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Exchange Core-Polarization Effects on Indirect Nuclear Spin Interactions—Application to Rubidium and Cesium Metals

S. D. Mahanti
Michigan State University, East Lansing, Michigan 48823

and

T. P. Das
University of Utah, Salt Lake City, Utah 84112

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The role of exchange core-polarization (ECP) effects in the study of indirect nuclear spin interactions (INSI) in the alkali metals rubidium and cesium is discussed. The ECP contributions to the INSI parameters A_{12} (Ruderman-Kittel) and B_{12} (pseudodipolar) are evaluated and compared with other contributions. The theoretical values of A_{12} are in reasonable agreement with experiment. However, the incorporation of the ECP contributions to B_{12}, $(B_{12})^{\text{dip}}_{\text{ECP}}$ (in this ECP process, the conduction electrons are polarized by the electron-nuclear dipolar interaction, and the exchanged polarized core electrons interact with the nucleus via the Fermi contact interaction) does not improve the order-of-magnitude disagreement between theory and experiment. The importance of additional ECP processes whose inclusion can improve the theoretical situation is briefly discussed.

I. INTRODUCTION

Both steady-state[1] and transient NMR[2] experiments yield parameters describing the indirect nuclear spin interactions (INSI)[3,4] in metals. There are two such INSI parameters, namely, the Rudermann-Kittel-Kasuya-Yosida (RKKY) parameter A_{12} and the pseudodipolar (PD) parameter B_{12}. The physical mechanism for the origin of these parameters is well understood, and the nature of the contributions to them from the conduction electrons has been discussed by several authors.[3-5] In an earlier paper,[5] we have made a quantitative evaluation of A_{12} and B_{12} from the conduction electrons for the two alkali metals rubidium and cesium, including relativistic effects.[6] In these calculations where single orthogonalized plane waves (OPW) were used for the conduction-electron wave function, A_{12} was found to be in reasonable agreement with the experiment. For example, the theoretical value of A_{12} for cesium including relativistic effects was found to be 187 cps, compared to the experimental value[1] 200 ± 10 cps. The theoretical and experimental values of A_{12} for rubidium were 24 and 50 ± 5 cps. More realistic representation of the conduction-electron wave function (for example, a linear combination of OPW) is expected to reduce the theoretical values. However, the quality of the agreement between theory and experiment for A_{12} is not expected to change appreciably.

In contrast, the agreement for B_{12} was found[5,6] to be quite poor, the theoretical values being an order of magnitude smaller than the experimental (for both metals). Although a certain degree of uncertainty can be associated with the experimental numbers because of their smallness (35 ± 5 for Cs and 11 ± 2 for Rb), the disagreement is quite puzzling. To investigate the cause of this disagreement between theory and experiment for the alkali metals, a different metal, lead, was chosen. For lead, the experimental values[2] have been obtained by transient NMR techniques (expected to be more accurate compared to steady-state measurements) and are quite large. The experimental values of B_{12} and A_{12} are 2200 ± 200 and 4800 ± 500 cps. The theoretical values[7] were found to be in good agreement with the experiment for both B_{12} (1490 cps) and A_{12} (4882 cps). The direct contribution to B_{12} associated with the polarization of the conduction electrons is quite large because of the appreciable p character in the wave function near the Fermi surface. The small direct contribution to B_{12} in the case of alkali metals can then be attributed to the weak p character of the conduction-electron wave function.

In these calculations[5,6] the core electrons surrounding the nuclei were assumed to be magnetically neutral and did not contribute to A_{12} and B_{12}. It has been shown[8,9] that for the alklai metals, the core electrons can contribute quite significantly to the Knight shift K_s and the nuclear spin relaxation time T_1 through exchange polarization by the conduction electrons. One therefore expects this exchange core-polarization (ECP) effect to be also important for the INSI. Thus, one of the nuclei, say, with spin $\vec{I}_1$ and located at the position $\vec{R}_1$, can polarize the conduction electrons via either the Fermi contact or the spin-dipolar interaction. The spin-polarized conduction electrons, besides interacting directly with a second nuclear spin $\vec{I}_2$ located at $\vec{R}_2$, can also exchange polarize the core electrons surrounding the second nucleus. These polarized core electrons can in turn interact with the nuclear spin $\vec{I}_2$ via either the Fermi contact or the spin-dipolar interaction leading to an effective additional INSI between the two nuclear spins $\vec{I}_1$ and $\vec{I}_2$.

