

Relativistic Effects on the Hyperfine Interactions in Alkali Metals*

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A relativistic formulation of the hyperfine properties of metals has been developed and applied to study the Knight shifts K_s , relaxation times T_1 , and Ruderman-Kittel A_{12} and pseudodipolar B_{12} interactions in the two alkali metals, rubidium and cesium. The calculations have been carried out using Dirac orthogonalized-plane-wave wave functions, and the relativistic expressions derived have been checked for correctness by proceeding to the nonrelativistic limit. The calculated values of K_s for rubidium and cesium are 0.60% and 1.42%, as compared to 0.65% and 1.49% from experiment. The values of T_1T for these metals are 1.293 and 0.128 deg sec, in good agreement with the experimental values of 1.235 and 0.130 deg sec, respectively. The relativistic values of A_{12} for rubidium and cesium are found to be 24.45 and 189.64 cps, as compared to 50 ± 5 and 200 ± 10 cps from resonance experiments. The theoretical values of B_{12} for the two metals are 0.45 and 2.65 cps, respectively, as compared to 11 ± 2 cycles and 35 ± 5 cps from recent steady-state NMR measurements. The relativistic results for all the properties, including $(T_1T)^{-1}$, are substantially larger (7% to 60%) than predicted by nonrelativistic theory, leading to improved agreement with experiment. Possible reasons for the poor agreement between experiment and theory for B_{12} in both metals are discussed.

I. INTRODUCTION

THE importance of relativistic effects on properties of heavy metals has been realized for some time. One of the properties that was analyzed earliest,¹ by an extension of the quantum defect method, was the cohesive energy of alkali metals. Subsequently, the influence of relativistic effects on band structure was highlighted by several calculations at symmetry points based on perturbation theory.² More detailed calculations, using Dirac theory adapted to orthogonalized-plane-wave (OPW) and augmented-plane-wave (APW) techniques, have been carried out for a number of heavy metals.³ The role of relativistic effects in the theory of g shifts in ESR has also been investigated.⁴ The influence of relativistic effects on the hyperfine properties of metals is the subject of study in the present work. Hyperfine effects depend sensitively on the wave function in the vicinity of the nucleus. Since this region is relatively unimportant for properties depending on band structure alone, the study of hyperfine properties thus provides a further test of the relativistic theory of metals.

More specifically, we shall be interested in the theory of Knight shifts, nuclear relaxation times, and Ruder-

man-Kittel (RK), and pseudodipolar (PD) interactions in two heavier alkali metals, rubidium and cesium. Nonrelativistic analyses^{5,6} for these metals have shown that there are significant departures from experiment which could be associated with relativistic effects. Since relativistic wave functions are now available for the corresponding atoms, it is possible to construct Dirac OPW wave functions for these metals. This, then, seems to be an appropriate time for a relativistic analysis of the various hyperfine properties.

In Sec. II, the definitions and terminology for Dirac OPW functions⁷ will be described and theoretical expressions will be derived for the various properties of interest. In Sec. III, numerical procedures and results will be presented. The significance of the results and possible improvements will be discussed in Sec. IV.

II. THEORY

The properties that we shall be concerned with, namely, Knight shift, relaxation times, and RK and PD interactions, require in some form or other an evaluation of matrix elements of the hyperfine Hamiltonian

$$\mathcal{H}_{\text{hfs}}^{\text{rel}} = \sum_i \epsilon \alpha_i \cdot \mathbf{A}_i \quad (1)$$

over conduction electron wave functions. In Eq. (1), the components of α represent the first three Dirac matrices and \mathbf{A}_i is the vector potential produced by the nuclear moment \mathbf{u}_I at the site of the i th electron \mathbf{r}_i .

$$\mathbf{A}_i = (\mathbf{u}_I \times \mathbf{r}_i) / r_i^3. \quad (2)$$

The evaluation of the hyperfine matrix elements for Dirac-Hartree-Fock (DHF) atomic functions has been

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¹ J. Callaway, Phys. Rev. **107**, 934 (1957).

² M. Asdente and J. Friedel, Phys. Rev. **124**, 384 (1961); J. Appel, *ibid.* **133**, A280 (1964); L. M. Falicov, *ibid.* **130**, 42 (1961); L. E. Johnson, J. B. Conklin, and G. W. Pratt, Jr., Phys. Rev. Letters **11**, 538 (1963); L. Liu, Phys. Rev. **126**, 1317 (1962); G. W. Lehman, *ibid.* **116**, 846 (1959); J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., *ibid.* **137**, A1282 (1965).

³ P. Soven, Phys. Rev. **137**, A1706 (1965); T. L. Loucks, *ibid.* **139**, (1965); S. Takada, Progr. Theoret. Phys. (Kyoto) **36**, 224 (1966).

⁴ A. Bienenstock and H. Brooks, Phys. Rev. **136**, A784 (1964).

⁵ J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964).

⁶ S. D. Mahanti and T. P. Das (to be published).

⁷ P. Soven, see Ref. 3.

presented in an earlier paper⁸ (hereafter referred to as TMD I). Several features of this analysis can be utilized in the present problem. However, one now has to work with relativistic wave functions appropriate to metals. For the Dirac OPW formalism which we shall adopt, the wave function for a state with wave vector \mathbf{k} and majority spin index σ is conventionally written⁷ as

$$\Psi_{\sigma}(\mathbf{k}, \mathbf{r}) = \frac{A(\mathbf{k})}{\Omega_0^{1/2}} [\chi_{\sigma}(\mathbf{k}, \mathbf{r}) - \sum_c B_c(\mathbf{k}, \sigma) \phi_c(\mathbf{r})], \quad (3)$$

where

$$\chi_{\pm}(\mathbf{k}, \mathbf{r}) = \left(\frac{1+W}{2W} \right)^{1/2} \begin{pmatrix} |\pm\rangle \\ \frac{\boldsymbol{\sigma} \cdot \mathbf{k}}{1+W} |\pm\rangle \end{pmatrix} e^{i\mathbf{k} \cdot \mathbf{r}} \quad (4)$$

are the four-component plane-wave wave functions with energy W (in units of mc^2) and $|\pm\rangle$ represent the spin functions

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

The components of $\boldsymbol{\sigma}$ in Eq. (4) are the Pauli matrices. The four-component core wave functions $\phi_c(\mathbf{r})$ in Eq. (3) are defined by the appropriate quantum numbers^{8,9} $n\kappa\mu$ and are given by

$$\phi_{n\kappa\mu}(\mathbf{r}) = \begin{pmatrix} g_{n\kappa}(r) \psi_{\kappa\mu} \\ i f_{n\kappa}(r) \psi_{-\kappa\mu} \end{pmatrix}, \quad (5)$$

where $g_{n\kappa}(r)$ and $f_{n\kappa}(r)$ are the radial wave functions for the major and minor components, respectively, and $\psi_{\kappa\mu}$ is the usual two-component angular spinor.^{8,9} The orthogonalization coefficients $B_c(\mathbf{k}, \sigma)$ in Eq. (3) are given by

$$B_{n\kappa\mu}(\mathbf{k}, \sigma) = \langle \phi_{n\kappa\mu} | \chi_{\sigma}(\mathbf{k}) \rangle. \quad (6)$$

For the sake of convenience, the Bloch wave function in Eq. (3) has been normalized to the Wigner-Seitz volume Ω_0 and $A(\mathbf{k})$ is the corresponding normalization factor. For ease of manipulation of the matrix elements of $\mathcal{H}_{\text{hfs}}^{\text{rel}}$, it is convenient to use an angular spinor representation for the Bloch functions in terms of which Eq. (3) may be rewritten as

$$\Psi_{\sigma}(\mathbf{k}, \mathbf{r}) = \sum_{\kappa\mu} a_{\kappa\mu}(\mathbf{k}, \sigma) \begin{pmatrix} b_{\kappa}(\mathbf{k}, r) \psi_{\kappa\mu} \\ i d_{\kappa}(\mathbf{k}, r) \psi_{-\kappa\mu} \end{pmatrix}, \quad (7)$$

where

$$a_{\kappa\mu}(\mathbf{k}, \sigma) = 4\pi i^{l} \left(\frac{1+W}{2W} \right)^{1/2} C(l\frac{1}{2}j; \mu - \sigma, \sigma) Y_{l\mu - \sigma}^{*}(\hat{\mathbf{k}}),$$

$$b_{\kappa}(\mathbf{k}, r) = \left[j_l(kr) - \sum_n D_{n\kappa}(k) g_{n\kappa}(r) \right] \frac{A(\mathbf{k})}{\Omega_0^{1/2}}, \quad (8)$$

$$d_{\kappa}(\mathbf{k}, r) = \left[\frac{kS_{\kappa}}{1+W} j_{l'}(kr) - \sum_n D_{n\kappa}(k) f_{n\kappa}(r) \right] \frac{A(\mathbf{k})}{\Omega_0^{1/2}}.$$

⁸ L. Tterlikkis, S. D. Mahanti, and T. P. Das, Phys. Rev. **176**, 10 (1968).

