incorporates the correct linewidth while at the same time reproducing of the results of perturbation theory through first order. Although the justification we have given here is based on a particularly simple interaction, it is plausible that our treatment is satisfactory for other types of off-diagonal perturbations as well.

APPENDIX B

In this Appendix we outline a calculation of the Fourier transform of $\langle S_zS_z(t)\rangle$ which is carried out with the help of Green's functions. The main results presented here are implicit in Ref. 5, to which the reader is referred for further details. The Fourier transform of the longitudinal correlation function can be written in the form[18]

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle S_zS_z(t)\rangle=\left.\frac{i[G(\omega+i\epsilon)-G(\omega-i\epsilon)]}{e^{\beta\hbar\omega}+1}\right|_{\epsilon\to 0_+}. \tag{B1}$$

Here $G(\omega)$ denotes the Fourier transform of the retarded Green's function $-i\theta(t)\langle S_z(t)S_z+S_zS_z(t)\rangle$, where $\theta(x)$ is the unit step function. As shown in Ref. 5, the use of spin-phonon interaction as an off-diagonal perturbation leads in lowest order to a Green's function of the form[19]

$$G(\omega\pm i\epsilon)=\frac{1}{4\pi}\,\frac{1\pm i(1/T_1\omega)\tanh^2\tfrac{1}{2}\beta\hbar\omega_0}{\omega\pm i/T_1}\mp(i/4)\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\,\delta(\omega). \tag{B2}$$

Hence we have

$$\frac{2}{\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle S_zS_z(t)\rangle=\frac{2}{e^{\beta\hbar\omega}+1}\times\left[(1-\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0))\frac{1/(\pi T_1)}{\omega^2+(1/T_1)^2}+\tanh^2(\tfrac{1}{2}\beta\hbar\omega_0)\,\delta(\omega)\right], \tag{B3}$$

in agreement with (4.5). As is the case in Appendix A, the calculation was carried out for a model interaction but is expected to hold for a wider class of off-diagonal perturbations.

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[18] D. N. Zubarev, Usp. Fiz. Nauk. **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

[19] Reference 5, Eq. (II, 22), in the limit $E\to\omega\pm i\epsilon$. In the one-phonon approximation a coupling of the form $S_z\Sigma_v B_v(a_v+a_v^\dagger)$ does not contribute significantly to $\langle S_zS_z(t)\rangle$.

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Theory of Indirect Nuclear Interactions in Rubidium and Cesium Metals*

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A quantitative evaluation has been made of the Ruderman-Kittel and pseudodipolar parameters A_{ij} and B_{ij} for Rb^{85} and Cs^{133} nuclei in the respective metals using one-orthogonalized-plane-wave functions and calculated band structures. All the possible mechanisms that contribute to A_{ij} and B_{ij} have been considered. For A_{ij} ,about 90.54 and 92.25 % of the total contribution for rubidium and cesium, respectively, are found to arise from the second-order effect of the contact hyperfine interaction. For B_{ij}, the corresponding figures are 89.95 and 88.84 %, arising from one order each in the electron-nuclear contact and dipole interactions. For each mechanism, the calculation involves an integration over the region of **k** space within the Fermi surface. The integrand is composed of three **k**-dependent factors, an expectation value over the wave functions, a density-of-states term, and a phase factor which depends on the distance between the nuclei. The final result depends sensitively on the k dependence of these factors, and in some cases there is a cancellation between positive and negative contributions from different regions of **k** space. In the light of this, a critical analysis is made of earlier approximations, where some of the **k**-dependent factors were replaced by their values at the Fermi surface. Self-consistency and correlation effects are explicitly included, and produce less than 10% correction for A_{ij} and B_{ij} in both metals. Our calculated values for A_{ij} are 22.73 and 124.65, respectively, for rubidium and cesium, as compared to recent experimental values 51±5 and 200±10 cps. For B_{ij}, the calculated values are 0.398 and 2.330, as compared to experimental values 11.80 and 35.00 cps. Possible sources for the discrepancies, and additional factors whose inclusion could lead to improved agreement with experiment, are discussed.

I. INTRODUCTION

THE role of conduction electrons in producing indirect coupling between two localized moments or between nuclear moments in a metal was first realized by Fröhlich and Nabarro.[1] For transition metals, Zener[2] proposed that this indirect exchange interaction between localized d-electron magnetic moments can lead to ferromagnetism. These authors only considered the diagonal contribution to the coupling, which is nonzero for the case of metals because of their Pauli paramagnetism. They did not take into account the contributions from second-order polarization effects

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* Supported by the National Science Foundation.

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[2] C. Zener, Phys. Rev. **81**, 440 (1951).

obtained from the nondiagonal excitations of the conduction electrons. A complete theory for the indirect exchange coupling was first proposed by Ruderman and Kittel[3] and Bloembergen and Rowland[4] in order to explain the anomalous linewidths observed in the nuclear magnetic resonance (NMR) of silver,[5] tin,[4] and thallium.[4] Bloembergen and Rowland also suggested that a combination of the Fermi-contact and classical dipolar interaction between electron and nuclear spins could give rise to a pseudodipolar coupling between the two nuclei. The Ruderman-Kittel and pseudodipolar interactions are usually described by two parameters A_{ij} and B_{ij} in the spin Hamiltonian of the form

$$H_{ij}=H_{ij}^{\mathrm{RK}}+H_{ij}^{\mathrm{PD}},$$

where

$$H_{ij}^{\mathrm{RK}}=A_{ij}\mathbf{I}_i\cdot\mathbf{I}_j \tag{1}$$

and

$$H_{ij}^{\mathrm{PD}}=B_{ij}[\mathbf{I}_i\cdot\mathbf{I}_j-3(\mathbf{I}_i\cdot\mathbf{R}_{ij})(\mathbf{I}_j\cdot\mathbf{R}_{ij})R_{ij}^{-2}], \tag{2}$$

$\mathbf{R}_{ij}$ being the radius vector joining the two nuclei i and j.

Kasuya[6] has investigated the indirect interaction between localized spins in systems like the rare-earth metals, through their interactions with the conduction electrons. For copper-manganese alloy systems, Yosida[7] has considered the similar indirect interaction between localized Mn^{++} moments and $\mathrm{Cu}^{63,65}$ nuclear spins and between two localized Mn^{++} moments as mediated by the conduction electrons. Van Vleck[8] has reviewed the relationships between the theoretical methods for indirect spin-spin interactions that have been adopted by various authors. It may be noted that essentially the same mechanism for indirect coupling between nuclei in molecules was proposed by Ramsey and Purcell[9] to explain spin-echo modulation effects observed by Hahn and Maxwell[10] and additional line splitting observed in steady-state NMR spectra by Gutowsky, McCall, and Slichter.[11] The details of the procedure for evaluating the indirect interaction are somewhat different for molecules because of their discrete energy states, in contrast to the Bloch orbitals in metals which are associated with continuous energy bands.

In the present work, we are interested in the evaluation of indirect exchange coupling between the nuclear spins in metals. Although this effect exists in all metals with finite nuclear spin, its magnitude is large enough to be experimentally detectable only in the case of relatively heavy metals. The various metals where this coupling has been measured so far are rubidium,[12] cesium,[12] platinum,[13] silver,[5] tin,[4] thallium,[4] and also in lead-bismuth alloys.[14] We shall confine ourselves to the case of Ruderman-Kittel and pseudodipolar interactions in alkali metals which have recently been measured by Poitrenaud[12] using an ingenious NMR line-shape analysis based on observations of absorption modes in weak fields and dispersion modes in strong fields.

The present work is part of a program for the study of metallic properties other than those that can be interpreted purely from band-shape information. Examples of the latter are density of states, cyclotron resonance, and de Haas–van Alphen effect. In contrast, one could consider other properties that require an explicit knowledge of conduction-electron wave functions for their interpretation. Among these are the indirect spin-spin interactions, nuclear relaxation times, Knight shifts which are obtained from NMR experiments, and electronic g shifts and relaxation times from conduction-electron spin-resonance experiments. In view of the current availability of improved methods for calculating conduction-electron wave functions[15] and recent advances in the understanding of correlation effects in metals,[16] one can now attempt a quantitative understanding of the Ruderman-Kittel (RK) and pseudodipolar (PD) interaction parameters and analyze the theory in detail to understand the respective roles of important contributory factors such as the $\mathbf{k}$ dependence of the interaction, band structure, and exchange and correlation effects.

It is well known from the analysis of band structure and wave functions in metals that as one goes from the center of the Brillouin zone towards an edge or corner, there is a significant change in the relative s, p, $d\cdots$ characters of the wave function. The RK interaction depends only on the s character of the conduction-electron wave function. The PD interaction, on the other hand, will be shown to also involve p character of the wave function, although all non-s components can make finite but small contributions. One therefore expects a change in the relative contributions to RK and PD from various $\mathbf{k}$ states as one proceeds from the zone center towards the zone boundary. It is well known that the anisotropic Knight shift also arises mainly from the p character of the conduction-electron wave function near the Fermi surface. However, the expectation value of the electron-nuclear dipole interaction which leads to the anisotropic Knight shift averages out to zero for cubic metals. The PD coupling constant thus provides an alternate mechanism for studying the p character of the wave function when the anisotropic Knight shift vanishes.

Concerning the role of band structure, there can be

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two important effects on these indirect interactions. First, there is a significant variation in the density of states as one varies **k** from the center to the edge of the Brillouin zone. It will be shown that this variation has an important influence on the strengths of the RK and PD interactions and has to be handled carefully in order to obtain quantitatively reliable results. A second influence of the details of the band structure manifests itself through the departure of the Fermi surface from sphericity. Roth, Zeiger, and Kaplan[17] have shown that for severe departures from sphericity one can obtain a rather slow variation of the RK interaction with internuclear separation. Such effects could be quite significant for the transition metals and semimetals. However, for the alkali metals, band-structure calculations[18,19] as well as de Haas–van Alphen data[20] indicate that the departure from sphericity is rather small.

The role of exchange and correlation effects is twofold. First, they can modify the zero-order wave functions through their influence on the potential. A second interesting effect arises from the role of the exchange and correlation among the conduction electrons in influencing their response to the magnetic fields produced by the nuclei.

Our present interest in the study of RK and PD interactions in alkali metals was dictated primarily by the availability of Poitrenaud's results. However, there are two other important reasons. First, since no significant effects are expected from Fermi-surface anisotropy, one can focus attention on the other contributing factors listed in the last paragraph. Secondly, the wave functions and energy bands of alkali metals have been obtained with enough accuracy that one can rely on the quantitative nature of the results and from comparison with experiment try to draw conclusions about the accuracy of the model in general.

In Sec. II, we develop the necessary theory for the various contributions to the isotropic exchange and PD coupling constants using orthogonalized-plane-wave (OPW) functions. Effects of band anisotropy in **k** space have been incorporated through the use of the calculated density of states. For a parabolic band approximation, our expression for the isotropic coupling constant reduces to that of Ruderman and Kittel.[3]

Section III deals with the contribution of electron-electron interaction to the coupling constants. A self-consistent field method[21] has been employed similar to that used in the calculation of wave-vector-dependent susceptibility, and leads to an enhancement factor. In Sec. IV we present the results of numerical calculation and discuss the significance of various contributions to A_{ij} and B_{ij}. The results appear to be very sensitive to a phase factor in the integrand in **k** space, and in the light of this, a critical analysis of the earlier approximations[3,4] is made. A quantitative comparison with experimental results brings out clearly the significance of the factors considered by us and allows us to speculate on the importance of other effects which have not been considered.

II. ONE-ELECTRON THEORY FOR RK AND PD INTERACTIONS

Let us consider a pair of nuclei with spins $\mathbf{I}_i$ and $\mathbf{I}_j$ and gyromagnetic ratios γ_i and γ_j, respectively, situated at positions $\mathbf{R}_i$ and $\mathbf{R}_j$ and interacting individually with the conduction electrons. The electron-nuclear part of the Hamiltonian in which we are interested is given by

$$\mathcal{H}=\mathcal{H}_i+\mathcal{H}_j=\sum_l[h_i(l)+h_j(l)], \tag{3}$$

where the hyperfine terms[22] associated with the nucleus i are given by

$$\begin{aligned}h_i(l)=&\tfrac{1}{3}(16\pi)\gamma_i\gamma_e\hbar^2\mathbf{I}_i\cdot\mathbf{S}_l\delta(\mathbf{r}_l-\mathbf{R}_i)\\&-2\gamma_e\gamma_i\hbar^2[-3(\mathbf{I}_i\cdot\mathbf{r}_{il})(\mathbf{S}\cdot\mathbf{r}_{il})/r_{il}^5+\mathbf{I}_i\cdot\mathbf{S}_l/r_{il}^3]\\&+2\gamma_i\gamma_e\hbar^2[\mathbf{I}_i\cdot\mathbf{L}(\mathbf{r}_{il})/r_{il}^3].\end{aligned} \tag{4}$$

The first term in (4) is the usual Fermi-contact interaction. The second term describes the dipolar interaction between the nuclear spin $\mathbf{I}_i$ and the electron spins γ_l. The third term is the nuclear spin-electron orbit interaction. An expression similar to h_i can be written for h_j by making the replacement $\mathbf{I}_i\rightarrow\mathbf{I}_j$ and $\mathbf{r}_{il}\rightarrow\mathbf{r}_{jl}$. Here $\mathbf{r}_{il}$ is the radius vector of electron l with respect to nucleus i and $\mathbf{L}(\mathbf{r}_{il})$ is the angular-momentum operator for the electron l with respect to nucleus i as center. In order to obtain the second-order correction to the energy of the total system one has to compute the total second-order energy for the electronic system due to $\mathcal{H}$. By standard second-order perturbation theory,

$$\Delta^2E=\sum_n{}'\langle 0\,|\,\mathcal{H}\,|\,n\rangle\langle n\,|\,\mathcal{H}\,|\,0\rangle/(E_0-E_n), \tag{5}$$

where $|\,0\rangle$ represents the ground-state wave function for the many-electron system and $|\,n\rangle$ the excited states. In the one-electron approximation, the wave function $|\,0\rangle$ is a determinantal function made up of all the occupied Bloch states within the Fermi surface. Since $\mathcal{H}$ is composed of a sum of one-electron operators, the excited states $|\,n\rangle$ will differ from $|\,0\rangle$ by having an empty orbital within the Fermi surface, and an occupied orbital outside. By the usual manipulations for matrix elements over determinantal states[23] one can

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[22] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 149.