The moment perturbation (MP) procedure[8,9] has been utilized for obtaining the core electron contributions to INSI. This procedure entails a perturbation of the core electron wave functions by the hyperfine interaction and the evaluation of their exchange energy with the spin-polarized conduction electrons.

In Sec. II we describe the general procedure for obtaining the ECP contributions to both A_{12} and B_{12}. The pertinent expressions are given in simplified forms amenable to numerical calculation. In Sec. III, we present the results of our numerical calculations on rubidium and cesium and compare the theoretical results with the experiment.

II. ECP CONTRIBUTIONS TO INSI–GENERAL EXPRESSIONS

The Hamiltonian representing the hyperfine interaction between the conduction electrons and the two nuclear spins $\vec{I}_1$ and $\vec{I}_2$ is given[10] by

$$\mathcal{H} = \mathcal{H}(\vec{R}_1) + \mathcal{H}(\vec{R}_2) , \tag{1}$$

with

$$\mathcal{H}(\vec{R}_i) = a_i \sum_l \vec{I}_i \cdot \vec{s}_l \, \delta(\vec{r}_{il}) - \gamma_i \gamma_e \hbar^2 \left[\frac{\vec{I}_i \cdot \vec{s}_l}{r_{il}^3} - \frac{3(\vec{I}_i \cdot \vec{r}_{il})(\vec{s}_l \cdot \vec{r}_{il})}{r_{il}^5} \right] \tag{2}$$

and

$$a_i = \tfrac{16}{3} \pi \gamma_i \gamma_e \hbar^2 , \tag{3}$$

where γ_i and γ_e are the gyromagnetic ratios of ith nucleus and electron, respectively, and r_{il} is the distance of the lth electron from the ith nucleus. The orbital hyperfine interaction has not been included in Eq. (2) since it does not contribute to ECP effects. The nuclear spins are assumed to be oriented along the z direction. In the absence of the hyperfine Hamiltonian [Eq. (1)], the net conduction-electron spin density $\sigma_z^0(\vec{r})$ (also in the z direction)

$$\sigma_z^0(\vec{r}) = \sum_{\vec{k}(\mathrm{occ})} \left[|\psi_{\vec{k}\alpha}^0(\vec{r})|^2 - |\psi_{\vec{k}\beta}^0(\vec{r})|^2 \right] \tag{4}$$

vanishes. In Eq. (4), $\psi_{\vec{k}\alpha}^0$ and $\psi_{\vec{k}\beta}^0$ are the conduction-electron wave functions in the absence of hyperfine perturbation and α and β refer to spin-"up" and spin-"down" states, respectively. To obtain the total energy of interaction between two nuclei via the ECP effect, let us assume that nucleus 1 perturbs the conduction electrons and nucleus 2 perturbs the core electrons. The perturbed conduction and core electron states $\psi_{\vec{k}\alpha}$ and $U_{j\alpha}$ are given by

$$\begin{aligned} \psi_{\vec{k}\alpha} &= \psi_{\vec{k}\alpha}^0 + \delta\psi_{\vec{k}\alpha}^{c,1} + \delta\psi_{\vec{k}\alpha}^{d,1} , \\ U_{j\alpha} &= U_{j\alpha}^0 + \delta U_{j\alpha}^{c,2} + \delta U_{j\alpha}^{d,2} , \end{aligned} \tag{5}$$