⁹ M. E. Rose, *Relativistic Electron Theory* (John Wiley & Sons, Inc., New York, 1961).

In Eq. (8), the functions $j_l(x)$ and $Y_{lm}(\hat{\mathbf{k}})$ are^{8,9} the spherical Bessel function and spherical harmonic, respectively, and $C(ls j; m_l, m_s)$ are Clebsch-Gordan coefficients. The summation over n is restricted to the occupied core states only, and the function $D_{n\kappa}$ is given by

$$D_{n\kappa}(k) = \int_0^{\infty} \left[g_{n\kappa}(r) j_l(kr) + f_{n\kappa}(r) \frac{kS_{\kappa}}{1+W} j_{l'}(kr) \right] r^2 dr. \quad (9)$$

In Eqs. (8) and (9), S_{κ} and l' , associated with the lower component of the Bloch-spinor, depend upon the parity of the particular core state under consideration and are given by

$$S_{\kappa} = 1; l = \kappa; l' = \kappa - 1; j = l - \frac{1}{2} \quad \text{for } \kappa > 0$$

and

$$S_{\kappa} = -1; l = -\kappa - 1; l' = -\kappa; j = l + \frac{1}{2} \quad \text{for } \kappa < 0. \quad (10)$$

It should be remarked here that for values of k within the Fermi-surface, $W \approx 1$, and hence one can safely approximate the factor $(1+W)/2W$ in $a_{\kappa\mu}(\mathbf{k}, \sigma)$ by unity and $(1+W)$ by 2 in the expression for $d_{\kappa}(\mathbf{k}, r)$ in Eq. (8).

Using Eq. (7) for the Bloch wave function, one obtains the matrix element of $\mathcal{H}_{\text{hfs}}^{\text{rel}}$ between two states $|\mathbf{k}, \sigma\rangle$ and $|\mathbf{k}', \sigma'\rangle$,

$$\langle \mathbf{k}\sigma | e\boldsymbol{\alpha} \cdot \mathbf{A} | \mathbf{k}'\sigma' \rangle = \sum_{\kappa_1\mu_1} \sum_{\kappa_2\mu_2} i e \mu_z a_{\kappa_1\mu_1}^*(\mathbf{k}, \sigma) a_{\kappa_2\mu_2}(\mathbf{k}', \sigma') \\ \times [W_{\kappa_1\kappa_2}(k, k') + W_{\kappa_2\kappa_1}(k', k)] \\ \times \langle \psi_{\kappa_1\mu_1} | (\hat{\boldsymbol{r}} \times \boldsymbol{\sigma})_z | \psi_{-\kappa_2\mu_2} \rangle, \quad (11)$$

where

$$W_{\kappa_1\kappa_2}(k, k') = \int_0^{\infty} b_{\kappa_1}^*(kr) d_{\kappa_2}(kr) dr. \quad (12)$$

In deriving Eq. (11), the nuclear moment has been assumed to point in the z direction. This general form of the hyperfine matrix element is useful in the analysis of both Knight shift as well as RK and PD interactions.

A. Knight Shift (K_s)

The evaluation of K_s requires a diagonal hyperfine matrix element over Bloch states at the Fermi surface. Since $(\hat{\boldsymbol{r}} \times \boldsymbol{\sigma})_z$ commutes with the z component J_z of the total angular momentum operator, the double sum over μ_1 and μ_2 in Eq. (11) will reduce to a single one. On substituting the hyperfine matrix element in the standard expression for the Knight shift, we obtain for K_s

$$K_s = -(2mc/\hbar) \langle \Phi(\mathbf{k}_F) \rangle_{\text{av}} \chi_s \Omega_0, \quad (13)$$

where χ_s is the Pauli susceptibility in cgs volume units

and

$$\begin{aligned} \Phi(\mathbf{k}) = & i(4\pi)^2 \sum_{\kappa_1 \kappa_2 \mu} (i)^{l_1 - l_2} C^*(l_1 \frac{1}{2} j_1; \mu - \sigma, \sigma) \\ & \times C(l_2 \frac{1}{2} j_2; \mu - \sigma, \sigma) (-1)^{\sigma - \mu} [(2l_1 + 1)(2l_2 + 1)]^{1/2} \\ & \times \begin{pmatrix} l_1 & 0 & l_2 \\ \sigma - \mu & 0 & \mu - \sigma \end{pmatrix} \begin{pmatrix} l_1 & 0 & l_2 \\ 0 & 0 & 0 \end{pmatrix} A_{\kappa_1 \kappa_2 \mu} Y_{l_1}^{\mu - \sigma*}(\hat{\mathbf{k}}) \\ & \times Y_{l_2}^{\mu - \sigma}(\hat{\mathbf{k}}) [W_{\kappa_1 \kappa_2}(k, k) + W_{\kappa_2 \kappa_1}(k_1, k)]. \quad (14) \end{aligned}$$

In Eq. (14),

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

are the Wigner's $3j$ symbols,¹⁰ while $A_{\kappa_1 \kappa_2 \mu}$ arises from the matrix element [on the right-hand side of Eq. (11)] of $(\hat{\mathbf{r}} \times \boldsymbol{\sigma})_z$ over the angular spinors $(\kappa_1 \mu)$ and $(-\kappa_2 \mu)$. The values of this matrix element for various choices of κ_1 and κ_2 have been listed elsewhere.^{8,9} In writing Eq. (13), it has been assumed that the susceptibility is not affected by relativistic effects, a reasonable assumption for rubidium and cesium, for which the Fermi surface is within the Brillouin zone and never reaches the zone boundary. In addition, a considerable simplification is achieved when one uses a spherical^{6,11} Fermi surface, since one can make use of the orthogonality property of the spherical harmonics in carrying out the average in Eq. (13). The expression for the Knight shift then reduces to

$$K_s = -(2mc/\hbar) \Phi(k_F) \chi_s \Omega_0 \quad (15)$$

with

$$\begin{aligned} \Phi(k_F) = & \pi [(16/3)W_{\overline{11}}(k_F, k_F) + (64/9)W_{\overline{22}}(k_F, k_F) \\ & + (16/9)W_{11}(k_F, k_F) + (32/9) \\ & \times (W_{\overline{21}}(k_F, k_F) + W_{1\overline{2}}(k_F, k_F))], \quad (16) \end{aligned}$$

where $\bar{n} = -n$, and it is immaterial whether the spin index σ is up or down.

The summation in Eq. (14) for $\Phi(k_F)$ leads to two distinct types of contributions to K_s , one involving matrix elements over similar angular momentum states such as s - s , p - p , and d - d , and the other involving combinations of different angular momenta, for example, s - d and p - f . The second contribution can be shown to vanish identically, using the symmetry property of the $3j$ symbols. The significance and numerical importance of the nonvanishing terms will be discussed in the next section. Unlike the nonrelativistic theory, where the contribution to K_s arises only from the s -character of the conduction electron wave function, all angular components contribute in the relativistic theory as shown in Eq. (16). The correctness of Eq. (16) can be assured by making a nonrelativistic reduction similar to that for atoms as in TMD I.

¹⁰ R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (Technology Press, Cambridge, Mass., 1959).

¹¹ F. S. Ham, *Phys. Rev.* **128**, 2524 (1962).

For this purpose, we shall separate the s and non- s -like contributions in Eq. (16). The Dirac equation for an electron in a Bloch state $|\mathbf{k}\sigma\rangle$ with energy $\epsilon(\mathbf{k}\sigma)$ is

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_c(\mathbf{r})] \Psi(\mathbf{k}\sigma) = \epsilon(\mathbf{k}\sigma) \Psi(\mathbf{k}\sigma). \quad (17)$$

Using the expansion for $\Psi(\mathbf{k}\sigma)$ in (7) one can separate Eq. (16) into different angular spinor components, a typical one being

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2 + V_c(r) - \epsilon(\mathbf{k}\sigma)] \begin{pmatrix} b_\kappa(k, r) \psi_{\kappa\mu} \\ id_\kappa(k, r) \psi_{-\kappa\mu} \end{pmatrix} = 0. \quad (18)$$

Equation (18) is analogous to the Dirac equation for atomic states and one can carry out the corresponding nonrelativistic (NR) reduction using the procedure outlined in TMD I. The NR reduction of the $\kappa = -1$ ($l=0$) term of Eq. (16) then leads to

$$\begin{aligned} W_{\overline{11}}(k_F, k_F) = & \int b_{\overline{1}}(k_F, r) d_{\overline{1}}(k_F, r) dr \\ & \rightarrow -\frac{\hbar}{4mc} b_{\overline{1}}^2(k_F, r) |_{r=0}. \quad (19) \end{aligned}$$

Using Eq. (8) for the definition of $b_\kappa(k_F, r)$, the right-hand side of Eq. (19) reduces to

$$-\frac{\hbar}{4mc} [1 - \sum_n B_{n, \overline{1}}(k_F) g_{n, s}(0)]^2 \frac{A^2(k)}{\Omega_0},$$

and consequently $\Phi(k_F)$ of Eq. (16) becomes

$$\Phi(k_F) = -(8\pi\hbar/6mc) \langle \Psi_{k_F}^2(0) \rangle.$$

This leads to the final reduced form of K_s as

$$K_s^{\text{NR}} = (8\pi/3) \langle \Psi_{k_F}^2(0) \rangle \chi_s \Omega_0, \quad (20)$$

which is the standard nonrelativistic expression for the Knight shift.