[23] D. R. Hartree, *Calculation of Atomic Structure* (John Wiley and Sons, Inc., New York, 1957).

reduce (5) to an expression involving one-electron states:

$$\Delta^2E=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}\frac{\langle n\mathbf{k}s\,|\,h\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h\,|\,n\mathbf{k}s\rangle}{\epsilon_n(\mathbf{k}s)-\epsilon_{n'}(\mathbf{k}'s')}\,. \tag{6}$$

In Eq. (6) the Bloch states $n\mathbf{k}s$ are labelled in the reduced zone scheme, n representing the band, $\mathbf{k}$ the reduced wave vector, and s the spin state. The sum on $n\mathbf{k}s$ runs over all the occupied states and $n'\mathbf{k}'s'$ runs over the unoccupied ones. Following the general procedure of Bloembergen and Rowland[4] and assigning superscripts to the different terms of (2), namely, contact, dipolar, and orbital, describing the different mechanisms, one obtains the following expressions for the second-order energy associated with various types of coupling between the two nuclei i and j under consideration:

$$\Delta^2E_{\mathrm{RK},1}=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}B[\langle n\mathbf{k}s\,|\,h_i^{\mathrm{cont}}(\mathbf{r}_i)\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{cont}}(\mathbf{r}_j)\,|\,n\mathbf{k}s\rangle+\text{c.c.}], \tag{7a}$$

$$\begin{aligned}\Delta^2E_{\mathrm{PD},1}=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}B[&\langle n\mathbf{k}s\,|\,h_i^{\mathrm{cont}}(\mathbf{r}_i)\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{dip}}(\mathbf{r}_j)\,|\,n\mathbf{k}s\rangle\\&+\langle n\mathbf{k}s\,|\,h_i^{\mathrm{dip}}(\mathbf{r}_i)\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{cont}}(\mathbf{r}_j)\,|\,n\mathbf{k}s\rangle+\text{c.c.}],\end{aligned} \tag{7b}$$

$$\Delta^2E_{\mathrm{RK},2}=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}B[\langle n\mathbf{k}s\,|\,h_i^{\mathrm{orb}}(\mathbf{r}_i)\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{orb}}(\mathbf{r}_j)\,|\,n\mathbf{k}s\rangle+\text{c.c.}], \tag{7c}$$

$$\Delta^2E_{\mathrm{RK},3}+\Delta^2E_{\mathrm{PD},2}=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}B[\langle n\mathbf{k}s\,|\,h_i^{\mathrm{dip}}(\mathbf{r}_i)\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{dip}}(\mathbf{r}_j)\,|\,n\mathbf{k}s\rangle+\text{c.c.}], \tag{7d}$$

where

$$B=[\epsilon_n(\mathbf{k}s)-\epsilon_{n'}(\mathbf{k}'s')]^{-1}.$$

In Eqs. (7) $\mathbf{r}_i$ describes the radius vector of an electron with respect to the nucleus i. These four equations give all possible contributions to the RK and PD interaction energies arising from the hyperfine Hamiltonian $\mathcal{H}$ given by (3) and (4). Physically, the various contributions to $\Delta^2E_{\mathrm{RK},k}$ and $\Delta^2E_{\mathrm{PD},i}$ can be described as follows. $\Delta^2E_{\mathrm{RK},1}$ results from the mutual magnetic polarization of the conduction electrons by the nuclei i and j through their contact interactions. After summing over the electronic orbital and spin states in (7a) one ends up with an interaction of the form (1). The energy $\Delta^2E_{\mathrm{RK},2}$ results from the polarization effects due to the electron-orbital interactions of nuclei i and j, while $\Delta^2E_{\mathrm{RK},3}$ arises from second-order effects due to the classical dipole-dipole interaction between the electron and nuclear spins. A similar second-order effect also contributes to the PD energy $\Delta^2E_{\mathrm{PD},2}$. The other type of PD coupling arises out of a combination of the contact interaction of nucleus i with the electron spins and the classical dipole interaction of the electron spins with nucleus j and vice versa. Following the manipulations of the second-order energies later in this section, it can be shown that no PD interaction between the nuclei can result from the mutual polarization of the conduction electrons by nuclear spin-electron orbit interactions.

The evaluation of the second-order energy terms in Eqs. (7a)–(7d) requires a knowledge of the Bloch functions $|\,n\mathbf{k}s\rangle=\psi_{n\mathbf{k}}(\mathbf{r})\,|\,s\rangle$ (where $|\,s\rangle=\alpha,\beta$ represents the spin state) for the conduction-electron states. We shall develop the algebra here for the OPW formalism. For the alkali metals of interest here, single OPW functions represent the Bloch functions very well. Thus, in common with the situation in other good metals[24] like beryllium, aluminium, and indium, one finds by actual calculation[19] with linear combination of OPW that the admixtures of higher OPW functions are rather small for alkali metals. For matrix elements involving the Fermi-contact interaction the algebra for many OPW is a simple extension of the case of single OPW. For the electron-nuclear dipole matrix elements, however, there is substantial simplification when one uses a single OPW. The extension to many OPW is straightforward following a procedure analogous to that presented here. Concerning the energy-band properties arising from the energy denominators we shall make use of the calculated band structure[19] in the many-OPW approximation.

We next proceed to the simplification of the relevant second-order energy expressions (7a)–(7d). The RK and PD coupling constants A_{ij} and B_{ij} can be obtained by reexpressing Δ^2E in the form of the spin Hamiltonian in Eqs. (1) and (2). For bookkeeping purposes we shall add superscripts (example A_{ij}^k, B_{ij}^k) to describe the various contributions to RK and PD coupling constants in Eqs. (7a)–(7d).

A. Derivation of Expression for A_{ij}^1

On substituting for h_i^{cont} from Eq. (4) in Eq. (7a) and using the periodic property of the Bloch functions which gives

$$\langle\mathbf{k}\,|\,f(\mathbf{r}-\mathbf{R})\,|\,\mathbf{k}'\rangle=\exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]\langle\mathbf{k}\,|\,f(\mathbf{r})\,|\,\mathbf{k}'\rangle,$$

we obtain

$$\begin{aligned}\Delta^2E_{\mathrm{RK},1}=\sum_{n\mathbf{k}s}\sum_{n'\mathbf{k}'s'}&B\{\exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}]\\&\times\langle n\mathbf{k}s\,|\,h_i^{\mathrm{cont}}(\mathbf{r})\,|\,n'\mathbf{k}'s'\rangle\langle n'\mathbf{k}'s'\,|\,h_j^{\mathrm{cont}}(\mathbf{r})\,|\,n\mathbf{k}s\rangle+\text{c.c.}\}.\end{aligned} \tag{8}$$

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[24] W. M. Shyu, Ph.D. thesis, University of California, Riverside, 1965 (unpublished); W. M. Shyu, G. D. Gaspari, and T. P. Das, Phys. Rev. **141**, 603 (1965); **152**, 270 (1966).

The spin summation in (8) is relatively simple and will be carried out first:

$$\sum_{ss'} \langle s \mid \mathbf{I}_i\cdot\mathbf{S} \mid s'\rangle\langle s' \mid \mathbf{I}_j\cdot\mathbf{S} \mid s\rangle = \tfrac{1}{2}\mathbf{I}_i\cdot\mathbf{I}_j. \qquad (9)$$

Replacing the sum over **k** and **k**′ in (8) by integrals and using Eq. (9) one obtains

$$A_{ij}{}^1 = \tfrac{1}{2}C \sum_{nn'} \int \frac{d^3k}{(2\pi)^3} \int \frac{d^3k'}{(2\pi)^3} \times \left[\frac{\Phi(n\mathbf{k}, n'\mathbf{k}')}{\epsilon_{n'}(\mathbf{k}') - \epsilon_n(\mathbf{k})} \exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}] + \text{c.c.} \right],$$

where

$$C = -(16\pi/3)^2 \gamma_i \gamma_j \gamma_e{}^2 \hbar^4, \qquad (10)$$

$$\Phi(n\mathbf{k}, n'\mathbf{k}') = \mid \psi_{n\mathbf{k}}(0) \mid^2 \mid \psi_{n'\mathbf{k}'}(0) \mid^2. \qquad (11)$$

As has been suggested by earlier authors,[3,4] in the spirit of the one-electron picture one can, to a very good approximation, ignore the effect of exclusion principle in the summation over excited states. As a result, the $n'\mathbf{k}'$ summation can be made to run over both the occupied and unoccupied regions of **k** space. In order to evaluate (10), we shall integrate over constant energy contours. Thus, instead of integrating over k, θ_k, φ_k, we shall use the variable ϵ, θ_k, φ_k, the value of ϵ defining a particular energy contour. Let us define a function $g(\theta_k, \varphi_k, \epsilon)$ such that

$$\begin{aligned} d^3\mathbf{k} &= k^2(\theta_k, \phi_k, \epsilon) \sin\theta_k d\theta_k d\phi_k (dk/d\epsilon) d\epsilon \\ &= g(\theta_k, \phi_k, \epsilon) d\epsilon d\theta_k d\phi_k. \end{aligned} \qquad (12)$$

Using Eq. (12), Eq. (10) can be rewritten as

$$A_{ij}{}^1 = \frac{1}{2} \frac{C}{(2\pi)^6} \int_0^{\epsilon_F} d\epsilon \int d\theta_k d\phi_k \int_0^\infty d\epsilon' \int d\theta_{k'} d\phi_{k'} \times \left[\frac{\Phi(k, k')}{\epsilon' - \epsilon} \exp(-i\{\mathbf{k}(\theta_k, \phi_k, \epsilon) - \mathbf{k}'(\theta_{k'}, \phi_{k'}, \epsilon')\}\cdot\mathbf{R}_{ij}) + \text{c.c.} \right] g(\theta_k, \phi_k, \epsilon) g(\theta_{k'}, \phi_{k'}, \epsilon'). \qquad (13)$$

We shall carry out the ϵ', $\theta_k{}'$, $\varphi_k{}'$ integration first. For convenience, we choose a coordinate axis system such that $\mathbf{R}_{ij}$ is along the z direction. In analogy with Ruderman and Kittel's procedure[3,4,8] it is convenient to analytically continue ϵ' to the complex energy plane E' and introduce a step function $\Theta(\text{Re}E')$ to avoid contributions from negative energy states. The integrations in (13) can be carried out in steps. Thus, the E', $\theta_k{}'$, $\varphi_k{}'$ part of the integral is given by

$$I(\epsilon) = \int_0^{2\pi} d\phi_{k'} \int_0^\pi d\theta_{k'} \left[\oint_c dE' \frac{\Phi(E', \epsilon)}{E' - \epsilon} \Theta(\text{Re}E') \times \exp[+ik'(\theta_{k'}, \phi_{k'}, E') R_{ij}\mu] g(\theta_{k'}, \phi_{k'}, E') \right], \qquad (14)$$

where $\mu = \cos\theta_k{}'$. Since μ can be both positive and negative when $\theta_k{}'$ goes from $0 \rightarrow \pi$, $\mu > 1$ represents an integration over a closed contour in the upper half of the E' plane while $\mu < 1$ refers to the lower half-plane. Introducing a quantity t in Eq. (14) such that

$$t = \pm 1 \quad \text{for} \quad \mu \gtrless 1,$$

one obtains

$$I(\epsilon) = i\pi \int_0^{2\pi} d\phi_{k'} \int_0^\pi d\theta_{k'} \Phi(\epsilon, \epsilon) t \Theta(\epsilon) \times \exp[ik'(\theta_{k'}, \phi_{k'}, \epsilon) R_{ij}\mu] g(\theta_{k'}, \phi_{k'}, \epsilon), \qquad (15)$$

where we have taken the principal value of the integral over E' in (14). Substituting (15) in Eq. (13) we get for the RK coupling constant

$$A_{ij}{}^1 = \frac{1}{2} \frac{C}{(2\pi)^6} \int_0^{\epsilon_F} d\epsilon \int_0^{2\pi} d\phi_k \int_0^\pi d\theta_k \times \{\exp[ik(\theta_k, \phi_k, \epsilon) R_{ij}\mu] I(\epsilon) g(\theta_k, \phi_k, \epsilon) t + \text{c.c.}\}, \qquad (16)$$

the upper limit of the integration over occupied energy states ϵ being ϵ_F. In principle, the angular integrations in both (15) and (16) can be evaluated from a knowledge of the constant energy contours, that is, of k as a function of θ_k, φ_k, and ϵ. For simplification, we shall use a spherical contour approximation so that k is only a function of ϵ, not necessarily parabolic. In the parabolic band approximation our result will reduce to Eq. (7) of Ref. 3. Thus, on substituting $k'(\epsilon, \theta_{k'}, \phi_{k'}) = k'(\epsilon)$ in (15), one can evaluate $I(\epsilon)$ quite easily and obtains

$$I(\epsilon) = (4\pi^2/R_{ij}) \Theta(\epsilon) \Phi(\epsilon, \epsilon) k(dk/d\epsilon) \cos(kR_{ij}). \qquad (17)$$

If one defines a k-dependent effective mass $m^*(k)$ such that

$$\epsilon(k) = k^2/m^*(k),$$

where $\epsilon(k)$ is in Rydbergs and $m^*(k)$ is in units of $2m_0$, then

$$k(dk/d\epsilon) = m^*(k)[2 - (k/m^*(k))(dm^*(k)/dk)]^{-1}.$$

Using a particular $\epsilon(k)$-versus-k relation of the form[15]

$$\epsilon(k) = E_2k^2 + E_{4,1}k^4 + E_{6,1}k^6 + \cdots, \qquad (18)$$

where E_2, E_{41}, and E_{61} have been obtained from band calculations,[19]

$$m^*(k) = [E_2 + 2E_{4,1}k^2 + 3E_{6,1}k^4]^{-1} \qquad (19)$$

and

$$k(dk/d\epsilon) = \tfrac{1}{2}m_t(k), \qquad (20)$$

where

$$m_t(k) = [E_2 + 2E_{4,1}k^2 + 3E_{6,1}k^4]^{-1}.$$

The quantity $m_t(k)$ is usually referred to as the thermal or density-of-states mass. Equation (17) can then be reexpressed in the form

$$I(\epsilon) = (2\pi^2/R_{ij}) \Theta(\epsilon) \Phi(\epsilon, \epsilon) m_t(\epsilon) \cos(kR_{ij}). \qquad (21)$$

Equation (21) holds for a general spherical band, which is typically expanded for a cubic lattice as in Eq.

(18). In the parabolic band approximation employed by Ruderman and Kittel and Bloembergen and Rowland, $m_t(\epsilon)=m^*$, from Eqs. (18) and (20), and is independent of ϵ and k. In the work of Roth, Zeiger, and Kaplan,[17] emphasis has been placed on contributions from some regions of special shape on the Fermi surface. For cases where the main contribution to A_{ij} arises from a small limited region of the Fermi surface one can replace $m_t(\epsilon)$ by its appropriate value in that region and this is equivalent to using the proper cyclotron mass in the expression for A_{ij}. For the alkali metals which are of main interest here, the Fermi surface is nearly spherical and Eq. (21) is adequate.