where the superscripts c and d refer to the perturbations by contact and dipolar parts of the hyperfine Hamiltonian. For simplicity we consider only one core state described by $j\alpha$. A similar set of equations as (5) holds for the down spin states $\psi_{\vec{k}\beta}$ and $U_{j\beta}$. Since we are interested in the INSI which is linear in the nuclear spins $\vec{I}_1$ and $\vec{I}_2$, the perturbed parts of both $\psi_{\vec{k}\alpha}$ and $U_{j\beta}$ need to be considered only up to first order in the nuclear moments. For example,

$$\delta\psi_{\vec{k}\alpha}^{c,1} = \sum_{\vec{k}'} \frac{\langle \vec{k}'\alpha | a_1 I_{1z} s_z \delta(\vec{r} - \vec{R}_1) | \vec{k}\alpha \rangle}{E(\vec{k}) - E(\vec{k}')} \psi_{k'\alpha}^0 , \tag{6}$$

where $|\vec{k}\alpha\rangle$ represents the unperturbed Bloch state $\psi_{\vec{k}\alpha}^0$. The band indices have been omitted in the summation over excited states in Eq. (6) and can be introduced whenever necessary. The energy $E(\vec{k})$ is assumed to be spin independent.

The total exchange energy associated with conduction electrons with spin α and a particular core electron $(j\alpha)$ is given by

$$E_{\mathrm{ex},\alpha}^j = - \sum_{\vec{k}(\mathrm{occ})} \langle \psi_{\vec{k}\alpha}(\vec{r}_1) U_{j\alpha}(\vec{r}_2 - \vec{R}_2) | e^2/r_{12} | \times U_{j\alpha}(\vec{r}_1 - \vec{R}_2) \psi_{\vec{k}\alpha}(\vec{r}_2) \rangle , \tag{7}$$

where $\vec{k}(\mathrm{occ})$ refers to the summation over occupied $\vec{k}$ states only. In Eq. (7), it is assumed that the perturbed core and conduction-electron wave functions $U_{j\alpha}$ and $\psi_{\vec{k}\alpha}$ are orthogonal. Corrections due to lack of orthogonality will be included in the numerical calculations. In evaluating the exchange energy (7), we have not included the possibility where the conduction electrons are polarized by nucleus 2 and the core electrons by nucleus 1. This leads to a contribution exactly equal to (7).

On substituting for the perturbed core and conduction-electron wave function in Eq. (7), one obtains several types of terms contributing to the exchange energy. We need to consider only those terms which lead to a coupling between the two nuclear spins $\vec{I}_1$ and $\vec{I}_2$. There are 16 such terms which can be divided into three different categories. The first one (A),

$$\begin{aligned} \Delta E_{\mathrm{ex},\alpha}^j(A) = - \sum_{\vec{k}(\mathrm{occ})} \Big[&\langle \psi_{\vec{k}\alpha}^0(\vec{r}_1) U_{j\alpha}^0(\vec{r}_2 - \vec{R}_2) | e^2/r_{12} | \delta U_{j\alpha}^{c,2}(\vec{r}_1 - \vec{R}_2) \delta\psi_{\vec{k}\alpha}^{c,1}(\vec{r}_2) \rangle \\ &+ \langle \psi_{\vec{k}\alpha}^0(\vec{r}_1) \delta U_{j\alpha}^{c,2}(\vec{r}_2 - \vec{R}_2) | e^2/r_{12} | \delta\psi_{\vec{k}\alpha}^{c,1}(\vec{r}_2) U_{j\alpha}^0(\vec{r}_1 - \vec{R}_2) \rangle + \mathrm{c.\,c.} \Big] , \end{aligned} \tag{8}$$

arising purely from the contact interaction, dominates the ECP contribution to RKKY coupling. In the second category, (B), we have terms which arise from one order of contact and one order of dipole perturbation and are the leading ECP contributors to PD coupling. These are

$$\Delta E^{j}_{\mathrm{ex},\alpha}(B) = -\sum_{\vec{k}}[\langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)U^{0}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{c,1}_{\vec{k}\alpha}(\vec{r}_2)\delta U^{d,2}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle + \langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)U^{0}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{d,1}_{\vec{k}\alpha}(\vec{r}_2)\delta U^{c,2}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle$$