The other three terms in Eq. (16) involving $\kappa = -2$ and 1 are associated with the p components of the wave function. The terms $W_{\overline{22}}$ and W_{11} refer to diagonal elements over $p_{3/2}$ and $p_{1/2}$ states, respectively, while $W_{\overline{21}}$ and $W_{1\overline{2}}$ refer to nondiagonal elements between these states. These terms can be reduced to nonrelativistic form using Table III of TMD I, where a separation into orbital and dipolar effects has been made. Thus,

$$\begin{aligned} -e\mu_I (64\pi/9) W_{\overline{22}}(k_F, k_F) & \rightarrow 4\pi\mu_B \mu_I \\ & \times \langle 1/r^3 \rangle_{\overline{2}} [40/9 - 40/45], \\ -e\mu_I (16\pi/9) W_{11}(k_F, k_F) & \rightarrow 4\pi\mu_B \mu_I \\ & \times \langle 1/r^3 \rangle_p [-8/9 - 40/45], \\ -e\mu_I (32\pi/9) [W_{\overline{21}}(k_F, k_F) + W_{1\overline{2}}(k_F, k_F)] & \rightarrow 4\pi\mu_B \mu_I \\ & \times \langle 1/r^3 \rangle_p [-32/9 + 80/45], \end{aligned}$$

where $\langle 1/r^3 \rangle_p$ is the expectation value of r^{-3} over the p part of the normalized nonrelativistic wave function. The first term in the square brackets on the right refers

to orbital contribution, while the second is for the dipolar effect in the nonrelativistic approximation. On adding up these contributions, we find that the orbital and dipolar effects vanish individually as expected from NR theory.

B. Indirect Nuclear Spin-Spin Interaction

In addition to the direct dipolar interaction, the nuclei in a metal are indirectly coupled to each other through their mutual hyperfine interactions with the conduction electrons. The isotropic part of the coupling between two nuclei is referred to in the literature as RK interaction,^{12,13} and is represented by an effective spin Hamiltonian

$$\mathcal{H}_{\text{RK}} = A_{12} \mathbf{I}_1 \cdot \mathbf{I}_2, \quad (21)$$

where \mathbf{I}_1 and \mathbf{I}_2 are the spins of the two nuclei concerned and A_{12} represents the strength of the coupling. In nonrelativistic theory, the RK interaction arises from the second-order effects of contact, dipolar, and orbital parts of the hyperfine interaction acting separately. In addition to the indirect isotropic interaction, there can also be a dipolarlike coupling between the nuclei of the form

$$\mathcal{H}_{\text{PD}} = B_{12} [\mathbf{I}_1 \cdot \mathbf{I}_2 - 3(\mathbf{I}_1 \cdot \mathbf{R}_{12})(\mathbf{I}_2 \cdot \mathbf{R}_{12})R_{12}^{-2}], \quad (22)$$

where \mathbf{R}_{12} is the radius vector joining the two nuclei.

This interaction is referred to as the pseudodipolar interaction^{13,14} and the dominant contribution to B_{12} arises in the nonrelativistic theory from a combination of one order each in the contact and dipolar hyperfine interactions. There is an additional contribution to B_{12} from second-order effects of dipole interaction alone. In the relativistic formalism, all the different hyperfine interactions, contact, dipolar, and orbital, of NR theory are embedded in the single perturbation Hamiltonian in Eq. (1). In order to evaluate A_{12} and B_{12} in a relativistic theory, the general expression for the second-order perturbation energy has to be separated into components involving scalar and tensor coupling as in Eqs. (21) and (22). We shall now proceed to sketch the relativistic theory.

For a system of two nuclei with spins \mathbf{I}_1 and \mathbf{I}_2 located at the lattice sites \mathbf{R}_1 and \mathbf{R}_2 , their hyperfine interaction with the conduction electrons is described by an extension of the Hamiltonian in Eq. (1).

$$\mathcal{H}_{\text{hfs}}^{\text{rel}}(1,2) = \sum_i e\alpha_i \cdot [\mathbf{A}_1(\mathbf{r}_i - \mathbf{R}_1) + \mathbf{A}_2(\mathbf{r}_i - \mathbf{R}_2)], \quad (23)$$

where the summation i is over all the electrons, and \mathbf{A}_1 and \mathbf{A}_2 are the vector potentials associated with the magnetic moments \mathbf{u}_1 and \mathbf{u}_2 of the two nuclei. Using conventional second-order perturbation theory and Slater determinants for the many-particle electronic wave functions, the expression for second-order coupling energy due to $\mathcal{H}_{\text{hfs}}^{\text{rel}}(1,2)$ in (23) is given by

$$\Delta E_{12} = 2 \sum_{n\mathbf{k}\sigma}^{\text{occ}} \sum_{n'\mathbf{k}'\sigma'}^{\text{unocc}} \left[\frac{\langle n\mathbf{k}\sigma | e\alpha \cdot \mathbf{A}_1(\mathbf{r} - \mathbf{R}_1) | n'\mathbf{k}'\sigma' \rangle \langle n'\mathbf{k}'\sigma' | e\alpha \cdot \mathbf{A}_2(\mathbf{r} - \mathbf{R}_2) | n\mathbf{k}\sigma \rangle}{\epsilon_n(\mathbf{k}\sigma) - \epsilon_{n'}(\mathbf{k}'\sigma')} \right]. \quad (24)$$

In Eq. (24), the wave vector \mathbf{k} is expressed in reduced zone scheme, and n, σ are the band and spin indices, respectively. The summation in $n'\mathbf{k}'\sigma'$ extends over the unoccupied states, while the $n\mathbf{k}\sigma$ summation is over the occupied \mathbf{k} space. As is well known, in the one-electron approximation, the effect of the Pauli principle can be ignored in the intermediate states,¹² so that one can extend the $n'\mathbf{k}'\sigma'$ summation in Eq. (24) over the entire \mathbf{k} space. In addition, using the periodic property of the Bloch functions, Eq. (24) reduces to

$$\Delta E_{12} = 2 \sum_{n\mathbf{k}\sigma}^{\text{occ}} \sum_{n'\mathbf{k}'\sigma'} \left[e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_{12}} \frac{\langle n\mathbf{k}\sigma | e\alpha \cdot \mathbf{A}_1(\mathbf{r}) | n'\mathbf{k}'\sigma' \rangle \langle n'\mathbf{k}'\sigma' | e\alpha \cdot \mathbf{A}_2(\mathbf{r}) | n\mathbf{k}\sigma \rangle}{\epsilon_n(\mathbf{k}\sigma) - \epsilon_{n'}(\mathbf{k}'\sigma')} \right], \quad (25)$$

where the summation in $n'\mathbf{k}'\sigma'$ now scans the entire \mathbf{k} space, both occupied and unoccupied. The \mathbf{R}_{12} dependence in Eq. (25) is contained in the $e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_{12}}$ term in the summand. The explicit form of the \mathbf{R}_{12} dependence is, however, determined by the shape of the energy band through the \mathbf{k}, \mathbf{k}' summation in Eq. (25). Using the spherical harmonic expansion for $e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_{12}}$ and

the relation

$$Y_{\mu}^{\nu}(\hat{R}_{12}) Y_{\mu'}^{\nu'*}(\hat{R}_{12}) = (-1)^{\nu} \sum_{LM} \left[\frac{(2\mu+1)(2\mu'+1)(2L+1)}{4\pi} \right]^{1/2} \times \begin{pmatrix} \mu' & L & \mu \\ -\nu' & M & \nu \end{pmatrix} \begin{pmatrix} \mu' & L & \mu \\ 0 & 0 & 0 \end{pmatrix} Y_{LM}^*(\hat{R}_{12}), \quad (26)$$

¹² M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

¹³ S. D. Mahanti and T. P. Das, Phys. Rev. **170**, 426 (1968).