On substituting Eq. (21) in Eq. (16) and carrying out the integrations over θ_k and ϕ_k, one obtains

$$A_{ij}{}^1=\frac{1}{2}\frac{C}{(2\pi)^3R_{ij}{}^2}\int_0^{k_F} km_t(k)\Phi(k,k)\sin(2kR_{ij})dk. \quad (22)$$

If one makes use of the parabolic band approximation and also replaces $\Phi(k,k)$ by $\Phi(k_F,k_F)$, its value at the Fermi surface, Eq. (22) reduces to the result for A_{ij} obtained by Ruderman and Kittel[3] and Bloembergen and Rowland.[4] The consequence of the k dependence of the entire integrand in (22), in influencing the result for A_{ij}, is important and will be discussed in Sec. IV.

B. Derivation of Expressions for $B_{ij}{}^1$, $B_{ij}{}^2$, $A_{ij}{}^2$, $A_{ij}{}^3$

For the derivation of suitable expressions for $B_{ij}{}^1$ as well as for the other contributions to A_{ij} and B_{ij}, it is convenient to introduce some additional notation. The normalized OPW for a state with wave vector $\mathbf{k}$ is given by

$$\psi_{\mathbf{k}}(\mathbf{r})=A(\mathbf{k})\left[e^{i\mathbf{k}\cdot\mathbf{r}}-\sum_t b_t(\mathbf{k})\Phi_t(\mathbf{r})\right],$$

with

$$b_t(\mathbf{k})=\langle\Phi_t\mid e^{i\mathbf{k}\cdot\mathbf{r}}\rangle, \quad (23)$$

the sum $\sum_t$ running over all the occupied core states $\phi_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\theta,\phi)$. Using the spherical harmonic expansion for $e^{i\mathbf{k}\cdot\mathbf{r}}$, $\psi_{\mathbf{k}}(\mathbf{r})$ can be rewritten as

$$\psi_{\mathbf{k}}(\mathbf{r})=\sum_{lm}4\pi i^l\chi_l(k,r)Y_{lm}{}^*(\theta_k,\phi_k)Y_{lm}(\theta,\phi), \quad (24)$$

where

$$\chi_l(k,r)=A(k)\left[j_l(kr)-\sum_n I_{nl}(k)R_{nl}(r)\right]$$

and

$$I_{nl}(k)=\int_0^\infty R_{nl}(r)j_l(kr)r^2dr. \quad (25)$$

For easier manipulation, the operators $h^{\mathrm{cont}}(\mathbf{r})$ and $h^{\mathrm{dip}}(\mathbf{r})$ can be reexpressed in irreducible tensor-operator notation.[25]

$$h^{\mathrm{cont}}(\mathbf{r})=\tfrac{1}{3}(16\pi)\gamma_i\gamma_e\hbar^2\delta(\mathbf{r})\left[I_zS_z+\tfrac{1}{2}(I_+S_-+I_-S_+)\right]. \quad (26)$$

The Fermi-contact Hamiltonian $h^{\mathrm{cont}}(\mathbf{r})$ is expressed as a scalar product of two tensors of rank unity built out of the components of the vectors $\mathbf{I}$ and $\mathbf{S}$. Correspondingly, $h^{\mathrm{dip}}(\mathbf{r})$ is a scalar product of two tensors of second rank, one built out of the components of $\mathbf{r}$ alone and another out of the components of both $\mathbf{I}$ and $\mathbf{S}$:

$$h^{\mathrm{dip}}(\mathbf{r})=2\gamma_i\gamma_e\hbar^2\sum_m O_m{}^2(\mathbf{r},\mathbf{I},\mathbf{S}), \quad (27)$$

where

$$O_m{}^2(\mathbf{r},\mathbf{I},\mathbf{S})=C_{2m}O_m{}^2(\mathbf{r})O_{-m}{}^2(\mathbf{I},\mathbf{S}), \quad (28)$$

$$O_m{}^2(\mathbf{r})=(1/r^3)Y_{2m}(\theta,\phi), \quad (29)$$

and

$$O_0{}^2(\mathbf{I},\mathbf{S})=-2I_z\mathrm{S}_z+\tfrac{1}{2}(I_+\mathrm{S}_-+I_-\mathrm{S}_+),$$
$$O_{\pm1}{}^2(\mathbf{I},\mathbf{S})=-\tfrac{1}{2}(I_\pm\mathrm{S}_z+I_z\mathrm{S}_\pm),$$
$$O_{\pm2}{}^2(\mathbf{I},\mathbf{S})=-\tfrac{1}{4}(I_\pm\mathrm{S}_\pm). \quad (30)$$

The coefficients C_{2m} are

$$C_{20}=(4\pi/5)^{1/2},$$
$$C_{2\pm1}=\pm(24\pi/5)^{1/2},$$
$$C_{2\pm2}=(96\pi/5)^{1/2}. \quad (31)$$

We proceed next to the evaluation of $B_{ij}{}^1$. Substituting the expressions in (26) and (27) for $h^{\mathrm{cont}}(\mathbf{r})$ and $h^{\mathrm{dip}}(\mathbf{r})$ in Eq. (7b) and using the periodic property of the Bloch functions, one obtains

$$\Delta^2E_{\mathrm{PD},1}=2D\sum_{\mathbf{k}s}\sum_{\mathbf{k}s'}[\epsilon(\mathbf{k}'s')-\epsilon(\mathbf{k}s)]^{-1}$$
$$\times\{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}]\sum_m C_{2m}\langle\mathbf{k}\mid O_m{}^2(\mathbf{r})\mid\mathbf{k}'\rangle$$
$$\times\langle\mathbf{k}'\mid\delta(\mathbf{r}')\mid\mathbf{k}\rangle\langle s\mid O_{-m}{}^2(\mathbf{I}_i,\mathbf{S})\mid s'\rangle\langle s'\mid\mathbf{I}_j\cdot\mathbf{S}\mid s\rangle+\text{c.c.}\},$$

where

$$D=\tfrac{1}{3}(32\pi)\gamma_i\gamma_j\gamma_e{}^2\hbar^4 \quad (32)$$

and the factor of 2 outside the summation in (32) arises from the interchange of i and j. The spin summation in (32) can be readily carried out, leading to

$$\sum_{ss'}\langle s\mid O_{-m}{}^2(\mathbf{I}_i,\mathbf{S})\mid s'\rangle\langle s'\mid\mathbf{I}_j\cdot\mathbf{S}\mid s\rangle=\tfrac{1}{2}O_{-m}{}^2(\mathbf{I}_i,\mathbf{I}_j). \quad (33)$$

We shall again use spherical energy contours for carrying out the angular integrations over the directions of $\mathbf{k}$ and $\mathbf{k}'$. Equation (32) then reduces to the form

$$\Delta^2E_{\mathrm{PD},1}=\sum_m T_{ij}{}^1C_{2m}O_{-m}{}^2(\mathbf{I}_i,\mathbf{I}_j)O_m{}^2(\mathbf{R}_{ij}), \quad (34)$$

$$T_{ij}{}^1=R_{ij}{}^3\left(\frac{6D}{5\pi^3}\right)\int_e^{k_F}k^2dk\int_{k_F}^\infty k'^2dk'$$
$$\times\left[\sum_{l,l'}\frac{(i)^{l-l'}}{\epsilon(k')-\epsilon(k)}\Delta(ll'2)Q_{l',l}(k',k)j_l(kR_{ij})\right.$$
$$\left.\times j_{l'}(k'R_{ij})\psi_{\mathbf{k}}{}^*(0)\psi_{\mathbf{k}'}(0)+\text{c.c.}\right], \quad (35)$$

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[25] A. K. Saha and T. P. Das, *Theory and Applications of Nuclear Interaction* (Saha Institute of Nuclear Physics, Calcutta, India, 1957), p. 254.

where

$$Q_{l',l}(k',k)=\int \chi_{l'}(k',r)(1/r^3)\chi_l(k,r)r^2dr. \quad (36)$$

The functions $\chi_{l'}(k',r)$ are as defined in the expansion of OPW in Eq. (24). The factor $\Delta(l'lL)$ defines the usual triangular relationship[25] between the angular momenta l', l, and L. Using Eq. (2) for the definition of B_{ij} it follows that

$$B_{ij}^1=R_{ij}^{-3}T_{ij}^1.$$

It will be shown in Sec. IV that from the various combinations $(s\text{-}d)$, $(p\text{-}p)$, $(p\text{-}f)$, $\cdots$ arising out of different combinations of l' and l the dominant contribution comes from the $(p\text{-}p)$ term. The PD interaction thus provides a measure of the p-wave part of the conduction-electron wave functions. It should be remarked that had we not used a spherical Fermi surface for our integrations over θ_k and ϕ_k we would have obtained additional terms in the spin-Hamiltonian which are different in form from those in Eqs. (1) and (2). In view of the near-spherical nature of the Fermi surface in the alkali metals, such additional terms are insignificant in strength.

Before proceeding further, we shall derive expressions for B_{ij}^2, A_{ij}^2, and A_{ij}^3 corresponding to (35), since a common procedure for integration over $\mathbf{k}$ and $\mathbf{k}'$ can be used for all of them. Substitution of the tensor form of the dipolar interaction from Eq. (27) into Eq. (7d) and use of the periodicity property of Bloch functions yields

$$\Delta^2E_{\text{RK},3}+\Delta^2E_{\text{PD},2}=F\sum_{\mathbf{k},\mathbf{k}'}\sum_{m,m'}\bigg[C_{2m}C_{2m'}\langle\mathbf{k}\,|\,O_m^2(\mathbf{r})\,|\,\mathbf{k}'\rangle \times\langle\mathbf{k}'\,|\,O_{m'}^2(\mathbf{r})\,|\,\mathbf{k}\rangle\frac{\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{ij}]}{\epsilon(\mathbf{k})-\epsilon(\mathbf{k}')} \times\langle s\,|\,O_{-m}^2(\mathbf{I}_i,\mathbf{S})\,|\,s'\rangle\langle s'\,|\,O_{-m'}^2(\mathbf{I}_j,\mathbf{S})\,|\,s\rangle+\text{c.c.}\bigg], \quad (37)$$

where

$$F=4\gamma_i\gamma_j\gamma_e^2\hbar^4.$$

One can easily carry out the space integrations in (37), using the angular expansion of the OPW functions in (24), a typical space matrix element being

$$\langle\mathbf{k}\,|\,O_m^2(\mathbf{r})\,|\,\mathbf{k}'\rangle=(4\pi)^2\sum_{l_1m_1}\sum_{l_1'm_1'}(i)^{l_1'-l_1} \times Q_{l_1,l_1'}(k,k')(-1)^{m_1}\left[\frac{(2l_1+1)(2l_1'+1)}{4\pi}\right]^{1/2} \times\begin{pmatrix}l_1 & 2 & l_1'\\ m_1 & m & m_1'\end{pmatrix}\begin{pmatrix}l_1 & 2 & l_1'\\ 0 & 0 & 0\end{pmatrix}Y_{l_1m_1}(\theta_k,\phi_k) \times Y_{l_1'm_1'}{}^*(\theta_{k'},\phi_{k'}), \quad (38)$$

where the

$$\begin{pmatrix}l & l' & L\\ m & m' & M\end{pmatrix}$$

are the usual Wigner's $3j$ symbols. In carrying out the spin summation it is convenient to introduce the following notation:

$$\{\mathbf{I}_i,\mathbf{I}_j\}_{m,m'}=\sum_{s,s'}\langle s\,|\,O_m^2(\mathbf{I}_i,\mathbf{S})\,|\,s'\rangle\langle s'\,|\,O_{m'}^2(\mathbf{I}_j,\mathbf{S})\,|\,s\rangle. \quad (39)$$

Proceeding exactly as in the case of B_{ij}^1, that is, expanding $\exp[i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{ij}]$ in terms of spherical harmonics and carrying out the angular integrations in $\mathbf{k}$ and $\mathbf{k}'$ space, we obtain the following expression for the second-order energy in (37):

$$\Delta^2E_{\text{RK},3}+\Delta^2E_{\text{PD},2}=F\int_0^{k_F}\frac{k^2dk}{(2\pi)^3}\int_{k_F}^{\infty}\frac{k'^2dk'}{(2\pi)^3}\frac{\delta^2E(k',k)}{\epsilon(k)-\epsilon(k')}, \quad (40)$$

where

$$\delta^2E(k',k)=5(4\pi)^4\sum_{LM}\Bigg\{\left(\frac{2L+1}{4\pi}\right)^{1/2}\Bigg[\sum_{\substack{l_1m_1\\ l_1'm_1'}}\sum_{\substack{l_2m_2\\ l_2'm_2'}}\sum_{\substack{l_5m_5\\ l_6m_6}}\sum_{\substack{m\\ m'}}C_{2m}C_{2m'}\{\mathbf{I}_i,\mathbf{I}_j\}_{-m,-m'} \times(i)^{l_1'+l_2+l_6-l_1-l_2'-l_5}Q_{l_1,l_1'}(k,k')Q_{l_2',l_2}(k',k)\,j_{l_5}(kR_{ij})\,j_{l_6}(k'R_{ij}) \times(2l_1+1)(2l_2+1)(2l_1'+1)(2l_2'+1)(2l_5+1)(2l_6+1)(-1)^{m_5-m_1-m_2} \times\begin{pmatrix}l_1 & 2 & l_1'\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2' & 2 & l_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2 & l_1 & l_5\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2' & l_1' & l_6\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_5 & l_6 & L\\ 0 & 0 & 0\end{pmatrix} \times\begin{pmatrix}l_1 & 2 & l_1'\\ -m_1 & m & m_1'\end{pmatrix}\begin{pmatrix}l_2' & 2 & l_2\\ -m_2' & m' & m_2\end{pmatrix}\begin{pmatrix}l_2 & l_1 & l_5\\ -m_2 & m_1 & m_5\end{pmatrix}\begin{pmatrix}l_2' & l_1' & l_6\\ -m_2' & m_1' & m_6\end{pmatrix}\begin{pmatrix}l_5 & l_6 & L\\ -m_5 & m_6 & M\end{pmatrix}\Bigg]Y_{LM}{}^*(\mathbf{R}_{ij}) +\text{c.c.}\Bigg\}. \quad (41)$$

In order to obtain the contribution A_{ij}^3 to the RK interaction from this general expression we have to collect only the $L=M=0$ terms in (41) and for the PD term B_{ij}^2 we have to consider only the $L=2$ term. Because of the complexities of the algebra we present only the p-wave contributions here arising out of the terms involving $l_1=l_1'=l_2=l_2'=1$ in (41). Contributions from s-d, p-f, and other such terms (see Table II) are much smaller in magnitude for the alkali metals, as in the case of B_{ij}^1. There will now be two contributions to A_{ij}^3 arising from $l_5=l_6=0$ and $l_5=l_6=2$ leading to

$$A_{ij}^3=\mathrm{I}A+\mathrm{II}A, \tag{42}$$

$$\mathrm{I}A=-F\frac{24}{5\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_0(kR_{ij})j_0(k'R_{ij})+\text{c.c.}], \tag{43a}$$

$$\mathrm{II}A=-F\frac{24}{25\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_2(kR_{ij})j_2(k'R_{ij})+\text{c.c.}]. \tag{43b}$$