$$+\langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)\delta U^{c,2}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{d,1}_{\vec{k}\alpha}(\vec{r}_2)U^{0}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle + \langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)\delta U^{d,2}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{c,1}_{\vec{k}\alpha}(\vec{r}_2)U^{0}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle + \mathrm{c.c.}\,] , \quad (9)$$

where for convenience we have replaced $|e^2/r_{12}|$ by $|\,|$. Finally, the third category, (C), is associated with purely dipolar contributions. These terms contribute both to A_{12} and B_{12} and are given by

$$\Delta E^{j}_{\mathrm{ex},\alpha}(C) = -\sum_{\vec{k}}[\langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)U^{0}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{d,1}_{\vec{k}\alpha}(\vec{r}_2)\delta U^{d,2}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle$$

$$+\langle \psi^{0}_{\vec{k}\alpha}(\vec{r}_1)\delta U^{d,2}_{j\alpha}(\vec{r}_2-\vec{R}_2)|\,|\delta\psi^{d,1}_{\vec{k}\alpha}(\vec{r}_1)U^{0}_{j\alpha}(\vec{r}_1-\vec{R}_2)\rangle + \mathrm{c.c.}\,] . \quad (10)$$

Before simplifying $\Delta E_{\mathrm{ex}}(A)$ to a form which can be computed numerically, we briefly discuss the other two contributions to the exchange energy $\Delta E_{\mathrm{ex}}(B)$ and $\Delta E_{\mathrm{ex}}(C)$. The latter and a part of the former involve perturbations of the core states by the electron-nuclear dipolar interaction. All the core states s, p, and d can take part in these contributions and their numerical evaluation becomes quite involved. $\Delta E_{\mathrm{ex}}(B)$ does not contribute to $(A_{12})_{\mathrm{ECP}}$. The contribution to $(B_{12})_{\mathrm{ECP}}$ from $\Delta E_{\mathrm{ex}}(B)$ can be divided into two parts. One, where the conduction electrons are perturbed by the dipolar interaction and the core electrons are perturbed by the Fermi contact interaction, we denote as $(B_{12})^{\mathrm{cont}}_{\mathrm{ECP}}$. The second, where the conduction electrons are perturbed by the contact interaction and the core electrons by the dipolar interaction, we denote as $(B_{12})^{\mathrm{dip}}_{\mathrm{ECP}}$. We have made a numerical evaluation of $(B_{12})^{\mathrm{cont}}_{\mathrm{ECP}}$ only. The importance of $(B_{12})^{\mathrm{dip}}_{\mathrm{ECP}}$ and the contribution to $(A_{12})_{\mathrm{ECP}}$ and $(B_{12})_{\mathrm{ECP}}$ from $E_{\mathrm{ex}}(C)$ [Eq. (10)] will be discussed in Sec. III.

In order to simplify $\Delta E_{\mathrm{ex}}(A)$, we rewrite $\delta\psi^{c,1}_{k\alpha}$ and $\delta U^{c,2}_{j\alpha}$ in Eq. (8) in the following form:

$$\delta\psi^{c,1}_{\vec{k}\alpha}(\vec{r}) = \tfrac{1}{2}I_{1z}a_1\sum_{\vec{k}'}\frac{\langle \vec{k}'\,|\,\delta(\vec{r})\,|\,\vec{k}\rangle}{E(\vec{k})-E(\vec{k}')}\,e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_1}\,\psi^{0}_{\vec{k}'\alpha}(\vec{r}) \quad (11)$$

and

$$\delta U^{c,2}_{j\alpha}(\vec{r}) = \tfrac{1}{2}I_{2z}a_2\delta\Phi_j(\vec{r}) = \left(\frac{2m}{a_0\hbar^2}\right)\frac{1}{2}I_{2z}a_2\,\frac{\delta P_j(r)}{r}\,Y_{00}(\hat{r}) , \quad (12)$$

