made for the effective electron-electron interaction. Hamann and Overhauser³² have used $\epsilon_{RPA}(q)$ for $\epsilon(q)$ in Eq. (A2), and have solved the integral equation for Λ_3 to obtain $\chi(\bar{q}, 0)/\chi_p^f$.

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