For the case of PD coupling B_{ij}^2 one has $L=2$, and by inspection only the (0, 2), (2, 0), and (2, 2) combinations of (l_5, l_6) are seen to contribute. After some manipulations involving products of $3j$ symbols, the final expressions come out in the proper tensor interaction form (2) and one obtains

$$B_{ij}^2=\mathrm{I}B+\mathrm{II}B+\mathrm{III}B, \tag{44}$$

where

$$\mathrm{I}B=-F\frac{42}{25\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_0(kR_{ij})j_2(k'R_{ij})+\text{c.c.}], \tag{45a}$$

$$\mathrm{II}B=-F\frac{42}{25\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_2(kR_{ij})j_0(k'R_{ij})+\text{c.c.}], \tag{45b}$$

$$\mathrm{III}B=-F\frac{4}{35\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_2(kR_{ij})j_2(k'R_{ij})+\text{c.c.}]. \tag{45c}$$

Finally, we derive the contribution to A_{ij}^2 from the effect of nuclear spin-electron-orbital current interaction, given in Eq. (7c). The operator $\mathbf{I}\cdot\mathbf{L}$ can be reexpressed as

$$\mathbf{I}\cdot\mathbf{L}=I_zL_z+\tfrac{1}{2}(I_+L_-+I_-L_+).$$

The spin summation in (7c) gives a factor of 2 and the angular integration proceeds exactly as for B_{ij}^1. Retaining only the contribution from the p-p mode,

$$A_{ij}^2=\mathrm{IV}A+\mathrm{V}A, \tag{46}$$

where

$$\mathrm{IV}A=-F\frac{16}{\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_0(kR_{ij})j_0(k'R_{ij})+\text{c.c.}] \tag{47a}$$

and

$$\mathrm{V}A=F\frac{16}{\pi^2}\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times[Q_{1,1}^2(k,k')j_2(kR_{ij})j_2(k'R_{ij})+\text{c.c.}]. \tag{47b}$$

In order to obtain the final results for the coupling constants one has to carry out the k and k' integrations in (35), (43), (45), and (47). As has been pointed out earlier one can ignore the effects of the exclusion principle in the excited states.

For convenience of notation we introduce the following integrals:

$$T(l,l')=\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times Q_{1,1}^2(k,k')j_l(kR_{ij})j_{l'}(k'R_{ij}) \tag{48}$$

and

$$S(l,l')=\int_0^{k_F}k^2dk\int_{k_F}^{\infty}\frac{k'^2dk'}{\epsilon(k')-\epsilon(k)}\times Q_{l,l'}(k',k)j_l(kR_{ij})j_{l'}(k'R_{ij})\Psi_k^*(0)\Psi_{k'}(0). \tag{49}$$

Only a few $T(l, l')$ and $S(l, l')$ for specific values of l and l' occur in the expression for B_{ij}^k and A_{ij}^k. One can carry out the integrations in (49) in an exactly similar manner as was done for A_{ij}^1 by taking principal values in the contour integrations over the complex energy plane. One then obtains

$$T(0,0)=\frac{\pi}{4R_{ij}^2}\int_0^{k_F}m_t(k)Q_{1,1}^2(k,k)k\sin(2kR_{ij})dk, \tag{50a}$$

$$T(2,2)=\frac{\pi}{2R_{ij}^3}\int_0^{k_F}m_t(k)Q_{1,1}^2(k,k)\times[(3-k^2R_{ij}^2)\cos(kR_{ij})+3kR_{ij}\sin(kR_{ij})]\times j_2(kR_{ij})dk, \tag{50b}$$

$$T(0,2)=\frac{\pi}{2R_{ij}^3}\int_0^{k_F}m_t(k)Q_{1,1}^2(k,k)\times[(3-k^2R_{ij}^2)\cos(kR_{ij})+3kR_{ij}\sin(kR_{ij})]j_0(kR_{ij})dk, \tag{50c}$$

$$T(2,0)=\frac{\pi}{2R_{ij}}\int_0^{k_F}k^2m_t(k)Q_{1,1}^2(k,k)j_2(kR_{ij})\times\cos(kR_{ij})dk, \tag{50d}$$

and

$$S(1,1)=\frac{\pi}{2R_{ij}^2}\int_0^{k_F}km_t(k)\mid\psi_k(0)\mid^2Q_{1,1}(k,k)\times[\cos(kR_{ij})+kR_{ij}\sin(kR_{ij})]\times[\sin(kR_{ij})-kR_{ij}\cos kR_{ij}](k^2R_{ij}^2)^{-1}dk, \tag{50e}$$

where k_F is the value of k associated with ϵ_F from Eq. (18). The remaining integrations over k in Eqs. (50) have to be performed numerically. Equation (50e) is equivalent to the expression (49) of Bloembergen and Rowland,[4] except that they used the Bardeen approximation[15] for the wave functions and had an error in the first square brackets of the phase factor in (50e), namely, a negative sign in front of $kR_{ij}\sin kR_{ij}$. A quantitative comparison of our results with this approximation will be made in Sec. IV.

Finally, for ready reference, we list the expressions for A_{ij}^2, A_{ij}^3, B_{ij}^1, and B_{ij}^2 in terms of the pertinent $T(l,l')$ and $S(l,l')$.

$$A_{ij}^2=-2F[(16/\pi^2)T(0,0)-(16/\pi^2)T(2,2)],$$

$$A_{ij}^3=-2F[(24/5\pi^2)T(0,0)+(24/25\pi^2)T(2,2)],$$

$$B_{ij}^1=D[(12/5\pi^3)S(1,1)],$$

$$B_{ij}^2=-F[(42/25\pi^2)(T(0,2)+T(2,0))+(4/35\pi^2)T(2,2)]. \tag{51}$$

III. EXCHANGE AND CORRELATION CONTRIBUTION TO RK INTERACTION

In this section, we shall study the effects of correlation and exchange among conduction electrons on the indirect coupling between nuclei. We shall specialize to the case of the dominant mechanism for RK interaction, namely A_{ij}^1, but from the nature and magnitude of the exchange and correlation corrections for this case one can make certain conclusions regarding the importance of such corrections for other coupling mechanisms. In addition, the treatment adopted here for A_{ij}^1 can be easily adapted to the indirect coupling between localized electron moments and nuclei and between localized moments in metals. To retain the generality of the procedure, we shall write the contact interaction in the form

$$h_i^{\text{cont}}(l)=\lambda_i\mathbf{I}_i\cdot\mathbf{S}_l f(\mathbf{r}_l-\mathbf{R}_i), \tag{52}$$

which encompasses both conduction-electron nuclear-moment and conduction-electron localized-electron-moment interactions. Using Eq. (52), the second-order energy in (7a) can be rewritten as

$$\Delta^2E_{\text{RK},1}=\sum_{\mathbf{k}s}\sum_{\mathbf{k}'s'}\left[\frac{\langle\mathbf{k}s\,|\,\lambda_i f(\mathbf{r}-\mathbf{R}_i)\mathbf{I}_i\cdot\mathbf{S}\,|\,\mathbf{k}'s'\rangle\langle\mathbf{k}'s'\,|\,\lambda_j f(\mathbf{r}-\mathbf{R}_j)\mathbf{I}_j\cdot\mathbf{S}\,|\,\mathbf{k}s\rangle}{\epsilon(\mathbf{k}s)-\epsilon(\mathbf{k}'s')}+\text{c.c.}\right]. \tag{53}$$

In analyzing the effects of exchange and correlation among the conduction electrons on the energy $\Delta^2E_{\text{RK},1}$, it is convenient to regard the contact interaction as resulting from the magnetic field $\sim\lambda_i f(\mathbf{r}-\mathbf{R}_i)\mathbf{I}_i$ due to the ith nuclear moment at the position of the electron spin. In this respect the problem is similar to that of the exchange enhancement of the magnetic susceptibility of conduction electrons in the presence of an external field, which has been studied by various authors[21,26] using the random-phase approximation. In the present problem, the magnetic field produced by the nucleus is not uniform. It is therefore more appropriate to Fourier analyze the field and study the effects of exchange and correlation on $\chi(\mathbf{q})$. One then Fourier transforms back into real space to obtain the correction to $\Delta^2E_{\text{RK},1}$. It should be remarked that the self-consistent perturbation treatment to be employed here and used by previous authors for susceptibility is somewhat analogous to the Hartree-Fock perturbation formulation developed by Dalgarno and others[27] for atomic polarization problems.

It is convenient to rewrite (53) as

$$\Delta^2E_{\text{RK},1}=\langle\delta\Psi_{(i)}^{(1)}\,|\,\mathcal{H}_{\text{pert}}^{j}\,|\,\Psi^{(0)}\rangle+\text{c.c.}, \tag{54}$$

where Ψ^0 is the zero-order determinantal function for the electrons, $\delta\Psi_{(i)}^{(1)}$ is the first-order perturbation in the wave function due to nucleus i, and $\mathcal{H}_{\text{pert}}^{(j)}$ is the perturbing potential due to nucleus j.

$$\mathcal{H}_{\text{pert}}(\mathbf{R}_i)=\sum_l h_i^{\text{cont}}(l). \tag{55}$$

The summation over l runs over all the conduction electrons. On Fourier analyzing the perturbation, $\mathcal{H}_{\text{pert}}(\mathbf{R}_i)$ can be rewritten as

$$\begin{aligned}\mathcal{H}_{\text{pert}}(\mathbf{R}_i)&=\sum_{\mathbf{q}}\mathcal{H}_{\text{pert}}(\mathbf{q},\mathbf{R}_i)\\&=\sum_{\mathbf{q}}\lambda_i f(\mathbf{q})\mathbf{I}_i\cdot\sum_l\exp(i\mathbf{q}\cdot\mathbf{r}_l)\mathbf{S}_l'\\&\qquad\times\exp(-i\mathbf{q}\cdot\mathbf{R}_i).\end{aligned} \tag{56}$$

For the time being we will suppress the index i. The various $\mathbf{q}$ components of the perturbation will be treated independently since one can show that up to second order there is no interference between different $\mathbf{q}$ components. In the absence of the external perturbation $h_{\text{pert}}(\mathbf{q})$, the one-particle Hartree-Fock equation for the conduction electron in the state $|\,\mathbf{k}s\rangle$ is given by

$$[h^0+O_k^0+C^0]\Psi_{\mathbf{k}s}^0=\epsilon_{\mathbf{k}s}\Psi_{\mathbf{k}s}^0, \tag{57}$$

where h^0 includes the kinetic energy operator and the contribution of the core electrons and nuclei to the single-particle potential. The operators O_k^0 and C_0

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[26] A. K. Rajagopal and S. D. Mahanti, Phys. Rev. **158**, 353 (1967).

[27] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1962); P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. **44**, 505 (1965).

describe the unperturbed exchange and Coulomb potentials arising from the conduction electrons and are as follows:

$$O_{\mathbf{k}}{}^{0}\phi_{\mathbf{k}t}(\mathbf{r})=-\sum_{\mathbf{k}'s'}{}' e^{2}\int \psi_{\mathbf{k}'s'}{}^{0*}(\mathbf{r}')\phi_{\mathbf{k}t}(\mathbf{r}')\times g(\mathbf{r},\mathbf{r}')\psi_{\mathbf{k}'s'}{}^{0}(\mathbf{r})\,d\mathbf{r}' \qquad (58)$$

and

$$C^{0}\phi_{\mathbf{k}t}(\mathbf{r})=\sum_{\mathbf{k}'s'} e^{2}\int |\psi_{\mathbf{k}'s'}(\mathbf{r}')|^{2}g(\mathbf{r},\mathbf{r}')\phi_{\mathbf{k}t}(\mathbf{r})\,d\mathbf{r}', \qquad (59)$$

where the primed summation in (58) is over only the parallel spin states and $g(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$. In our calculation, we shall neglect the effect of the magnetic field on the core-conduction one-electron potential since the magnetic field is too weak to excite the strongly bound core electrons. The exchange and Coulomb operators $O_k{}^0$ and C^0, being state-dependent, will themselves change in the presence of the perturbation. Assuming that the perturbed one-electron states are orthogonal, the Schrödinger equation for the first-order perturbed electronic states can be shown to be

$$[h^{0}+h_{\text{pert}}(\mathbf{q})+O_{\mathbf{k}}(\mathbf{q})+C(\mathbf{q})]\psi_{\mathbf{k}s}(\mathbf{q})=\epsilon_{\mathbf{k}s}(\mathbf{q})\psi_{\mathbf{k}s}(\mathbf{q}), \qquad (60)$$

where O_k and C are given by Eqs. (58) and (59) but with $\psi_{\mathbf{k}s}{}^0$ replaced by $\psi_{\mathbf{k}s}$. It should be noted that in contrast to $\psi_{\mathbf{k}s}{}^0$, $\psi_{\mathbf{k}s}$ can be a mixed spin state. For cubic metals, the RK interaction is isotropic and it turns out that one can derive $A_{ij}{}^1$ from $\Delta^2E_{\text{RK},1}$ in Eq. (53), using any of the terms $I_{i\mu}\mathbf{S}_\mu$ ($\mu=x, y, z$) in the perturbation. For the sake of simplicity we shall use $\mu=x$, in which case the perturbed one-electron wave functions can be written as

$$\psi_{\mathbf{k}s}(\mathbf{q})=\psi_{\mathbf{k}s}{}^{0}+\delta\psi_{\mathbf{k}s}(\mathbf{q}), \qquad (61)$$

$\delta\psi_{\mathbf{k}s}(\mathbf{q})$ having a spin opposite to $\psi_{ks}{}^0$. The exchange and Coulomb operators O_k and C can be separated into zero-order and first-order parts:

$$O_{\mathbf{k}}(\mathbf{q})=O_{\mathbf{k}}{}^{0}+\delta O_{\mathbf{k}}(\mathbf{q}),$$
$$C(\mathbf{q})=C^{0}+\delta C(\mathbf{q}). \qquad (62)$$