where a_1 and a_2 are already defined in Eq. (3), m is the electron mass, and a_0 is the Bohr radius. The second-order exchange energy associated with A-type terms is then given by

$$\Delta E_{\mathrm{ex}}(A) = 8I_{1z}I_{2z}a_1a_2\frac{1}{4}\sum_{j}\sum_{\vec{k}\,\vec{k}'}\frac{\langle \vec{k}'\,|\,\delta(\vec{r})\,|\,\vec{k}\rangle}{E(\vec{k})-E(\vec{k}')}\,e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_{12}}$$

$$\times[F^{1}_{j}(\vec{k},\vec{k}') + F^{2}_{j}(\vec{k},\vec{k}')] . \quad (13)$$

The factor of 8 is the product of three factors of 2 each from spin summation, complex conjugation, and interchange of the roles of the two nuclear spins $\vec{I}_1$ and $\vec{I}_2$. $F^{i}_{j}(\vec{k},\vec{k}')$ are the two exchange integrals defined by

$$F^{1}_{js}(\vec{k},\vec{k}') = -\langle \psi^{0}_{\vec{k}'}(\vec{r}_1)U^{0}_{js}(\vec{r}_2)|\,|\psi^{0}_{\vec{k}}(\vec{r}_2)\delta\Phi_{js}(\vec{r}_1)\rangle \quad (14)$$

and

$$F^{2}_{js}(\vec{k},\vec{k}') = -\langle \psi^{0}_{\vec{k}'}(\vec{r}_1)\,\delta\Phi_{js}(\vec{r}_2)|\,|\psi^{0}_{\vec{k}}(\vec{r}_2)\,U^{0}_{js}(\vec{r}_1)\rangle . \quad (15)$$

The summation on j in Eq. (13) goes over all the occupied s cores (js). In deriving the expression for $\Delta E_{\mathrm{ex}}(A)$, the nuclear spins were assumed to be oriented along the z direction. For the cubic systems of interest here, the coefficients of $I_{1x}I_{2x}$ and $I_{1y}I_{2y}$ terms are exactly same.

The exchange integrals $F^{i}_{js}(\vec{k},\vec{k}')$ can be evaluated using properly normalized Bloch functions $\psi^{0}_{\vec{k}}$ and moment perturbed functions $\delta\Phi_j$. On expanding the Bloch functions in spherical harmonics,[5,9] Eqs. (14) and (15) lead to

$$F^{i}_{js}(\vec{k},\vec{k}') = \frac{4\pi}{\Omega}\left(\frac{e^2}{a_0}\,\frac{2m}{a_0\hbar^2}\right)\sum_{l} G^{i,l}_{js}(k,k')\,P_l(\vec{k}\cdot\vec{k}') , \quad (16)$$

where $P_l(x)$ represents the lth-order Legendre polynomial. The quantities $G^{i,l}_{js}$ are given by (in atomic units)

$$G^{1,l}_{js}(k,k') = -4\pi\int_0^{r_s}\int_0^{r_s}\chi_l(k',r)\,\frac{\delta P_{js}(r)}{r}\,\chi_l(k,r')$$

$$\times\,\frac{P_{js}(r')}{r'}\,\frac{r_<^{l}}{r_>^{l+1}}\,r^2r'^2\,dr\,dr' , \quad (17)$$

$$G^{2,l}_{js}(k,k') = -4\pi\int_0^{r_s}\int_0^{r_s}\chi_l(k',r)\,\frac{P_{js}(r)}{r}\,\chi_l(k,r')$$

$$\times\,\frac{\delta P_{js}(r')}{r'}\,\frac{r_<^{l}}{r_>^{l+1}}\,r^2r'^2\,dr\,dr' ,$$

TABLE I. Various contributions to A_{12} calculated in single-OPW approximation and estimated using many-OPW approximation. All the numbers are in units of cps. cont is the Fermi contact contribution, ECP is the exchange core polarization; NR is nonrelativistic; Rel is relativistic [additional relativistic contribution beyond $(A_{12})_{\mathrm{NR}}$]; expt is the experiment; tot is the total theoretical value.