¹⁴ N. Bloembergen and T. J. Rowland, Phys. Rev. **97**, 1679 (1955).

together with Eq. (11) for the hyperfine matrix element, leads to the somewhat complicated but general expression for the second-order energy given in Eq. (A1) of the Appendix, valid for a Fermi surface of any shape. This expression contains various types of coupling between the nuclei which can be recognized by collecting terms associated with the pertinent values of LM . Thus, the isotropic part of Eq. (A1) determined by the $Y_0^0(\hat{R}_{12})$ gives the relativistic RK interaction.

For a spherical Fermi surface, the only term with $L=2$ that occurs in Eq. (A1) after \mathbf{k}, \mathbf{k}' integration has a $Y_2^0(\hat{R}_{12})$ dependence. In order to derive the $Y_2^{\pm 1}(\hat{R}_{12})$ and $Y_2^{\pm 2}(\hat{R}_{12})$ terms in the pseudodipolar coupling Hamiltonian \mathcal{H}_{CPD} in Eq. (22), one would have to consider the μ_x and μ_y components of the hyperfine Hamiltonian along with μ_z . However, the coefficients of the Y_2^M terms in \mathcal{H}_{CPD} are simply related to that for the Y_2^0 , and no separate calculations are necessary. For general departures (less than cubic) from spherical symmetry, an examination of Eq. (A1) shows that there can be additional coupling terms besides the RK and PD interactions as defined in Eqs. (21) and (22). In particular, for a distorted Fermi surface, one can obtain finite Y_1^M terms which would indicate a vector interaction between the nuclear spins. There is no counterpart of this term in nonrelativistic theory.

For quantitative analysis, it is necessary to carry out the summations and corresponding simplification in Eq. (A1) for RK and PD interactions separately.

C. Ruderman-Kittel Interaction

This interaction is obtained from the scalar Y_0^0 term of Eq. (A1). On using the expressions for $a_{\kappa\mu}$ as defined in Eq. (8) and carrying out the angular integrations in \mathbf{k} and \mathbf{k}' space, Eq. (A1) reduces to

$$\Delta E_{12}^{(0)} = 2e^2\mu_{1z}\mu_{2z} \times \sum_{\sigma\sigma'} \int_0^{k_F} \int_0^\infty \frac{T_{\sigma\sigma'}^{(0)}(k, k')}{\epsilon(\mathbf{k}\sigma) - \epsilon(\mathbf{k}'\sigma')} k^2 k'^2 dk dk', \quad (27)$$

where the Fermi surface has been assumed spherical and $T_{\sigma\sigma'}^{(0)}(k, k')$ is again a rather complicated expression given in Eq. (A2) of the Appendix. It is to be noticed that in contrast to Eq. (A1), Eq. (A2) does not involve any summation over μ' , since for the $L=0$ interaction, the pertinent Wigner $3j$ symbols in Eq. (A1) lead to $\mu=\mu'$. Using Eq. (21) the RK parameter A_{12}^0 can be expressed in terms of $\Delta E_{12}^{(0)}$ of Eq. (27) as

$$A_{12} = \Delta E_{12}^{(0)} / I_{1z} I_{2z}. \quad (28)$$

The R_{12} dependence of A_{12} is determined by the pertinent phase factor $j_\mu(kR_{12}) j_\mu(k'R_{12})$ associated with $T_{\sigma\sigma'}^{(0)}(k, k')$ in Eq. (27). For the sake of uniformity, we shall denote the contribution to A_{12} from the $\mu=\mu'$ term in Eq. (A2) as $A_{12}^{\mu\mu}$. Terms involving $\mu > 2$ will be neglected since they make quantitatively

insignificant contribution¹³ to A_{12} . For a particular choice of μ in Eq. (A2), l_2 and l_4 are no longer independent but are determined by l_1 and l_3 . Various combinations of $l_1 l_2$ and $l_3 l_4$ will be characterized as $(ss-ss)$, $(ss-p\bar{p})$, $(p\bar{p}-p\bar{p})$, \dots contributions to $A_{12}^{\mu\mu}$. Among the terms with $\mu \leq 2$, A_{12}^{00} is the most dominant and will be considered first.

For A_{12}^{00} , Eq. (A2) shows that only diagonal contributions such as $(ss-ss)$, $(p\bar{p}-p\bar{p})$, and $(d\bar{d}-d\bar{d})$ can exist. It is interesting to note that the $(p\bar{p}-p\bar{p})$ and $(d\bar{d}-d\bar{d})$ terms derive contributions from both $\sigma=\sigma'$ and $\sigma \neq \sigma'$. This is a consequence of spin-orbit effects built into the relativistic theory which makes a particular σ state an admixture of up and down spin states. For the $(ss-ss)$ contribution, the effects of spin-orbit interaction are absent, and hence, no terms with $\sigma \neq \sigma'$ exist. After the summations in Eqs. (27) and (A2) are carried out using the properties of $(3j)$ symbols, Eq. (28) reduces to

$$A_{12}^{00} = 2\gamma_1\gamma_2\hbar^2 e^2 \times \int_0^{k_F} \int_0^\infty \frac{P^0(k, k')}{\epsilon(\mathbf{k}) - \epsilon(\mathbf{k}')} k^2 k'^2 dk dk', \quad (29)$$

where

$$P^0(k, k') = -(8/\pi^2) [(4/9)Q_{\text{II,II}}(k, k') + (4/9)Q_{\text{II,II}}(k, k') + (32/4\pi)Q_{\text{II,II}}(k, k') + (2/9)Q_{\text{II,II}}(k, k') + (2/9)Q_{\text{II,II}}(k, k')] j_0(kR_{12}) j_0(k'R_{12}) \quad (30)$$

with

$$Q_{\kappa_1\kappa_2, \kappa_3\kappa_4}(k, k') = [W_{\kappa_1\kappa_2}(k, k') + W_{\kappa_2\kappa_1}(k', k)] \times [W_{\kappa_3\kappa_4}(k, k') + W_{\kappa_4\kappa_3}(k', k)],$$

where only $(ss-ss)$ and $(p\bar{p}-p\bar{p})$ terms have been retained, the higher l terms being unimportant.¹³

The integration over k' involving the entire k space, both occupied and unoccupied, can be avoided by the technique utilized by Ruderman and Kittel.¹³ As a further simplification, we assume $\epsilon(\mathbf{k})$ to be independent of direction of \mathbf{k} , a reasonable approximation for the alkali metals of interest. The integration over k' may be replaced by one over $\epsilon(k')$ using the relation

$$dk = d\epsilon(dk/d\epsilon) = \frac{1}{2}[m_i(k)/k]d\epsilon, \quad (31)$$

where $m_i(k)$ is the thermal mass¹³ characterizing the density of states. Using these steps, Eq. (29) is re-expressed in the form

$$A_{12}^{00} = (16/\pi^2)\gamma_1\gamma_2\hbar^2 e^2 [(4/9)I_{\text{II,II}} + (32/45)I_{\text{II,II}} + (4/9)I_{\text{II,II}} + (2/9)I_{\text{II,II}} + (2/9)I_{\text{II,II}}], \quad (32)$$

where

$$I_{\kappa_1\kappa_2, \kappa_3\kappa_4} = -\frac{\pi}{4R_{12}^2} \int_0^{k_F} k m_i(k) \sin(2kR_{12}) \times Q_{\kappa_1\kappa_2, \kappa_3\kappa_4}(k, k) dk. \quad (33)$$

The suffixes $(\kappa_1\kappa_2, \kappa_3\kappa_4)$ in Eq. (32) designate processes connected with $(s_{1/2}s_{1/2} - s_{1/2}s_{1/2})$, $(p_{3/2}\bar{p}_{3/2} - \bar{p}_{3/2}p_{3/2})$, $(p_{1/2}\bar{p}_{1/2} - \bar{p}_{1/2}p_{1/2})$, $(p_{3/2}\bar{p}_{1/2} - \bar{p}_{3/2}p_{1/2})$, and $(p_{1/2}\bar{p}_{3/2} - \bar{p}_{1/2}p_{3/2})$ hyperfine matrix elements.