One can then lump $\delta O_{\mathbf{k}}$ and δC with $h_{\text{pert}}(\mathbf{q})$ and regard them as additional self-consistency perturbations with $\delta O_{\mathbf{k}}(\mathbf{q})$ and $\delta C(\mathbf{q})$ given by

$$\delta O_{\mathbf{k}}(\mathbf{q})\varphi_{\mathbf{k}t}(\mathbf{r})=-e^{2}\sum_{\mathbf{k}''s''}\int[\delta\psi_{\mathbf{k}''s''}(\mathbf{q},\mathbf{r})\psi_{\mathbf{k}''s''}{}^{0*}(\mathbf{r}')+\delta\psi_{\mathbf{k}''s''}{}^{*}(\mathbf{q},\mathbf{r}')\psi_{\mathbf{k}''s''}{}^{0}(\mathbf{r})]g(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}t}(\mathbf{r}')\,d\mathbf{r}' \qquad (63)$$

and

$$\delta C(\mathbf{q})\varphi_{\mathbf{k}t}(\mathbf{r})=e^{2}\sum_{\mathbf{k}''s''}\int[\delta\psi_{\mathbf{k}''s''}{}^{*}(\mathbf{q},\mathbf{r}')\psi_{\mathbf{k}''s''}(\mathbf{r}')+\delta\psi_{\mathbf{k}''s''}(\mathbf{q},\mathbf{r}')\psi_{\mathbf{k}''s''}{}^{*}(\mathbf{r}')]g(\mathbf{r},\mathbf{r}')\varphi_{\mathbf{k}t}(\mathbf{r})\,d\mathbf{r}', \qquad (64)$$

integrations over spin states being implied. Since $\delta\psi_{\mathbf{k}''\mathbf{s}''}$ has opposite spin from $\psi_{k''s''}{}^0$ it follows from (64) that $\delta C(\mathbf{q})=0$. We shall therefore work with the effective one-electron perturbation Hamiltonian

$$h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})=h_{\text{pert}}(\mathbf{q})+\delta O_{\mathbf{k}}(\mathbf{q}),$$

where

$$h_{\text{pert}}(\mathbf{q})\equiv h_{\text{pert}}(\mathbf{q},\mathbf{R}_i)=\tfrac{1}{2}\lambda_i f(\mathbf{q})\,\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{R}_i)]I_{ix}\sigma_x. \qquad (65)$$

For calculating $\Delta^2E_{\text{RK},1}$ as given by Eq. (54), but using

$$\mathcal{H}_{\text{pert}}{}^{\text{eff}}=\sum_{\mathbf{q}}h_{\text{pert}}{}^{\text{eff}}(\mathbf{q},\mathbf{R}_i), \qquad (66)$$

it is convenient to express the Bloch orbitals in the form

$$\psi_{\mathbf{k}\alpha}{}^{0}(\mathbf{r})=\sum_{n}a(\mathbf{k}+\mathbf{K}_n)\,\exp[i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}]\,|\alpha\rangle, \qquad (67)$$

where the sum runs over the reciprocal-lattice vectors. In the presence of the $h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})$, the perturbation in the one-particle state $\psi_{k\alpha}{}^0$ is given by $\delta\psi_{\mathbf{k}\alpha}$, where

$$\delta\psi_{\mathbf{k}\alpha}=\psi_{\mathbf{k}\alpha}-\psi_{\mathbf{k}\alpha}{}^{0}=\sum_{\mathbf{k}'}\frac{\langle\langle\mathbf{k}'\beta\,|\,h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})\,|\,\mathbf{k}\alpha\rangle\rangle}{\epsilon(\mathbf{k},\alpha)-\epsilon(\mathbf{k}',\beta)}\,{}_{\mathbf{k}}\psi'{}_{\beta}{}^{0}. \qquad (68)$$

Here we have only included the nondiagonal terms in the spin space because of the specific choice of the nuclear spin orientation (I_{ix}). The notation $\langle\langle\ \rangle\rangle$ indicates matrix elements over Bloch states as distinct from $\langle\ \rangle$ for plane-wave states. The perturbed wave function is normalized to first order since the perturbation correction to the normalization is of second order. On substituting (67) in (68), we get

$$\delta\psi_{\mathbf{k}\alpha}=\sum_{\mathbf{k}'nn'}a^{*}(\mathbf{k}'+\mathbf{K}_{n'})a(\mathbf{k}+\mathbf{K}_n)\times\frac{\langle\mathbf{k}'+\mathbf{K}_{n'},\beta\,|\,h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})\,|\,\mathbf{k}+\mathbf{K}_n,\alpha\rangle}{\epsilon(\mathbf{k},\alpha)-\epsilon(\mathbf{k}',\beta)}\psi_{\mathbf{k}'\beta}{}^{0}.$$

Using the expression for $h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})$, the orthogonal properties of plane-wave states, and redefining $\mathbf{K}_n-\mathbf{K}_{n'}=\mathbf{G}$, which is another reciprocal-lattice vector, $\delta\psi_{\mathbf{k}\alpha}$ takes the form

$$\delta\psi_{\mathbf{k}\alpha}=\sum_{n\mathbf{G}}a^{*}(\mathbf{k}+\mathbf{q}+\mathbf{K}_n)a(\mathbf{k}+\mathbf{K}_n)\times\frac{\langle\mathbf{k}+\mathbf{K}_n+\mathbf{q},\beta\,|\,h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})\,|\,\mathbf{k}+\mathbf{K}_n,\alpha\rangle}{\epsilon(\mathbf{k},\alpha)-\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G},\beta)}\psi_{\mathbf{k}+\mathbf{q}+\mathbf{G},\beta}{}^{0}. \qquad (69)$$

We shall handle the contributions to $\delta\psi_{\mathbf{k}\alpha}$ due to the external and exchange perturbation parts of $h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})$ separately. Using Eq. (63) for the exchange perturbation and some algebraic manipulations, one obtains for the off-diagonal matrix elements of this operator over plane-wave basis states,

$$\langle \mathbf{k}+\mathbf{K}_n+\mathbf{q},\beta \,|\, h_{\text{pert}}{}^{\text{exch}}(\mathbf{q}) \,|\, \mathbf{k}+\mathbf{K}_n,\alpha\rangle = \sum_{\mathbf{k}'',\mathbf{K}n'} \langle \mathbf{k}''+\mathbf{K}_{n'}+\mathbf{q},\beta \,|\, h_{\text{pert}}{}^{\text{eff}}(\mathbf{q}) \,|\, \mathbf{k}''+K_{n'},\alpha\rangle$$

$$\times\left[\sum_{\mathbf{G}} \frac{a^*(\mathbf{k}''+\mathbf{K}_{n'}+\mathbf{q})\,a(\mathbf{k}''+\mathbf{K}_{n'})}{\epsilon(\mathbf{k}'')-\epsilon(\mathbf{k}''+\mathbf{q}+\mathbf{G})} M(\mathbf{k},\mathbf{q},\mathbf{k}'';\mathbf{G},K_n)\right.$$

$$\left. +\sum_{\mathbf{G}} \frac{a(\mathbf{k}''+\mathbf{K}_{n'}+\mathbf{q})\,a^*(\mathbf{k}''+\mathbf{K}_{n'})}{\epsilon(\mathbf{k}'')-\epsilon(\mathbf{k}''+\mathbf{q}+\mathbf{G})} M^*(\mathbf{k}-\mathbf{q},-\mathbf{q};\mathbf{k}'',\mathbf{G},\mathbf{K}_n)\right], \quad (70)$$

where

$$M(\mathbf{k},\mathbf{q},\mathbf{k}'';\mathbf{G},\mathbf{K}_n) = \langle \mathbf{k}+K_n+\mathbf{q} \,|\, \psi_{\mathbf{k}''+\mathbf{q}+\mathbf{G}}{}^0(\mathbf{r}')\,g(\mathbf{r},\mathbf{r}')\,\psi_{\mathbf{k}''}{}^{0*}(\mathbf{r}) \,|\, \mathbf{k}+K_n\rangle. \quad (71)$$

On adding the matrix element of $h_{\text{pert}}(\mathbf{q})$ to both sides of Eq. (70) one obtains the integral equation

$$L_{\mathbf{K}_n}(\mathbf{k},\mathbf{q}) = f(\mathbf{q}) + \sum_{\mathbf{k}'',\mathbf{K}n'} \mathfrak{M}_{K_n,K_n'}{}^{\mathbf{q}}(\mathbf{k},\mathbf{k}'')\,L_{\mathbf{K}_{n'}}(\mathbf{k}'',\mathbf{q}) \quad (72)$$

for

$$L_{\mathbf{K}_n}(\mathbf{k},\mathbf{q}) = \langle \mathbf{k}+\mathbf{K}_n+\mathbf{q},\beta \,|\, h_{\text{pert}}{}^{\text{eff}}(\mathbf{q}) \,|\, \mathbf{k}+\mathbf{K}_n,\alpha\rangle. \quad (73)$$

In the matrix element for $L_{\mathbf{K}_n}(\mathbf{k},\mathbf{q})$, given by Eq. (73), the factor $\frac{1}{2}\lambda_i\mathbf{I}_i \exp(-i\mathbf{q}\cdot\mathbf{R})$ has been taken out from $h_{\text{pert}}{}^{\text{eff}}(\mathbf{q})$. The kernel of the integral Eq. (72) is related to $M(\mathbf{k},\mathbf{q},\mathbf{k}'',\mathbf{G},\mathbf{K}_n)$ of Eq. (71) by the relation

$$\mathfrak{M}_{\mathbf{K}_n,\mathbf{K}_n'}{}^{\mathbf{q}} = \sum_{\mathbf{G}} \frac{a(\mathbf{k}''+\mathbf{K}_n+\mathbf{q})\,a^*(\mathbf{k}''+\mathbf{K}_{n'})}{\epsilon(\mathbf{k}'')-\epsilon(\mathbf{k}''+\mathbf{q}+\mathbf{G})}$$

$$\times M(\mathbf{k},\mathbf{q},\mathbf{k}'',\mathbf{G},\mathbf{K}_n) + \text{the other term.} \quad (74)$$

It is to be noted that the matrix elements for both $h_{\text{pert}}{}^{\text{eff}}$ and $h_{\text{pert}}{}^{\text{exch}}$ are independent of the spin of the initial state; this is why no spin indices are introduced in $L_{\mathbf{K}_n}(\mathbf{k},\mathbf{q})$. The effect of correlation can be incorporated by screening the Fourier transform of the Coulomb potential by the RPA dielectric constant.[16] One thus has to solve the integral Eq. (72) for the self-consistent-field screened-exchange model in order to obtain the requisite perturbed one-electron states and the second-order energy. Equation (72) represents a generalization of Hamann and Overhauser's[21] procedure for the case of Bloch electrons within the framework of the screened-exchange model. They have, however, presented a more rigorous treatment of correlation effects for free electrons using Landau Fermi-liquid theory.

The solution of the Eq. (72) for a general Bloch function is a rather formidable task. Since we are interested only in estimating the importance of exchange and correlation effects as corrections to the one-electron theory result of Sec. II, we shall be content with an evaluation of these effects appropriate to a free-electron model. This is equivalent to dropping terms associated with all nonzero reciprocal-lattice vectors $\mathbf{K}_n$, $\mathbf{K}_{n'}$, and $\mathbf{G}$ in Eqs. (72) and (74). One might remark that this is not a very serious approximation for alkali metals since they are quite free-electron-like outside of the volume occupied by the core electrons. This latter volume is only a small fraction of the volume of the Wigner-Seitz cell. With this approximation, Eq. (72) reduces to

$$L(\mathbf{k},\mathbf{q}) = f(\mathbf{q}) + \sum_{\mathbf{k}''} \mathfrak{M}^{\mathbf{q}}(\mathbf{k},\mathbf{k}'')\,L(\mathbf{k}'',\mathbf{q}), \quad (75)$$

where

$$\mathfrak{M}^{\mathbf{q}}(\mathbf{k},\mathbf{k}'') = \left[\frac{1}{\epsilon(\mathbf{k}'')-\epsilon(\mathbf{k}''+\mathbf{q})}\right.$$

$$\times\langle \mathbf{k}+\mathbf{q} \,|\, \exp[-i(\mathbf{k}''+\mathbf{q})\cdot\mathbf{r}']\exp(i\mathbf{k}''\cdot\mathbf{r})\,g(\mathbf{r},\mathbf{r}') \,|\, \mathbf{k}\rangle$$

$$+\frac{1}{\epsilon(\mathbf{k}'')-\epsilon(\mathbf{k}''+\mathbf{q})}$$

$$\times\langle \mathbf{k}+\mathbf{q} \,|\, \exp(-i\mathbf{k}''\cdot\mathbf{r})\exp[i(\mathbf{k}''+\mathbf{q})\cdot\mathbf{r}']\,g(\mathbf{r},\mathbf{r}') \,|\, \mathbf{k}\rangle. \quad (76)$$

Equation (71) has been utilized in obtaining Eq. (76).

The integral equation (75) reduces to an algebraic equation if we neglect the $\mathbf{k}$ dependence of $L(\mathbf{k},\mathbf{q})$. One can then write

$$L(\mathbf{q}) = f(\mathbf{q})/[1-F(\mathbf{q})], \quad (77)$$

where

$$F(\mathbf{q}) = \sum_{\mathbf{k}''} \mathfrak{M}^{\mathbf{q}}(\mathbf{k},\mathbf{k}'') \quad (78)$$

depends parametrically on $\mathbf{k}$. Since most of the electrons taking part in the differential response to the external field are those near the Fermi surface, one can evaluate $F(\mathbf{q})$ for $\mathbf{k}$ near the Fermi surface and consider it essentially $\mathbf{k}$-independent, in accordance with the assumed $\mathbf{k}$ independence of $L(\mathbf{k},\mathbf{q})$. The enhancement factor in (77) depends sensitively upon the choice of the screening parameter used for screening the potential. Three different types of screening[26] have been utilized. Thomas-Fermi and self-consistent-type screening do not give rise to any appreciable enhancement. On the other hand, a screening parameter obtained from plasma-cutoff considerations gives values of the enhancement factors for various **q** which are in reasonable agreement with the results of Hamann and Overhauser,[21] who have solved the integral Eq. (75) numerically.