In an analogous manner, expressions for A_{12}^{11} and A_{12}^{22} corresponding to $\mu=1$ and 2, respectively, can be derived using Eqs. (27) and (A2)

$$A_{12}^{11} = -(32/\pi^2)\gamma_1\gamma_2\hbar^2e^2[(16/27)J_{\text{II},\overline{22}} + (4/27)J_{\text{II},11} + (16/27)J_{\text{II},1\overline{2}} + (16/27)J_{\text{II},\overline{21}}], \quad (34)$$

where

$$J_{\kappa_1\kappa_2,\kappa_3\kappa_4} = -\frac{\pi}{2R_{12}^2} \int_0^{k_F} km_t(k) Q_{\kappa_1\kappa_2,\kappa_3\kappa_4}(k,k) \times j_1(kR_{12}) [\cos kR_{12} + kR_{12} \sin kR_{12}] dk. \quad (35)$$

The first term in Eq. (34) originates from a process described by the product of the relativistic matrix elements ($s_{1/2}-s_{1/2}$) and ($p_{3/2}-p_{3/2}$). The other terms have similar interpretation. The expression for A_{12}^{22} is given by

$$A_{12}^{22} = (128/15\pi^2)\gamma_1\gamma_2\hbar^2e^2 \times [(256/225)K_{\overline{22},\overline{22}} + (34/27)K_{\overline{21},\overline{21}}],$$

where

$$K_{\kappa_1\kappa_2,\kappa_3\kappa_4} = \frac{\pi}{2R_{12}^3} \int_0^{k_F} m_t(k) Q_{\kappa_1\kappa_2,\kappa_3\kappa_4}(k,k) j_2(kR_{12}) \times \{[(3-k^2R_{12}^2) \cos(kR_{12})] + 3kR_{12} \sin kR_{12}\} dk. \quad (36)$$

D. Pseudo-Dipolar Interaction

The tensor $Y_2^0(\hat{R}_{12})$ of Eq. (A1) describing the PD interaction [Eq. (22)] will be considered next. By analogous steps as those used in deriving Eq. (27), one obtains

$$\Delta E_{12}^{(2)} = e^2\mu_{1z}\mu_{2z} \sum_{\sigma\sigma'} \int_0^{k_F} \int_0^\infty \frac{T_{\sigma\sigma'}^{(2)}(k,k')}{\epsilon(\mathbf{k}\sigma) - \epsilon(\mathbf{k}'\sigma')} \times k^2k'^2 dk dk', \quad (37)$$

where $T_{\sigma\sigma'}^{(2)}(k,k')$ is exactly similar to $T_{\sigma\sigma'}^{(0)}(k,k')$ defined in Eq. (A2) with the terms

$$Y_0^{0*}(\hat{R}_{12}) \begin{pmatrix} \mu & 0 & \mu \\ \nu & 0 & -\nu \end{pmatrix} \begin{pmatrix} \mu & 0 & \mu \\ 0 & 0 & 0 \end{pmatrix}$$

replaced by

$$Y_2^{0*}(\hat{R}_{12}) \begin{pmatrix} \mu & 2 & \mu \\ \nu & 0 & -\nu \end{pmatrix} \begin{pmatrix} \mu & 2 & \mu \\ 0 & 0 & 0 \end{pmatrix}$$

and an additional factor of $\sqrt{5}$ coming from the $(2L+1)^{1/2}$ term in Eq. (A1). To determine B_{12} conveniently from Eq. (37), one has to reexpress the PD Hamiltonian in Eq. (22) in a spherical tensor representation:

$$\mathcal{H}_{\text{CPD}} = B_{12} \sum_m C_{2m} O_{-m}^2(\mathbf{I}_1, \mathbf{I}_2) Y_2^m(\hat{R}_{12}),$$

where

$$C_{20} = (4\pi/5)^{1/2}, \quad C_{2\pm 1} = \pm (24\pi/5)^{1/2}, \quad C_{2\pm 2} = (96\pi/5)^{1/2} \quad (38)$$

and

$$O_0^2(\mathbf{I}_1, \mathbf{I}_2) = -2I_{1z}I_{2z} + \frac{1}{2}(I_{1+}I_{2-} + I_{1-}I_{2+}),$$

$$O_{\pm 1}^2(\mathbf{I}_1, \mathbf{I}_2) = -\frac{1}{2}(I_{1\pm}I_{2z} + I_{1z}I_{2\pm}),$$

$$O_{\pm 2}^2(\mathbf{I}_1, \mathbf{I}_2) = -\frac{1}{4}(I_{1\pm}I_{2\pm}),$$

and equate coefficients of $Y_2^{0*}(\hat{R}_{12})$ in Eqs. (37) and (38). In contrast to the case of A_{12} where only the $\mu'=\mu$ terms survive in the summations of Eq. (A1), for the case of B_{12} an examination of $T_{\sigma\sigma'}^{(2)}$ indicates that two types of terms can survive, namely,

$$\mu = \mu' = 1 \quad \text{and} \quad 2$$

and

$$\begin{aligned} \mu = 0, \quad \mu' = 2, \\ \mu = 2, \quad \mu' = 0. \end{aligned} \quad (39)$$

Of the various combinations of μ and μ' in Eq. (39), the one with $\mu=\mu'=2$, and both the second type of terms together, constitute the relativistic counterparts of second-order dipole effects in NR theory. Expressions for these terms will not be presented here since they are very complicated, and also quite ineffective in their contributions by virtue of the fact that they do not depend on the dominant s character of the wave functions. The dominant contribution arises from the $\mu=\mu'=1$ term. The R_{12} dependence for this term is described by a phase factor $j_1(kR_{12})j_1(k'R_{12})$ similar to the A_{12}^{11} contribution to the RK interaction. In the NR theory, B_{12}^{11} arises out of a cross interaction between contact and dipolar hyperfine operators. Further, as in the case of A_{12}^{11} , most important combinations of $(\kappa_1\kappa_2)$ and $(\kappa_3\kappa_4)$ are those associated with $(s_{1/2}-s_{1/2})$ and $(p_\mu-p_\mu)$ matrix elements. After some algebraic manipulations similar to those for A_{21} , one obtains

$$B_{12}^{11} = -(128/\pi^2)\gamma_1\gamma_2\hbar^2e^2 \times [2J_{\text{II},\overline{22}} + \frac{4}{3}J_{\text{II},11} - \frac{1}{2}J_{\text{II},\overline{21}} - \frac{1}{2}J_{\text{II},1\overline{2}}], \quad (40)$$

where $J_{\kappa_1\kappa_2,\kappa_3\kappa_4}$ has been defined in Eq. (35).

E. Reduction to Nonrelativistic Limit

As in the case of the Knight shift, both for physical interest as well as a check on the relativistic theory, it is useful to carry out the Breit reduction of Eqs. (32), (34), (36), and (40) to compare with earlier expressions¹³ for A_{12} and B_{12} derived by a NR procedure. In particular, the first and the dominant term of Eq. (32) can be shown to reduce to the NR expression for A_{12} arising from two orders of contact interaction. The last three terms of Eq. (32) should similarly reduce to the second-order contribution from orbital and dipolar interactions in NR theory. For the purpose of illustration, we will carry out the NR reduction of A_{12}^{11} in (34) in some detail, as it embodies some features of both A_{12}^{00} and B_{12}^{11} in Eqs. (32) and (40). Additionally, A_{12}^{11} is of interest since it has no NR counterpart.

The expression A_{12}^{11} involves matrix elements over both s and p components of the conduction electron

wave function. The nonrelativistic reduction of the former follows similar lines as for the Knight shift. The reduction of the non- s -like terms is however a little subtle. The NR reduction in this case cannot be carried out directly from Eq. (34), since terms associated with different values of ν in Eq. (A2) reduce differently. This follows because the values of ν determine μ_4 for the relevant hyperfine matrix elements over p_{j,μ_4} states, which may be seen to depend on μ_4 from Table III of TMD I. A typical p -type matrix element in (A2) involves $A_{\bar{2}\bar{2}}^{\mu_4} W_{\bar{2}\bar{2}}(k,k)$. For $\mu_4 = \frac{3}{2}$, using Table III (TMD I),

$$2A_{\bar{2}\bar{2}}^{3/2} W_{\bar{2}\bar{2}}(k,k) \xrightarrow{\text{NR}} (8/5)(\hbar/mc) Q_{pp}(k,k), \quad (41)$$

where

$$Q_{pp}(k,k) = \langle \chi_p(k,r) | 1/r^3 | \chi_p(k,r) \rangle,$$

$\chi_p(k,r)$ being the radial part of the p component of the nonrelativistic OPW function. On carrying out a similar reduction for all the terms in $T_{\sigma\sigma}^{(0)}$ appropriate to A_{12}^{11} , one can show that A_{12}^{11} vanishes in the NR limit, the terms associated with $\nu=0$ being cancelled by the sum of the $\nu=\pm 1$ terms. This cancellation holds separately for the dipolar and orbital hyperfine terms in the NR approximation.

In an analogous manner, Eq. (32) for A_{12}^{00} reduces to the NR form

$$A_{12}^{00}(\text{NR}) = A_{12}^{00}(\text{cont}) + A_{12}^{00}(\text{orb}) + A_{12}^{00}(\text{dip}), \quad (42)$$

where the three terms correspond to second-order effects of contact, orbital, and dipolar hyperfine interactions and are given by

$$\begin{aligned} A_{12}^{00}(\text{cont}) &= \frac{1}{2} \left(\frac{1}{2\pi} \right)^3 \left(\frac{16\pi}{3} \right)^2 \gamma_1 \gamma_2 \gamma_e^2 \hbar^4 \frac{1}{R_{12}^2} \int_0^{k_F} k m_t(k) \\ &\quad \times |\psi_k(0)|^4 \sin(2kR_{12}) dk, \\ A_{12}^{00}(\text{orb}) &= -\frac{32}{\pi} \gamma_1 \gamma_2 \gamma_e^2 \hbar^4 \frac{1}{R_{12}^2} \int_0^{k_F} k m_t(k) Q_{1,1}^2(k,k) \\ &\quad \times \sin(2kR_{12}) dk, \quad (43) \\ A_{12}^{00}(\text{dip}) &= -\frac{48}{\pi} \gamma_1 \gamma_2 \gamma_e^2 \hbar^4 \frac{1}{R_{12}^2} \int_0^{k_F} k m_t(k) Q_{1,1}^2(k,k) \\ &\quad \times \sin(2kR_{12}) dk, \end{aligned}$$

which are exactly the same as those derived by NR theory.¹³ Similarly for B_{12}^{11} , in Eq. (40), the NR reduction leads to the result

$$\begin{aligned} B_{12}^{11}(\text{NR}) &= \frac{64}{\pi} \gamma_1 \gamma_2 \gamma_e^2 \hbar^4 \frac{1}{R_{12}^2} \int_0^{k_F} k m_t(k) |\psi_k(0)|^2 \\ &\quad \times Q_{1,1}(k,k) [\cos kR_{12} + kR_{12} \sin kR_{12}] \\ &\quad \times [\sin kR_{12} - kR_{12} \cos kR_{12}] (k^2 R_{12}^2)^{-1} dk. \end{aligned}$$

This result agrees exactly with that from a NR procedure and is described in the NR approximation as a cross interaction between contact and dipolar hyperfine effects. In the reduction process for B_{12}^{11} , one arrives at a set of terms that can be identified with a cross interaction between contact and orbital hyperfine effects in NR theory. These terms add to zero on using the relevant matrix elements from Table III (TMD I). This is in agreement with the NR result.

It is interesting at this point to examine the predicted R_{12} dependence of RK and PD interactions. In order to obtain R_{12} dependence, one has to express the integral in Eq. (36) in terms of reduced variable kR_{12} . One cannot do this analytically for the function $m_t(k) \times Q_{\kappa_1 \kappa_2; \kappa_3 \kappa_4}(k,k)$ in the integrand. If this latter function were k -independent, Eq. (34) would indicate an R_{12}^{-4} dependence. However, both in relativistic and non-relativistic theory, $m_t Q_{\kappa_1 \kappa_2; \kappa_3 \kappa_4}$ is a function of k and so the actual R_{12} dependence can only be found by numerical calculations. Similar remarks apply to PD interaction.

III. RESULTS AND DISCUSSION

The expressions derived in Sec. II have been utilized for quantitative calculations of the Knight shift, RK, and PD interactions for rubidium and cesium. The Knight-shift results are discussed first.

A. Knight Shift

Accurate experimental results^{15,16} for the Knight shifts in these metals are available from a number of measurements over the past few years. While we are interested in comparing our theoretical results with experiment, our major emphasis is on the importance of relativistic effects. Since relativistic effects are primarily determined by the hyperfine matrix elements, we shall first make a comparison of these with nonrelativistic theory and try to understand the physical origin of various sources that contribute to relativistic effects. In the calculation of the hyperfine matrix elements, single Dirac OPW functions have been used. For the core states, we have employed the atomic relativistic Hartree-Fock wave functions of Coulthard.¹⁷

In Table I, the contributions from the individual matrix elements in Eq. (16) are separately displayed, together with the corresponding nonrelativistic matrix elements for one-OPW wave functions. The W_{II} term which is related to the nonrelativistic s contribution is seen to predominate, but the p -like terms individually make significant nonvanishing contributions. However, on adding up the p -like contributions as in the sixth column, the sum is small, though nonvanishing. This

¹⁵ D. F. Holcomb and R. E. Norberg, Phys. Rev. **98**, 1074 (1955).

¹⁶ D. F. Holcomb, J. A. Kaeck, and J. H. Strange, Phys. Rev. **150**, 306 (1966).

¹⁷ M. A. Coulthard, Proc. Phys. Soc. (London) **91**, 44 (1967).

TABLE I. Relativistic hyperfine matrix elements (expressed in units of χ_s) occurring in the Knight-shift expression.

Rel. contrs. Metal	I ^a W_{II} ($s_{1/2}-s_{1/2}$)	II ^a W_{II} ($p_{3/2}-p_{3/2}$)	III ^a $W_{1,1}$ ($p_{1/2}-p_{1/2}$)	IV ^a $W_{21}+W_{12}$ ($p_{3/2}-p_{1/2}$) + ($p_{1/2}-p_{3/2}$)	Sum ^a II+III+IV (Total p contribution)	Total ^a I+II+III+IV	NR appr. ^a
Rb ⁸⁶	7691.30	403.86	-211.83	-197.92	- 5.89	7685.41	7162.64
Cs ¹³³	18521.14	898.54	-516.64	-431.15	-49.25	18471.89	14081.78

^a The entries in these columns include the numerical factors in Eq. (16) and have been multiplied by the factor $(-2mc/\hbar)$ of Eq. (15).

nonvanishing result is a characteristic feature of relativistic effects. However, in terms of magnitude, the difference between relativistic and nonrelativistic s contribution is much more pronounced, and can be associated with the effects of the mass velocity and Darwin terms in Foldy-Wouthuysen⁹ language. The magnitude of this effect is seen from columns 7 and 8 to be about 7.3% for rubidium and 31.2% for cesium. The smaller result for rubidium is to be expected because it is a lighter metal and the extent of variation from cesium to rubidium indicates that for other alkali metals, potassium, sodium, and lithium, the relativistic corrections will be insignificant.

To compare the Knight shift from relativistic theory with experiment, we need a knowledge of Pauli susceptibility χ_s . It would be ideal if direct experimental values of χ_s for the two metals were available, so that one could test the correctness of hyperfine matrix element. Unfortunately, no experimental values of χ_s from spin-resonance measurements exist in rubidium and cesium. One has, therefore, to fall back on theoretical estimates of the susceptibility. Using density of states obtained from band structure calculations,^{6,11} the Pauli susceptibilities come out as

$$\begin{aligned} (\chi)_{\text{Band}}^{\text{Rb}} &= 0.605 \times 10^{-6} \text{ cgs vol units,} \\ (\chi)_{\text{Band}}^{\text{Cs}} &= 0.592 \times 10^{-6} \text{ cgs vol units.} \end{aligned} \quad (44)$$

However, one has to correct these values for the exchange enhancement in the presence of the magnetic field.¹⁸ There are several alternative approaches to incorporate this effect. One that seems most plausible is due to Silverstein¹⁹

$$(\chi_s^*)_{\text{Band}} = \chi_s / [1 + (m_0/m_t - 1)(\chi_s/\chi_0)]. \quad (45)$$

In Eq. (45), χ_s on the right-hand side refers to the susceptibility, including the effects of exchange enhancement and without band corrections, while χ_0 is the free-electron susceptibility corresponding to the densities in these metals, m_t is the density-of-states mass given by

$$m_t = \hbar^2 k \left. \frac{dk}{dE} \right|_{k=k_F}, \quad (46)$$

and m_0 is the free electron mass. The values of m_t/m_0

¹⁸ C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV.

¹⁹ S. D. Silverstein, Phys. Rev. **130**, 1703 (1963).

from band-structure calculations are

$$\begin{aligned} \left(\frac{m_t}{m_0} \right)_{\text{Rb}} &= 1.210, \\ \left(\frac{m_t}{m_0} \right)_{\text{Cs}} &= 1.304. \end{aligned} \quad (47)$$

The corrected values of $(\chi_s^*)_{\text{Band}}$ to be used in the Knight shift are

$$\begin{aligned} (\chi_s^*)_{\text{Band}}^{\text{Rb}} &= 0.7804 \times 10^{-6} \text{ cgs vol units,} \\ (\chi_s^*)_{\text{Band}}^{\text{Cs}} &= 0.7696 \times 10^{-6} \text{ cgs vol units.} \end{aligned} \quad (48)$$

Using these values of $(\chi_s^*)_{\text{Band}}$, the Knight shifts in relativistic and nonrelativistic approximations are tabulated in Table II. The near-exact agreement between the relativistic result for cesium and experiment is fortuitous in view of the neglect of such effects as the core-polarization and core-conduction correlation. The importance of these and other possible sources of correction will be discussed in Sec. IV. The most important feature of the results is the ratio between the relativistic and nonrelativistic K_s , which equals the corresponding ratio between the matrix elements, and is quite substantial for cesium.