The function $L(\mathbf{q})$ in (77) represents the analog of the one-electron function $f(\mathbf{q})$ after inclusion of screened exchange. We shall next use $L(\mathbf{q})$ to compute the total second-order energy and hence the correction to $A_{ij}{}^1$. Summing over the contributions from all **q** components, the net first-order change in the one-electron wave function is given by

$$\delta\psi_{\mathbf{k}\alpha}{}^{(i)}(\mathbf{r}) = -\sum_{\mathbf{q},\mathbf{G}} \frac{f(\mathbf{q})}{1-F(\mathbf{q})} \times \frac{\langle\langle \mathbf{k}+\mathbf{q} \mid \exp(i\mathbf{q}\cdot\mathbf{r}-\mathbf{R}_i) \mid \mathbf{k}\rangle\rangle^*}{\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G})-\epsilon(\mathbf{k})} \psi_{\mathbf{k}+\mathbf{q}+\mathbf{G},\beta}{}^0(\mathbf{r}). \tag{79}$$

From the second-order energy expression in Eq. (54) we get

$$\Delta^2 E_{\mathrm{RK},1} = \sum_{\mathbf{k}s} [\langle \delta\psi_{\mathbf{k}s}{}^{(i)} \mid h_{\mathrm{pert}}(\mathbf{r}_j) \mid \psi_{\mathbf{k}s}{}^0\rangle + \mathrm{c.c.}], \tag{80}$$

where $\delta\psi_{\mathbf{k}s}{}^{(i)}$ in (80) arises from the hyperfine effect of nucleus i. On substituting for $\delta\psi_{k\alpha}$ in (80)

$$\Delta^2 E_{\mathrm{RK},1} = -\sum_{\mathbf{k}s} \sum_{\mathbf{q}s'} \sum_{\mathbf{G}} \left[\frac{1}{1-F(\mathbf{q})} \langle \mathbf{k}+\mathbf{q}, s' \mid h_{\mathrm{pert}}(\mathbf{q}, \mathbf{R}_i) \mid \mathbf{k}s\rangle \times \langle\langle \mathbf{k}+\mathbf{q} \mid e^{i\mathbf{q}\cdot\mathbf{r}} \mid \mathbf{k}\rangle\rangle \frac{\langle\langle \mathbf{k}+\mathbf{q}+\mathbf{G}, s' \mid h_{\mathrm{pert}}(\mathbf{r}_j) \mid \mathbf{k}s\rangle\rangle}{\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G})-\epsilon(\mathbf{k})} + \mathrm{c.c.} \right]. \tag{81}$$

On making the substitution

$$1/[1-F(\mathbf{q})] = F(\mathbf{q})/[1-F(\mathbf{q})]+1$$

and using the identity

$$\sum_{\mathbf{k}'} \frac{\langle\langle \mathbf{k}' \mid B(\mathbf{r}) \mid \mathbf{k}\rangle\rangle}{\epsilon(\mathbf{k})-\epsilon(\mathbf{k}')} \psi_{\mathbf{k}'}{}^0(\mathbf{r}) = \sum_{\mathbf{G}\mathbf{q}} \frac{\langle \mathbf{k}+\mathbf{q} \mid B(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}} \mid \mathbf{k}\rangle \langle\langle \mathbf{k}+\mathbf{q} \mid e^{i\mathbf{q}\cdot\mathbf{r}} \mid \mathbf{k}\rangle\rangle}{\epsilon(\mathbf{k})-\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G})} \psi_{\mathbf{k}+\mathbf{q}+\mathbf{G}'}{}^0(\mathbf{r}),$$

one obtains

$$\Delta^2 E_{\mathrm{RK},1} = \Delta^2 E_{\mathrm{RK},1}{}^0 + \Delta^2 E_{\mathrm{RK},1}{}^{\mathrm{corr}},$$

where

$$\Delta^2 E_{\mathrm{RK},1}{}^0 = -\sum_{\mathbf{k}s} \sum_{\mathbf{k}'s'} \left[\frac{\langle\langle \mathbf{k}s \mid h_{\mathrm{pert}}(\mathbf{r}_i) \mid \mathbf{k}'s'\rangle\rangle \langle\langle \mathbf{k}'s' \mid h_{\mathrm{pert}}(\mathbf{r}_j) \mid \mathbf{k}s\rangle\rangle}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k})} + \mathrm{c.c.} \right] \tag{82}$$

and

$$\Delta^2 E_{\mathrm{RK},1}{}^{\mathrm{corr}} = -\sum_{\mathbf{k}s} \sum_{\mathbf{q}s'} \sum_{\mathbf{G}} \left[\frac{F(\mathbf{q})}{1-F(\mathbf{q})} \langle\langle \mathbf{k}+\mathbf{q} \mid e^{i\mathbf{q}\cdot\mathbf{r}} \mid \mathbf{k}\rangle\rangle \times \langle \mathbf{k}+\mathbf{q}, s' \mid h_{\mathrm{pert}}(\mathbf{q}, \mathbf{R}_i) \mid \mathbf{k}s\rangle \frac{\langle\langle \mathbf{k}+\mathbf{q}+\mathbf{G}, s' \mid h_{\mathrm{pert}}(\mathbf{r}_j) \mid \mathbf{k}s\rangle\rangle}{\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G})-\epsilon(\mathbf{k})} + \mathrm{c.c.} \right]. \tag{83}$$

Thus $\Delta^2 E_{\mathrm{RK},1}$ is now separated into two parts. One part, $\Delta^2 E_{\mathrm{RK},1}{}^0$, is the one-electron contribution in (82) that has been considered already in Sec. II. The other part, $\Delta^2 E_{\mathrm{RK},1}{}^{\mathrm{corr}}$, is the result of the susceptibility enhancement from exchange and correlation effects as described by the function $F(\mathbf{q})/[1-F(\mathbf{q})]$. The rest of this section will deal with the evaluation of $\Delta^2 E_{\mathrm{RK},1}{}^{\mathrm{corr}}$ in (83).

There are two main parts to the calculation of $\Delta^2 E_{\mathrm{RK},1}{}^{\mathrm{corr}}$. The first is the evaluation of the function responsible for the enhancement, namely $F(\mathbf{q})$, and secondly, that of finding suitable methods for carrying out the integrations and reciprocal-lattice summation in Eq. (83). We consider the evaluation of $F(\mathbf{q})$ first. One notices from Eq. (76) that the limit $\mathbf{q}\rightarrow 0$ has to be handled specially because of singularities in $\mathfrak{M}^{\mathbf{q}}(\mathbf{k}, \mathbf{k}'')$. One way to avoid this difficulty is to use a stationary perturbation $\cos(\mathbf{q}\cdot\mathbf{r})$ rather than $e^{i\mathbf{q}\cdot\mathbf{r}}$. On making this replacement in (76) and carrying out the necessary integration, one gets

$$F(0) = \lim_{\mathbf{q}\rightarrow 0} \frac{8\pi}{2} \sum_{\mathbf{k}''} \left[\frac{1}{\epsilon(\mathbf{k}''+\mathbf{q})-\epsilon(\mathbf{k}'')} \frac{1}{|\mathbf{k}-\mathbf{k}''|^2} + \frac{1}{\epsilon(\mathbf{k}''-\mathbf{q})-\epsilon(\mathbf{k}'')} \frac{1}{|\mathbf{k}+\mathbf{q}-\mathbf{k}''|^2} \right]. \tag{84}$$

For evaluating $F(\mathbf{q})$ no special precaution is necessary and one can make direct use of Eqs. (76) and (78), which lead to

$$F(\mathbf{q}) = 8\pi \sum_{\mathbf{k}''} \frac{1}{\epsilon(\mathbf{k}''+\mathbf{q})-\epsilon(\mathbf{k}'')} \frac{1}{|\mathbf{k}-\mathbf{k}''|^2}. \tag{85}$$

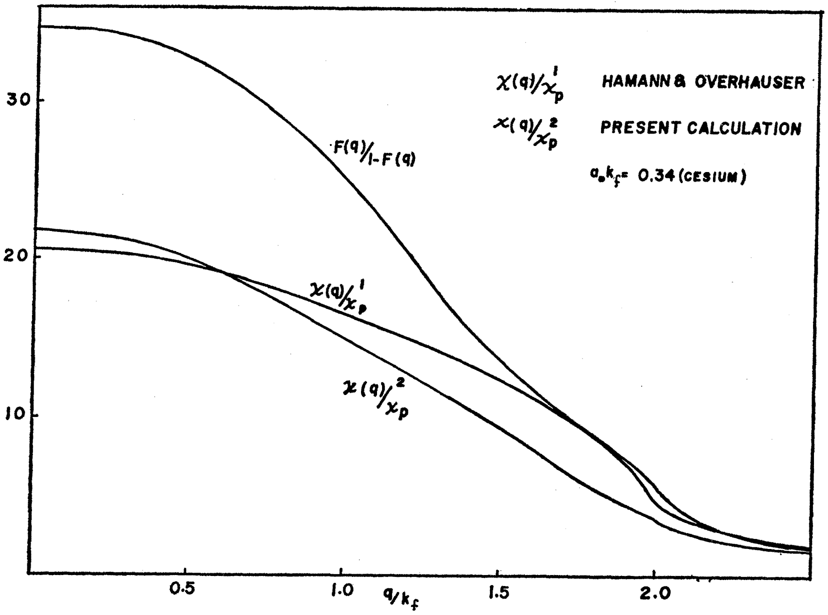

FIG. 1. Dependence of the enhancement factor $F(q)/[1-F(q)]$ due to correlation on q in cesium. Also plotted is $\chi(q)/\chi_{\rm Pauli}$, with corresponding values of Hamann and Overhauser.

At this stage one can introduce the effects of correlation using the screened-exchange approximation, which is equivalent to replacing

$$1/|\mathbf{k}-\mathbf{k}''|^2 \quad \text{by} \quad 1/(|\mathbf{k}-\mathbf{k}''|^2+\xi^2k_F^2)$$

in the Fourier component of the potential, being a suitably chosen screening parameter. It is well known that the Thomas-Fermi screening overestimates the correlation effect and cuts off the potential much too sharply. As a matter of fact, this particular choice of the screening does not lead to a paramagnetic instability for $r_s \sim 10$. Another possibility is to choose the screening parameter from plasma cutoff considerations, $\xi_{\rm cutoff}$ being given by

$$\alpha r_s/\pi = \xi_{\rm cutoff}^2[(\xi_{\rm cutoff}+2)\ln(\xi_{\rm cutoff}+2/\xi_{\rm cutoff})-2]^{-1}, \tag{86}$$

where

$$\alpha = 0.521.$$

A detailed description of this type of screening has been given by Rajagopal and Mahanti.[26] For this particular type of screening, $\chi(0)$ shows an instability at $r_s = 10.93$, which is reasonably close to the value obtained by Hamman and Overhauser[21] by solving the requisite integral equation in the self-consistent field approximation. This indicates that the prescription for $\xi_{\rm cutoff}$ in Eq. (86) is a reasonable one. For densities appropriate to rubidium and cesium, namely, $r_s = 5.289$ and 5.640, respectively, one gets from Eq. (86) $\xi_{\rm Rb} = 1.0484$ and $\xi_{\rm Cs} = 1.0728$.

With the screened-exchange approximation and replacing the summation in (85) by integration over the Fermi volume, one gets, using an effective-mass approximation for simplicity,

$$F(\mathbf{q}) = \frac{m^*}{\pi^2}\int_0^{k_F} \frac{k''^2dk''d\Omega_{\mathbf{k}}''}{(q^2+2\mathbf{q}\cdot\mathbf{k}'')\{|\mathbf{k}-\mathbf{k}''|^2+\xi^2k_F^2\}}. \tag{87}$$

The reduction of $F(0)$ as given by (84) requires a more careful consideration. The summations are now best carried out by introducing Fermi functions to take care of the occupied $\mathbf{k}$ space and extend the limits of integration to infinity. This procedure, along with suitable expansions for Fermi functions for small q, leads to

$$F(0) = -\frac{m^*}{\pi k_F}\,\tfrac{1}{4}\ln\left|\frac{(k-k_F)^2+\xi^2k_F^2}{(k+k_F)^2+\xi^2k_F^2}\right|. \tag{88}$$

To carry out the angular integration in (87) we first remind ourselves that according to our earlier approximations we are only interested in a spherical average of $F(\mathbf{q})$ over directions of $\mathbf{k}$ and also with $k = k_F$. Carrying out the averaging procedure first simplifies the integration over $d\Omega_{\mathbf{k}}''$ and leads to

$$F(\mathbf{q}) = -\frac{m^*}{4\pi qk_F}\int_0^{k_F} dk''\ln\left|\frac{q+2k''}{q-2k''}\right| \times \ln\left|\frac{(k_F-k'')^2+\xi^2k_F^2}{(k_F+k'')^2+\xi^2k_F^2}\right|. \tag{89}$$

$F(0)$ and $F(q)$ have been numerically computed for various values of r_s. In Fig. 1 we present our calculated enhancement factor $F(q)/[1-F(q)]$ as a function of q for a value of r_s appropriate to cesium. In Fig. 2, $1/[1-F(0)]$ is plotted as a function of r_s. In both figures, comparable results of Hammann and Overhauser[21] are presented for reference. The agreement between our results and theirs justifies the validity of the screened-exchange approximation.

We shall next consider the summations in Eq. (83) for $\Delta^2E_{\rm RK,1}{}^{\rm corr}$. Equation (83) is quite general and applies to any type of indirect interaction, between nuclei, localized moments, and between nuclei and localized moments with the proper substitutions for

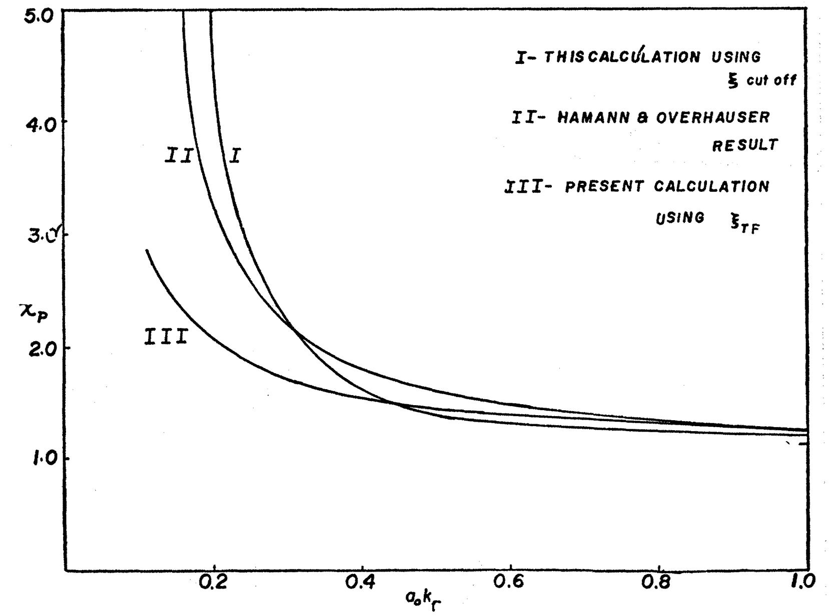

FIG. 2. Calculated Fermi-momentum dependence of $1/[1-F(0)]$ for different screening parameters, compared with Hamann and Overhauser's results (Ref. 21).

λ_{ij} and $f(\mathbf{r}-\mathbf{R}_j)$ in the expression (52) for $h_{\text{pert}}(\mathbf{r}_j)$. We shall now specialize to our case of interest, namely, the RK interaction between nuclei, making the requisite substitutions for $h_{\text{pert}}(\mathbf{r}_j)$ from (4). With this step and replacing the summation over $\mathbf{k}'$ by $\mathbf{q}'=\mathbf{k}'-\mathbf{k}$, Eq. (83) reduces to

$$A_{ij}^{\text{corr}}=\tfrac{1}{2}C\sum_{\mathbf{kqG}}\frac{F(\mathbf{q})}{1-F(\mathbf{q})}\left[\frac{\langle\langle\mathbf{k}+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,\mathbf{k}\rangle\rangle}{\epsilon(\mathbf{k}+\mathbf{q}+\mathbf{G})-\epsilon(\mathbf{k})}\right.$$
$$\left.\times\psi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^{*}(0)\psi_{\mathbf{k}}(0)\exp(-i\mathbf{q}\cdot R_{ij})+\text{c.c.}\right],\quad(90)$$

where C is defined in Eq. (10).