B. Spin-Lattice Relaxation Time

The other important property that depends upon the hyperfine matrix element at the Fermi surface is the spin-lattice relaxation time T_1 . As in the case of the Knight shift, one again has to correct for the influence of correlation and exchange among conduction electrons. Since we now have a dynamic process to deal with, one has to include the influence of dynamic correlation among electrons instead of the static effects for the susceptibility. Such effects can only be approximately treated at the present time. Since our main concern here is the role of relativistic effects, we shall

TABLE II. Nonrelativistic and relativistic values of Knight shift (K_s) compared with experiment.

Metal \ K_s	Nonrelativistic	Relativistic	Experimental
Rb ⁸⁶	0.0056	0.0060	0.0065
Cs ¹³³	0.01086	0.01419	0.0149

TABLE III. Nonrelativistic, relativistic, and experimental values of (T_1T) in deg sec.

Metal \ (T_1T)	Nonrelativistic	Relativistic	Experiment
Rb ⁸⁵	1.485	1.293	1.234±0.10
Cs ¹³³	0.219	0.128	0.130±0.01

merely quote the expression²⁰ of T_1 in the literature without including the effects of dynamic correction.

$$(T_1T)^{-1} = (2\pi/\hbar)k\rho^2(\epsilon_F)F, \quad (49)$$

where

$$F = \frac{1}{2}(8\pi/3)^2 \gamma_N^2 \gamma_e^2 \hbar^4 \langle |\psi_{k_F}(0)|^2 \rangle \quad (50)$$

in the nonrelativistic case. For the relativistic case

$$F = \frac{1}{2}e^2 \gamma_N^2 \hbar^2 \langle \phi(k_F) \rangle^2. \quad (51)$$

Using the values of the matrix elements in Table I and substituting appropriate values for other quantities, we obtain the theoretical values of (T_1T) listed in the third column of Table III. The second column lists the NR results in one-OPW approximation and the last column gives the most recent experimental results. Again, the close agreement between the results of relativistic calculation of T_1 and experiment should not be taken seriously in view of the neglected effects of dynamic correlation and additional contributions to the hyperfine field pointed out in the case of K_s . The more significant results are the 12.9% and 41.4% decreases in the values of (T_1T) for rubidium and cesium on including relativistic effects. These corrections are relatively larger compared to the corresponding corrections for K_s , since the square of the hyperfine matrix element occurs in the expression for T_1^{-1} .

C. Ruderman-Kittel Interaction

To obtain better insight, we have listed the contributions from the various component terms in Eqs.

(32) and (34) for A_{12}^{00} and A_{12}^{11} separately in Table IV (a). In Table V, we tabulate the theoretical results for the RK parameter A_{12} in rubidium and cesium and compare it when experiment²¹ and earlier nonrelativistic¹³ results.

The most important contribution to A_{12} arises from the A_{12}^{00} expression in Eq. (32). As in the case of Knight shift, the major part (almost 99%) of A_{12}^{00} is associated with the $I_{II,II}$ term, which reduces to the second-order result from contact interaction in NR theory. The other three terms in Eq. (32) are associated with second-order contribution from the $p_{3/2}$ and $p_{1/2}$ components by themselves and through their cross product. The cross terms have the same sign as the diagonal terms for the p -like contributions in contrast to the situation for the Knight shift. This difference of relative signs in the two cases occurs probably because the Knight shift involves simple matrix elements, while the RK interaction involves products. However, these p contributions are all seen to be individually rather small. They represent the contributions from orbital and dipolar hyperfine interactions in NR theory, where their effects are also minimal. The effects of higher l components (d, f, \dots) of the wave functions were found to be negligible, and are not listed.

The terms in the expression (34) for A_{12}^{11} , which have no nonrelativistic counterparts are found from Table IV(b) to be rather small, compared to the leading term of A_{12}^{00} , but they are an order of magnitude larger than the p -component contributions to A_{12}^{00} . This behavior can be understood since the terms in A_{12}^{11} involve matrix elements connected with the predominant s component of the wave function which does not occur for the p -component terms of A_{12}^{00} . The net effect of the A_{12}^{11} term is seen to be exceedingly small because of some cancellations among them. The A_{12}^{22} contribution was not found to be significant and has not been listed.

TABLE IV. (a) Contributions to A_{12}^{00} in cycles from various angular components of the wave function. (b) Contributions to A_{12}^{11} in cycles from various angular components of the wave function.

Metal \ Contrs. ^a to A_{12}^{00}	Part (a)				Total
	$I_{II,II}$ ($s_{1/2}s_{1/2} - s_{1/2}s_{3/2}$)	$I_{22,22}$ ($p_{3/2}p_{3/2} - p_{3/2}p_{1/2}$)	$I_{11,11}$ ($p_{1/2}p_{1/2} - p_{1/2}p_{3/2}$)	$I_{21,21} + I_{12,12}$ ($p_{1/2}p_{3/2} - p_{1/2}p_{1/2}$) + ($p_{3/2}p_{1/2} - p_{3/2}p_{3/2}$)	
Rb ⁸⁵	24.00	0.02	0.06	0.00	24.08
Cs ¹³³	187.17	0.16	0.50	0.02	187.85

Metal \ Contrs. ^b to A_{12}^{11}	Part (b)			Total
	$J_{II,22}$ ($s_{1/2}s_{1/2} - p_{3/2}p_{3/2}$)	$J_{II,11}$ ($s_{1/2}s_{1/2} - p_{1/2}p_{1/2}$)	$J_{II,12} + J_{II,21}$ ($s_{1/2}s_{1/2} - p_{1/2}p_{3/2}$) + ($s_{1/2}s_{1/2} - p_{3/2}p_{1/2}$)	
Rb ⁸⁵	-0.60	0.32	0.65	0.37
Cs ¹³³	-3.45	1.84	3.40	1.79

^a The numbers quoted include the numerical factors in Eq. (34).

^b The numbers quoted include the numerical factors in Eq. (36).

²⁰ T. Moriya, J. Phys. Soc. Japan **18**, 516 (1963).

²¹ J. Poitrenaud, J. Phys. Chem. Solids **28**, 161 (1967).

The final result from relativistic theory for A_{12} in cesium is in very good agreement (about 95%) with experiment. The situation for rubidium is not as good, the theoretical result now being about 50% of experiment. Possible reasons for this discrepancy will be discussed in Sec. IV. Again, the ratio of relativistic and nonrelativistic results is perhaps of greater interest than the specific agreement with experiment. We notice from Table IV that relativistic effects increase A_{12} by about 16% for rubidium and 60% for cesium. These corrections are more than twice as large as those obtained for the Knight shift, which is not unexpected, since squares of hyperfine matrix elements are again involved as in the case of relaxation times. Since the dominant contribution to A_{12} , and hence the major relativistic correction, arises from the s component of the conduction electron wave function, it again appears that the main relativistic effect in these metals is of the mass-velocity and Darwin type.

D. Pseudo-Dipolar Interaction

Various contributions to PD coupling constants are listed in Table VI for both metals together with results from NR theory and experiment²¹ for comparison. Equation (40) consists of four terms. These terms involve the products of the $(s_{1/2}-s_{1/2})$ matrix element with the diagonal $(p_{3/2}-p_{3/2})$ and $(p_{1/2}-p_{1/2})$ terms and the nondiagonal $(p_{3/2}-p_{1/2})$ and $(p_{1/2}-p_{3/2})$ terms. The nondiagonal terms are grouped together in the fourth column of Table VI, while the diagonal terms are given separately in the first two columns. All three terms are seen to be comparable in magnitude with each other and corresponding terms in A_{12} ,¹¹ because the latter involves products [Eq. (33)] of similar matrix elements. The results in both metals are found to be more than an order of magnitude smaller than experiment, as was the case with nonrelativistic theory. Thus, relativistic corrections cannot alone produce agreement with experiment, and the source of discrepancy has to be sought elsewhere. We shall discuss this point further in Sec. IV. A comparison of relativistic and nonrelativistic results indicates that there is about 5.5% increase due to relativistic effects in rubidium and about 14% in cesium. These corrections are comparable to those for the Knight shift, which is not surprising, since the major relativistic effect is associated with the contact term, which occurs linearly in both the Knight shift and PD interaction.

TABLE V. Relativistic results for A_{12} in cycles compared with experiment and nonrelativistic theory.

Metal	A_{12}^{00}	A_{12}^{21}	$A_{12} = A_{12}^{00} + A_{12}^{21}$ Relativistic	A_{12} Non-relativistic	A_{12} Experiment
Rb ⁸⁵	24.08	0.37	24.45	21.00	50 ± 5
Cs ¹³³	187.85	1.79	189.64	117.55	200 ± 10

IV. CONCLUSION

A formalism for relativistic analysis of hyperfine properties of metals has been developed and applied to two alkali metals, rubidium and cesium. The results clearly demonstrate the importance of including relativistic effects for heavy metals. The improvement found over the results of nonrelativistic analysis in these metals was observed to decrease significantly from cesium to rubidium as expected. While it was sufficient for the case of alkali metals to deal with a single occupied band, the expressions derived in this paper can be easily extended to include more than one band, which will be necessary in the analysis of the hyperfine properties of heavier polyvalent metals such as lead, thallium, and platinum; in particular, the RK and PD interactions in these metals. Also in our analysis, we have utilized relativistic single-OPW functions, which is a good approximation for the monovalent alkali metals except lithium. Since our primary interest here was in the assessment of the importance of relativistic effects, rather than in obtaining good agreement with experiment, we have not sought to analyze the effect of using more than one-OPW functions. The use of many-OPW functions is expected in general to reduce the s character somewhat and, therefore, our estimates of the Knight shift and RK parameter. On the other hand, the PD parameter B_{12} should not be affected significantly by the use of many-OPW functions, since any decrease of s character is likely to be compensated by the gain in the p character of the wave function. Further, since relativistic effects on hyperfine properties arise primarily from the core region, the percentage wise corrections over NR theory should not be expected to change appreciably in going from single- to many-OPW wave functions for both relativistic and NR theories.

As far as comparison with experiment, relativistic effects appear to improve the results for the Knight shifts, relaxation times, and RK parameters, and produce good agreement with experiment. The agreement with experiment is not as good for the RK parameter in

TABLE VI. Results for PD coupling parameter B_{12} expressed in cycles.

Metal	$J_{II,22}$ ($s_{1/2}s_{1/2}-s_{1/2}s_{1/2}$)	$J_{II,11}$ ($s_{1/2}s_{1/2}-p_{1/2}p_{1/2}$)	$J_{II,12}+J_{II,21}$ ($s_{1/2}s_{1/2}-p_{1/2}p_{3/2}$) + ($s_{1/2}s_{1/2}-p_{3/2}p_{1/2}$)	Total B_{12} ^a (Rel)	B_{12} (NR)	B_{12} Experiment
Rb ⁸⁵	-0.12	+0.65	-0.08	0.45	0.40	11 ± 2
Cs ¹³³	-0.69	+3.66	-0.42	2.65	2.33	35 ± 5

^a The entries in this and previous columns include the numerical factors of Eq. (42).

rubidium, while for the PD constants in both metals, there is a rather strong disagreement between theory and experiment. In making a final assessment between theory and experiment, it would be necessary to include other mechanisms that could influence the magnitudes of hyperfine properties. Two possible important mechanisms are core-polarization^{22,23} and core-conduction correlation effects. A quantitative analysis of the core-conduction correlation effects would be rather difficult. However, in view of the dynamic independence of core and conduction electrons,²⁴ its effect may be expected to be small. For the core-polarization effects, one could make use of one-electron procedures available in the literature.^{22,23} It would be interesting to investigate these effects particularly for the RK and PD interactions, as they involve products of hyperfine matrix elements leading to an enhancement in the importance of core polarization as was also found in the case of relativistic effects. A definitive assessment of agreement between theory and experiment can be made only after an analysis of CP effects is available. However, it does not seem to us that the order-of-magnitude dif-

ference between present theory and experiment for the PD constant can be removed by inclusion of core-polarization and core-conduction correlation effects. It would be helpful if some remeasurements of the PD constants were carried out, perhaps using powerful echo techniques. Similar results for the RK parameter in rubidium would be also helpful in explaining the much less important difference between theory and experiment. In addition, further light can be shed on the experimental-versus-theoretical situations by calculating RK and PD parameters in heavier metals like lead,²⁵ platinum,²⁶ and thallium,^{27,14} where accurate experiments have been carried out.

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APPENDIX: SECOND-ORDER ENERGY EXPRESSIONS IN THEORY OF INDIRECT NUCLEAR SPIN-SPIN INTERACTION

For the sake of brevity in the text and retaining continuity in the discussions, the second-order energy expressions occurring in the theory of indirect spin-spin interaction among nuclei will be presented in this Appendix.

Using Eq. (11) for the hyperfine matrix elements in the second-order energy expression in Eq. (25), we obtain the following expression for ΔE_{12} which holds for a Fermi-surface of any general shape.

$$\begin{aligned} \Delta E_{12} = & 2e^2 \mu_{1z} \mu_{2z} \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} \left\{ [\epsilon(\mathbf{k}\sigma) - \epsilon(\mathbf{k}'\sigma')]^{-1} \sum_{LM} \sum_{\mu\nu} \sum_{\mu'\nu'} (-)^{\nu'} Y_{\mu\nu}^*(\hat{k}) Y_{\mu'\nu'}(\hat{k}') Y_L^{M*}(\hat{R}_{12}) j_{\mu}(kR_{12}) j_{\mu'}(k'R_{12}) \right. \\ & \times \left[\frac{(2\mu+1)(2\mu'+1)(2L+1)^{-1/2}}{4\pi} \begin{pmatrix} \mu' & L & \mu \\ -\nu' & M & \nu \end{pmatrix} \begin{pmatrix} \mu' & L & \mu \\ 0 & 0 & 0 \end{pmatrix} \sum_{\kappa_1\kappa_2\mu_1} \sum_{\kappa_3\kappa_4\mu_4} a_{\kappa_1\mu_1}^*(\mathbf{k},\sigma) a_{\kappa_2\mu_1}(\mathbf{k}',\sigma') \right. \\ & \left. \left. \times a_{\kappa_3\mu_4}^*(\mathbf{k}',\sigma') a_{\kappa_4\mu_4}(\mathbf{k},\sigma) A_{\kappa_1\kappa_2}^{\mu_1} A_{\kappa_3\kappa_4}^{\mu_4} [W_{\kappa_1\kappa_2}(k,k') + W_{\kappa_2\kappa_1}(k',k)] [W_{\kappa_3\kappa_4}(k,k') + W_{\kappa_4\kappa_3}(k',k)] \right] \right\}. \quad (A1) \end{aligned}$$

In Eq. (A1), the band indices n and n' are dropped for brevity and will be recalled wherever necessary. For the alkali metals, no specification of n and n' is required because there is only a single occupied band.

Equation (A1) can be reduced further by introducing the definition of $a_{\kappa\mu}$ in Eq. (8) and carrying out angular integration in \mathbf{k} space. Equation (27) results in this manner with $T_{\sigma\sigma'}^{(0)}(k,k')$ given by

$$\begin{aligned} T_{\sigma\sigma'}^{(0)}(k,k') = & \frac{16}{\pi} \sum_{\mu\nu} (-1)^{\nu} Y_0^{0*}(\hat{R}_{12}) \begin{pmatrix} \mu & 0 & \mu \\ \nu & 0 & -\nu \end{pmatrix} \begin{pmatrix} \mu & 0 & \mu \\ 0 & 0 & 0 \end{pmatrix} (2\mu+1)^2 j_{\mu}(kR_{12}) j_{\mu}(k'R_{12}) \\ & \times \sum_{\kappa_1\kappa_2\mu_1} \sum_{\kappa_3\kappa_4\mu_4} (-1)^{l_1+l_3-l_2-l_4} \left[\frac{(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)^{-1/2}}{4\pi} \right] (-1)^{\sigma+\sigma'-2\mu_1} C^*(l_1\frac{1}{2}j_1; \mu_1-\sigma, \sigma) \\ & \times C(l_2\frac{1}{2}j_2; \mu_1-\sigma', \sigma') C(l_3\frac{1}{2}j_3; \mu_4-\sigma', \sigma') C(l_4\frac{1}{2}j_4; \mu_4-\sigma, \sigma) A_{\kappa_1\kappa_2}^{\mu_1} A_{\kappa_3\kappa_4}^{\mu_4} \begin{pmatrix} l_1 & \mu & l_4 \\ \sigma-\mu_1 & \nu & \mu_4-\sigma \end{pmatrix} \begin{pmatrix} l_1 & \mu & l_4 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \begin{pmatrix} l_2 & \mu & l_3 \\ \sigma'-\mu_1 & \nu & \mu_4-\sigma' \end{pmatrix} \begin{pmatrix} l_2 & \mu & l_3 \\ 0 & 0 & 0 \end{pmatrix} \{ W_{\kappa_1\kappa_2}(k,k') + W_{\kappa_2\kappa_1}(k',k) \} \{ W_{\kappa_3\kappa_4}(k',k) + W_{\kappa_4\kappa_3}(k',k) \}. \quad (A2) \end{aligned}$$

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