The exact evaluation of A_{ij}^{corr} in (90) is a rather formidable task because it involves a triple summation over three variables $\mathbf{k}$, $\mathbf{q}$, and $\mathbf{G}$. In fact, it involves an integration over nine variables corresponding to the magnitudes and directions of three vectors. We have made a reasonable estimate of the results to be expected from the summations by examining the sensitiveness of the dependence of the summands on the variables involved. The following sequence of approximations has been made:

(1) The matrix element $\langle\langle\mathbf{k}+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,\mathbf{k}\rangle\rangle$ has been replaced by its value at $\mathbf{k}=\mathbf{k}_F$. This is justified because this matrix element, which would be unity for plane waves, varies only about 2% for OPW functions inside the Fermi volume.

(2) The quantity $\psi_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^{*}(0)\psi_{\mathbf{k}}(0)$ has been replaced by $\psi_{\mathbf{k}_F+\mathbf{q}+\mathbf{G}}^{*}(0)\psi_{\mathbf{k}_F}(0)$, with $\mathbf{k}_F$ taken along the (111) direction. This approximation was based on the observation that the dependence of this quantity on the magnitude and direction of $\mathbf{k}$ was rather slight in the process of carrying out the other summations and integrations involved.

(3) The dependence of the integrand, except for the phase factor $\exp(-i\mathbf{q}\cdot\mathbf{R}_{ij})$ on the direction of $\mathbf{q}$, was found to be weak by testing with three directions (111), (110), and (100) for $\mathbf{q}$. With these approximations and carrying out the integration over angles of $\mathbf{k}$ in the denominator one obtains

$$A_{ij}^{\text{corr}}=\tfrac{1}{2}Cm^{*}\frac{1}{(2\pi)^5}\int_0^\infty q^2dq\,d\Omega_q\left[\frac{F(q)}{1-F(q)}\exp(-i\mathbf{q}\cdot R_{12})\right.$$
$$\left.\times\sum T(k_F,|\,\mathbf{q}+\mathbf{G}\,|)I(|\,\mathbf{q}+\mathbf{G}\,|,k_F)+\text{c.c.}\right],\quad(91)$$

where

$$I(|\,\mathbf{q}+\mathbf{G}\,|,k_F)=\int_0^{k_F}\frac{k^2dk}{2k\,|\,\mathbf{q}+\mathbf{G}\,|}\ln\frac{|\,\mathbf{q}+\mathbf{G}\,|+2k}{|\,\mathbf{q}+\mathbf{G}\,|-2k}$$
$$=\tfrac{1}{4}k_F\left[1+(2X)^{-1}(1-X^2)\ln\left|\frac{1+X}{1-X}\right|\right],$$
$$X=\frac{|\,\mathbf{q}+\mathbf{G}\,|}{2k_F},\quad(92)$$

and

$$T(k_F,|\,\mathbf{q}+\mathbf{G}\,|)$$
$$=\langle\langle\mathbf{k}+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,\mathbf{k}\rangle\rangle_{\text{Av}}[\Psi_{\mathbf{k}_F+\mathbf{q}+\mathbf{G}}(0)\Psi_{\mathbf{k}_F}(0)]_{\text{av}}.$$

Next the summation in $\mathbf{G}$ was performed over the first 228 reciprocal-lattice vectors. The convergence in $\mathbf{G}$ was quite good, primarily because of the decrease in $\Psi_{\mathbf{k}_F+\mathbf{q}+\mathbf{G}}(0)$ for large values of $\mathbf{k}_F+\mathbf{q}+\mathbf{G}$. For brevity we define

$$B(k_F,q)=\sum_{\mathbf{G}}\Psi_{k_F+|\mathbf{q}+\mathbf{G}|}(0)I(k_F,|\,\mathbf{q}+\mathbf{G}\,|),\quad(93)$$

where a separate summation has to be carried out for

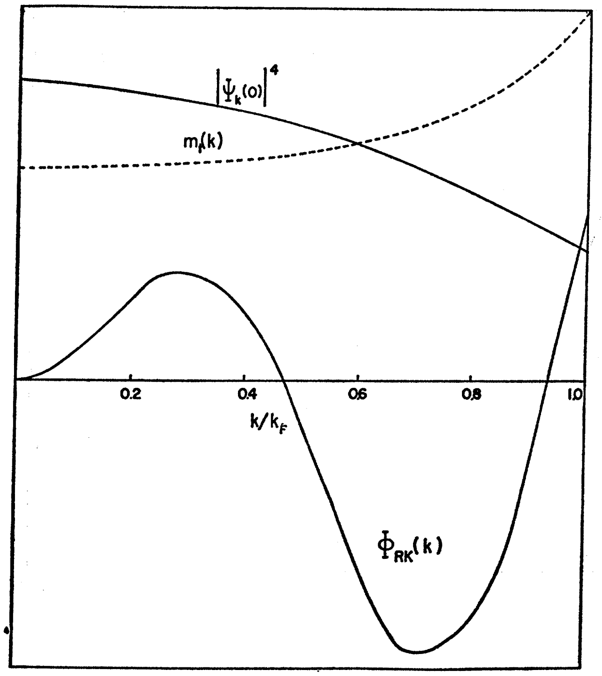

FIG. 3. Variation of $|\psi_k(0)|^4$, thermal mass $m_t(k)$, and phase factor $\Phi_{\rm RK}(k)$ with k for RK interaction in cesium.

each value of **q**. Finally, integrating over **q**, Eq. (91) reduces to

$$A_{ij}{}^{\rm corr}=\frac{c}{(2\pi)^4}\,2m^*\Psi_{k_F}(0)\,(R_{ij})^{-1}\int_0^\infty\frac{qF(q)}{1-F(q)}$$
$$\times[B(k_F,q)\,\sin(qR_{ij})\,\langle\langle\mathbf{k}_F+\mathbf{q}\,|\,e^{i\mathbf{q}\cdot\mathbf{r}}\,|\,k_F\rangle\rangle+\text{c.c.}]dq. \tag{94}$$

The evaluation of $A_{ij}{}^{\rm corr}$ from (94) has been carried out numerically and the results will be discussed in the next section.

IV. RESULTS AND DISCUSSION

The results of our calculations will be analyzed in two steps. First, we shall study the relative importance of various contributions to A_{ij} and B_{ij} for which expressions have been derived in Secs. II and III. Such an analysis enables one to make a critical evaluation of earlier calculations[3,4,12] as well as a general assessment of the relative importance of the different contributing factors. Information of this type should be helpful in channeling efforts towards only the most important contributions in future calculations on other metals. The second step in the analysis concerns the comparison of our results with experiment. The nature of the agreement between theory and experiment for A_{ij} and B_{ij} will be utilized for assessing both the correctness of electronic wave functions and the importance of effects which have not been taken into account in our calculation. In particular, we shall be interested in information on the influence of relativistic and exchange polarization effects on A_{ij} and B_{ij}.

A. RK Coupling Constant A_{ij}

We first consider the one-electron results for A_{ij} based on Eqs. (22), (46), and (42) for $A_{ij}{}^1$, $A_{ij}{}^2$, and $A_{ij}{}^3$, respectively, derived in Sec. II. The principle contribution to A_{ij} comes from $A_{ij}{}^1$, which arises out of the contact interactions alone. It is instructive to first study the k dependence of the various terms in the integrand of Eq. (22). In Fig. 3, the different functions $|\psi_k(0)|^4$, $m_t(k)$ and the phase factor $\Phi_{\rm RK}(k)=k\sin(2kR_{ij})$ are all plotted as functions of k, for the case of cesium. Core wave functions required in the construction of the OPW functions $\psi_{\mathbf{k}}(\mathbf{r})$ were taken from both Hartree-Fock[28] and Hartree-Fock-Slater[28] calculations for cesium atom. The values of $\psi_{\mathbf{k}}(0)$ for the two cases were very close to each other, indicating that the results would not be too different if one had available and made use of actual core-electron wave functions in the metal. The value of $\psi_k(0)$ varies from 51.49 $a_0{}^{-3/2}$ for $k=0$ to 41.82 $a_0{}^{-3/2}$ for $k=k_F$, a 20% change. The decrease in $|\psi_k(0)|^4$ is considerably more magnified, namely about 55%. The phase factor $\Phi_{\rm RK}$ also shows drastic variation in the range $k=0$ to k_F and in particular it changes sign at $k=0.5k_F$ and $0.9k_F$. Such a behavior produces a significant cancellation between the contributions to $A_{ij}{}^1$ arising from the regions $k<0.5k_F$ and $0.5k_F<k<0.9k_F$. The thermal mass $m_t(k)$, defined in Eq. (20), also shows sizeable variation in the range $0<k<k_F$. In particular, it varies from 0.73 m at $k=0$ to 1.32 m at $k=k_F$. In view of these rather drastic variations of all the three k-dependent factors that occur in the expression for $A_{ij}{}^1$, the replacement of $m_t\phi(k,k)$ in (22) by its value at k_F can be rather inaccurate.[3,12]

The rapid variation of the various contributory factors to A_{ij} with k should lead to a sensitive depend-

TABLE I. Contributions to A_{ij} in cycles.

	Cesium	Rubidium
$A_{ij}{}^1$	115.00	20.58
$A_{ij}{}^2$	2.55	0.42
$A_{ij}{}^3$	4.0×10^{-4}	1.7×10^{-3}
$A_{ij}{}^{\rm corr}$	7.10	1.73
A_{ij} (total)	124.65	22.73
A_{ij} (experiment)	200±10	51±5
A_{ij} (approximate)[a]	97.92	19.34

[a] This row gives the value obtained by making an approximation similar to Ruderman and Kittel (Ref. 3) but using actual wave functions.

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[28] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963); T. L. Gilbert (private communication); We thank Dr. Gilbert for making the Hartree-Fock wave function for Cs and Rb available. These were calculated using a program written by Dr. C. Froese Fisher.

ence of A_{ij} on the dimensions of the Fermi surface. One would therefore expect to see important variations in A_{ij} with external factors which distort the Fermi surface, such as applied pressure or alloying. No such data are currently available for A_{ij} but they should be accessible to measurement with either steady-state[12] or echo techniques.[14] A sensitive k dependence, analogous to what has been found here, has also been obtained for the coupling between localized moments in transition metals by Watson and Freeman.[29]

In Table I, the contributions to A_{ij} for cesium and rubidium from both A_{ij}^1 as well as A_{ij}^2 and A_{ij}^3 are listed together with our total A_{ij}, experiment, and the value that would be obtained by the RK-like approximation of using the Fermi-surface result. The contribution A_{ij}^2 arising from second-order effects of the orbital interactions is seen to be smaller than A_{ij}^1 by two orders of magnitude. This is understandable because A_{ij}^1 arises from the predominant s density of the electronic wave function while A_{ij}^2 is obtained from the p and higher components of the wave function which can only contribute through the $\langle 1/r^3\rangle$ term. The tensor-tensor contribution A_{ij}^3 is about five orders of magnitude smaller than A_{ij}^1 and three orders smaller than A_{ij}^2. A_{ij}^3 also arises from the non-s components of the wave function; its smallness with respect to A_{ij}^2 is due to the cancellation of two terms in (51) arising from the phase factor $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}]$. Similar factors for A_{ij}^2, on the other hand, interfere constructively. Correlation corrections have not been applied to A_{ij}^2 and A_{ij}^3 because their magnitudes are rather small.

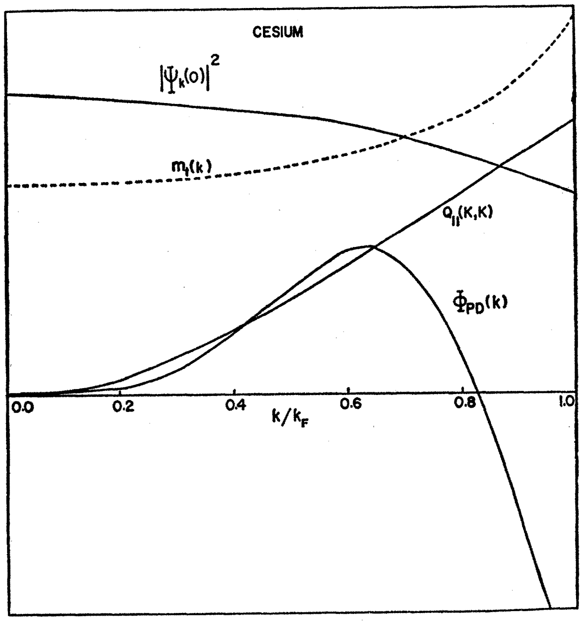

FIG. 4. Variation of $|\psi_k(0)|^2$, $Q_{11}(k,k)$, thermal mass $m_t(k)$, and phase factor $\Phi_{PD}(k,k)$ with k for PD interaction in cesium, indicating the sensitive k dependence of integrand in Eq. (50e).

TABLE II. Dependence of $Q_{l,l'}(k,k)$ on l and l' in cesium.[a]

k in units of k_F	$Q_{02}(k,k)$ (sd)	$Q_{11}(k,k)$ (pp)	$Q_{13}(k,k)$ (pf)
0.0	0.0	0.0	0.0
0.25	0.1253	3.8183	0.0475
0.50	0.0993	13.2928	0.0410
0.75	0.0831	25.8087	0.0378
1.0	0.0640	37.6198	0.0353

[a] Results for $Q_{ll'}$ are in atomic units (α_0^{-3}).

The correction factors for A_{ij}^1 are found to be respectively 6.2 and 9.9% for cesium and rubidium from numerical computations using Eq. (94) together with effective masses $m^*=1.32$ (cesium) and 1.24 (rubidium). By virtue of the various approximations made in deriving (94), some uncertainty is expected in these correction factors. However, even an overconservative estimate of a factor of 2 for the uncertainty would still make these corrections less than 15% of the one-electron results. The smallness of the correlation enhancement factor as compared to that for uniform fields ($\mathbf{q}=0$) can be understood from Fig. 1 for $F(q)/[1-F(q)]$. The Fourier spectrum of $\delta(\mathbf{r}-\mathbf{R}_i)$, namely $f(\mathbf{q})$ in (56), is a white spectrum which leads to an integration of $\mathbf{q}$ over all values from 0 to ∞ in Eq. (94). Since $F(q)/[1-F(q)]$ falls off rapidly for large values of q, the correction factor to A_{ij}^1 turns out to be small. The one-electron value of A_{ij} for cesium in Table I obtained from Eq. (22) using the predicted variations of different factors with k' in Fig. 4 is to be compared with the value 97.92 that one obtains using a parabolic band approximation ($m^*\equiv m_t=0.91$) and replacing $\Phi(k,k)$ in Eq. (22) by $\Phi(k_F,k_F)$. This was the approximation proposed by Ruderman and Kittel.[3] The smaller approximate value can be understood from Fig. 3, since $|\psi_k(0)|^4$ decreases continually from $k=0$ to k_F; however, Poitrenaud,[12] using the Fermi-surface approximation, has obtained a value of 214 cycles, which is fortuitously close to the experimental value. Here large theoretical value is the combined result of using $m^*=0.89$ and the arbitrary approximation $\psi_{k_F}^2(0)=\psi_{at}^2(0)\Omega$, where $\psi_{at}^2(0)$ is the density at the nucleus for the free cesium atom and Ω is the volume of the Wigner-Seitz cell. This approximation overestimates the density at the nucleus by a factor of about 1.7 and would also lead to a gross overestimation of the Knight shift.[30] A discussion of the reasons for disagreement between our value and experiment will be made after presenting the results on PD interaction. All features of the results for cesium metal seem to apply to rubidium as well, as seen from Table I.

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[29] R. E. Watson and A. J. Freeman, Phys. Rev. **152**, 566 (1966).

[30] Analysis of the Knight shift will be given in a subsequent paper dealing with the band structure of cesium.

TABLE III. Contributions to B_{ij} in cycles.

	Cesium	Rubidium
B_{ij}^1	2.07	0.36
B_{ij}^2	0.26	0.04
B_{ij} (total)	2.33	0.40
B_{ij} (experiment)	35.00	11.80
B_{ij} (approximate)[a]	12.96	2.42

[a] This row gives the result of an approximation similar to Bloembergen and Rowland (Ref. 4) but using calculated OPW functions.

B. PD Interaction

In calculating B_{ij}^1, one obtains contributions from the l and l' components of the wave function, where $l=l'\pm 2$, and l', the latter possibility being excluded for $l=l'=0$. One can label such contributions as (ll') terms. Thus one can get contributions from (pp), (pf), $(sd)\cdots$terms. From Table II, it can be seen that the pp term is by far the major contributor to $Q_{ll'}(kk')$, the contributions decreasing rapidly as l and l' increase. Such a behavior can be understood by examining the various l components of the wave functions, the p part starting from zero at $k=0$ and rapidly increasing as one approaches k_F. The d part also starts with zero value at $k=0$ but increases much more slowly in approaching $k=k_F$. One can thus obtain a fair estimate of $Q_{ll'}(kk')$ by keeping only the p-p contribution.

The PD interaction B_{ij}^1 has a much stronger k dependence than A_{ij}. Part of the reason for this sensitive dependence is due to the stronger variation of $Q_{11}(k,k)$ with k than is the case for $|\psi_k(0)|^2$. Thus for the case of cesium, Q_{11} starts out with a zero value at $k=0$ and increases to 37 at $k=k_F$. In addition, there is now a much more sensitive cancellation between positive and negative contributions to B_{ij}^1 from different regions of k than was the case for A_{ij}^1. The phase factor, $\Phi_{\mathrm{PD}}=k(\cos kR_{ij}+kR_{ij}\sin kR_{ij})x(\sin kR_{ij}-kR_{ij}\cos kR_{ij})/(kR_{ij})^2$ is positive over a large region $k=0$ to $0.812k_F$ and negative over the remainder of the Fermi radius. While the product of $Q_{11}(k,k)$ and $|\psi_k(0)|^2$ in the integrand has smaller values over the positive phase factor region, the larger extent of this region overwhelms the negative region and leads to the positive result listed in Table III. Because of this sensitive cancellation effect, a small change in k_F by external means can have a more drastic change on B_{ij}. Another consequence of the rapid variation with k in the case of B_{ij}^1 is that one now makes a much larger error by replacing[4] the integrand in Eq. (50e) (except for Φ_{PD}), by its value at $k=k_F$. Thus, in Table III, such an average approximation is seen to lead to a value about four times larger than the actual theoretical value obtained by k integration. The relative largeness of the approximate value of B_{ij}^1 can be understood from Fig. 4 by noticing that the Fermi-surface average overestimates the positive value of the integrand in regions of small k.

The tensor-tensor contribution B_{ij}^2 to B_{ij} has been obtained by a numerical evaluation of the requisite equation in (51). From Table III, this contribution is seen to be an order of magnitude smaller than B_{ij}^1. This order of smallness is to be compared to the even larger order of smallness ($\sim 10^{-5}$) for A_{ij}^3 as compared to A_{ij}^1. The larger ratio for the PD case occurs because B_{ij}^1 involves the combined effects of s and p characters while B_{ij}^2 involves p character alone (the contributions from higher l components is again small). This is in contrast to the case of RK interaction where A_{ij}^3 involves only p character, whereas A_{ij}^1 involves only s character. One might remark here that in transition metals where higher non-s orbital components, particularly d character, can predominate, the contributions A_{ij}^1 and B_{ij}^1 will be expected to be comparatively less predominant than other contributions which depend strongly on non-s components. We have not made any estimates of exchange and correlation corrections for B_{ij}^1. However, the general procedure to be followed is the same as for the RK case, the only modification is that wherever $f(\mathbf{r}-\mathbf{R})$ refers to dipolar interaction it has to be replaced by $(3\cos^2\theta_i-1)/r_i^3$. The spectrum for the Fourier components is now no longer a white spectrum as it was for $\delta(\mathbf{r}-\mathbf{R}_i)$ but it should still be quite broad because of the localized nature of the interaction. We therefore expect a similar or perhaps slightly stronger enhancement than for the RK interaction. Using a factor of 10% for the enhancement, our theoretical value from Table III comes out as 2.56 cycles for cesium. The features of the PD interaction in rubidium are closely analogous to those in cesium, except that the contribution to the variation in B_{ij} due to $m_t(k)$ is now less pronounced because of the more parabolic nature of the Fermi surface. A similar comment also applies to the A_{ij} results in rubidium.

We next turn our attention to comparison with experiment. From the results in Table I, the theoretical values of A_{ij} are seen to be about 60% of experiment for cesium and 50% for rubidium. On the other hand, from Table III, the theoretical values of B_{ij} are an order of magnitude smaller than experimental ones. There are primarily two sources of error which could influence the theoretical results. First, there are those connected with approximations adopted in the process of our calculation. Secondly, there are some additional causes which have not been considered in the present work. In considering the former source, it is convenient to discuss A_{ij} and B_{ij} separately.

In the construction of OPW functions, one should use crystal-core wave functions rather than atomic ones. However, the difference between the atomic- and metallic-core wave functions can at best be comparable to that between Hartree-Fock-Slater and

Hartree-Fock atomic wave functions. Since, as mentioned earlier in this section, only a rather small ($\sim 3\%$) difference in A_{ij} was found with these two types of core wave functions, one does not expect the error due to the use of atomic core functions instead of actual ones to amount to more than 3%. A possibly more important source of error within the framework of our calculation is the use of one-OPW instead of a linear combination of such functions. However, calculations[24,31] in beryllium, aluminum, and indium indicate that a one-OPW representation is reasonably adequate for the conduction-electron wave function. Furthermore it has been found[19] from band-structure calculations for cesium that admixture of higher OPW's is rather small. Thus the amplitude $C_{|\mathbf{k}+\mathbf{K}|}$ is less than 6% for the higher OPW, with $|\mathbf{k}+\mathbf{K}|$ nearest to the reduced vector and rapidly decreases for increasing **K**. It can be shown that $\psi_k(0)$ falls off rapidly beyond $k=k_F$. Since the magnitude of the nearest **K** vector will be of the order of $2k_F$, the many-OPW correction will be quite small, due to the smallness of both $C_{|\mathbf{k}+\mathbf{K}|}$ and $\psi_{|\mathbf{k}+\mathbf{K}|}(0)$.

In the case of B_{ij}, we are concerned with both s and p characters of the conduction-electron wave function. The choice of atomic p cores again is not expected to affect the p character of OPW function significantly. This point was again confirmed from tests with Hartree-Fock and Hartree-Fock-Slater cores. The effect of including higher OPW functions could be different in this case than for A_{ij}. The amplitude factor is, of course, similar in nature. The variation of $Q_{1,1}(k,k)$, on the other hand, is somewhat different in nature than $\psi_k^2(0)$. Thus $Q_{1,1}(k,k)$ keeps increasing beyond $1.5k_F$, where it is about 30% larger than at k_F. For $k>1.5k_F$, the function $Q_{1,1}(k,k)$ falls off rapidly and is quite small beyond $k=3k_F$. The effect on B_{ij} of including higher OPW's is expected to be more important than for A_{ij}, but not by anything more than 30%. This change is far short of the order-of-magnitude increase required to explain the experimental B_{ij} for both metals. To further confirm that it is not the accuracy of the OPW functions which is in question to explain the experimental B_{ij}, we have evaluated $Q_{1,1}(k,k)$ and $\psi_k^2(0)$ for several values of k, using Callaway's cellular wave functions for cesium, based on the Bardeen approximation. The values of $Q_{1,1}(k,k)$ with these functions are always about 20% larger than that from one-OPW functions over the range $0 \leq k \leq k_F$, while the values of $\psi_k^2(0)$ from both functions agree within 5%.

Two other approximations that have been utilized in our calculation are spherical Fermi-surface (except in the k dependence of m_t) and the use of free-electron gas approximation to evaluate correlation corrections. We believe that the Fermi surface of rubidium is very nearly spherical and therefore nonsphericity corrections cannot be more than a few percent. Cesium, although it has a slightly more distorted Fermi surface, is still not distorted enough to expect a large nonsphericity correction. The use of free-electron approximation for the exchange-correlation enhancement is not expected to be serious either, because of the predominantly free-electron-like nature of the wave functions over most of the Wigner-Seitz sphere except near the cores, and also because the exchange-correlation enhancement is itself rather small. It is therefore clear that one has to look for an answer to the discrepancy between experiment and theory elsewhere. This brings us to the consideration of the second type of sources of error.

The second kind of error can occur because of the omission of certain neglected factors that have not been considered in our work but which can significantly influence the theoretical values of A_{ij} and B_{ij}. These factors are: (a) relativistic effects, (b) isotropic and anisotropic core-polarization effects, (c) core-conduction correlation and to a less important extent, core-core correlation. Casimir[32] has demonstrated that relativistic effects can have important influence on the hyperfine interaction for atoms with large atomic number. Preliminary results from recent calculations[33] on relativistic corrections to the hyperfine constant in the ground states of the two alkali atoms of interest indicate that this correction is about 25% for rubidium atom and 48% for cesium. Since the RK and PD parameters both involve hyperfine interactions between the nuclei and conduction electrons it is quite possible that relativistic effects can make similar sizeable contributions to A_{ij} and B_{ij}. The second mechanism that can produce significant corrections to A_{ij} and B_{ij} is the spin polarization[24,34] of the core electrons surrounding the nuclei. The hyperfine interactions of both the scalar and tensor types in Eqs. (3) and (4) can be considered as producing magnetic fields at the positions of the conduction electrons and polarizing them. This conduction-electron spin polarization can induce a similar effect on the core through exchange interaction. The cores which were otherwise spin-symmetric now get polarized with different up and down spin density, the up and down directions being in reference to the direction of surplus conduction-electron spin. The net core magnetization can interact with the nucleus via both contact and dipolar interactions. This core-polarization effect can lead to either positive or negative corrections. Calculations by Goodings on sodium and potassium atoms indicate that it produces a positive correction to the hyperfine constant in both cases. The positive effect may be a property of s-valence electrons.[24,34] However, for lithium metal,[24,34] whose conduction electrons at the Fermi surface seem to have

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[31] G. D. Gaspari and T. P. Das, Phys. Rev. **167**, 660 (1968).

[32] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (W. H. Freeman & Co., San Francisco, Calif., 1963).

[33] L. Tterlikkis (private communication).

[34] M. H. Cohen, D. A. Goodings, and V. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

substantial amounts of both s and p characters (as is also the case for rubidium and cesium metals), the core-polarization contributions from these two different angular-momentum components have a tendency to cancel. Therefore, actual calculations of the spin-polarization effects in cesium and rubidium metals are very desirable, in the absence of which nothing definite can be said about the relative importance of such effects.

The third factor that could provide corrections to A_{ij} and B_{ij} is the correlation effect between core and conduction electrons. From recent calculations of Nesbet,[35] Kelly,[36] and Chang[37] for the ground state of the lithium atom, intershell correlations do not seem to have much effect on the energy while hyperfine calculations[35,37] indicate that the $2s$-$1s$ correlation can give rise to a 20% enhancement in the hyperfine constant. Core-conduction correlations in metals represent the parallel of intershell correlations in atoms. However, no satisfactory procedure is available currently for handling core-conduction correlations quantitatively. The Brueckner-Goldstone theory[36,37] is specially adapted to correlation effects between localized electrons and has in fact been applied only to atoms so far. The dielectric formalism[16] is applicable primarily to delocalized systems. Core-conduction correlation effects form the twilight zone between the two types of correlation and neither of these procedures is well suited for our problem. Another type of correlation effect that could influence the theoretical results for A_{ij} and B_{ij} is the correlation among core electrons themselves. This type of correlation is expected to be of less importance than the core-conduction exchange because of the following reason: Since the core electrons have paired spins, pure correlation effects among them cannot directly contribute to hyperfine interaction. However, core-core correlation could indirectly influence the spin polarization[24] of core electrons produced by conduction electrons. Any or all of the above mechanisms could explain the nearly 40% difference between experimental results and theoretical values of A_{ij} for rubidium and cesium. However, these factors are not expected to influence the theoretical values of B_{ij} sufficiently enough to produce agreement with experiment. The explanation of the smallness of the theoretical B_{ij} for both metals thus presents a dilemma. It is possible that the experimental results are in error since the values of B_{ij} are quite small, and their accurate measurements by steady-state line-shape technique presents some difficulty. Echo measurements that have recently been applied[14] to other metals could perhaps lead to more accurate values of B_{ij}. In addition, it would be quite interesting to obtain theoretical values of B_{ij} in platinum and lead along the lines developed here to see if the theoretical result is again an underestimate. It is hoped that this combination of experimental and theoretical efforts will help us understand better the difference in the nature of agreement between current theory and experiment for B_{ij} in alkali metals.

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[35] R. K. Nesbet, Phys. Rev. **155**, 51 (1967).

[36] H. P. Kelley, Phys. Rev. **144**, 39 (1966).

[37] E. S. Chang, Ph.D. thesis, University of California, Riverside, 1967 (unpublished); E. S. Chang, T. P. Das, and R. T. Pu, Bull. Am. Phys. Soc. **12**, 68 (1967).