	One OPW		Many OPW	
	Cs	Rb	Cs	Rb
$(A_{12})_{\mathrm{NR}}^{\mathrm{cont}}$	115.0	20.6	80.5	14.4
$(A_{12})_{\mathrm{ECP}}$	43.3	9.4	30.3	6.6
$(A_{12})_{\mathrm{Rel}}^{\mathrm{cont}}$	72.2	3.4	50.5	2.4
$(A_{12})_{\mathrm{other}}$[a]	9.7	2.2	9.7	2.2
$(A_{12})_{\mathrm{tot}}$	240.2	35.6	171.0	25.6
$(A_{12})_{\mathrm{expt}}$	200.0 ± 10	50.0 ± 5		

[a] other = (second-order dipolar) + (orbital) + (correlation) (see Ref. 5).

where $\chi_l(k, r)$ is the radial part of the conduction-electron wave function associated with the lth angular component.[5] It is straightforward to derive an expression for the ECP contribution $(A_{12})_{\mathrm{ECP}}$ to A_{12} using Eqs. (13), (16), and (17). The summations over $\vec{k}$ and $\vec{k}'$ in Eq. (13) are carried out in a spherical band approximation. The details of such summations have been given earlier[5] and will not be reproduced. One thus has

$$(A_{12})_{\mathrm{ECP}} = \sum_l (A_{12})_{\mathrm{ECP},l} = \sum_l \sum_j \beta_{12} I_{lj} \ , \tag{18}$$

where

$$\beta_{12} = -\frac{\Omega}{R_{12}^4}\left(\frac{2m}{\hbar^2}\right)^2 \frac{e^2}{a_0^3} \frac{1}{(2\pi)^3} a_1 a_2 \ , \tag{19}$$

and

$$I_{0j} = 2\int_0^{\chi_F} m_t(k)\,|\psi_k(0)|^2 G_{js}^{1;0}(k,k)\,\chi\sin\chi\,d\chi \ , \tag{20}$$

$$I_{1j} = 4\int_0^{\chi_F} m_t(k)\,|\psi_k(0)|^2 G_{js}^{1;1}(k,k)\,(\chi\sin\chi + \cos\chi) \times(\sin\chi - \chi\cos\chi)\,\frac{d\chi}{\chi} \ , \tag{21}$$

$$I_{2j} = 2\int_0^{\chi_F} m_t(k)\,|\psi_k(0)|^2 G_{js}^{1;2}(k,k) \times[(3-\chi^2)\cos\chi + 3\chi\sin\chi]\,j_2(\chi)\,d\chi \ , \tag{22}$$

where $\chi = kR_{12}$, $\chi_F = k_F R_{12}$, $m_t(k)$ is the thermal (density-of-states) mass, and $j_2(\chi)$ is the second-order spherical Bessel function. It is interesting to compare $(A_{12})_{\mathrm{ECP},s}$ with $(A_{12})_{\mathrm{NR}}^{\mathrm{cont}}$, the direct second-order contribution to INSI associated with the Fermi contact interaction. Using Eq. (22) of Ref. 5, we have

$$\frac{(A_{12})_{\mathrm{ECP},s}}{(A_{12})_{\mathrm{NR}}^{\mathrm{cont}}} = 4\left[\int_0^{k_F} kR_{12} m_t(k)\left(\sum_j G_{js}^{1;0}(k,k)\right)|\psi_k(0)|^2 \sin 2kR_{12}\,d(kR_{12}) \bigg/ \int_0^{k_F} kR_{12}\,|\psi_k(0)|^4 \sin 2kR_{12}\,d(kR_{12})\right] . \tag{23}$$

The factor 4 is quite important and increases the strength of ECP effects on A_{12}. In Sec. III we present the results of our numerical calculation for $(A_{12})_{\mathrm{ECP}}$ in rubidium and cesium using Eqs. (20)–(22).

An expression for $(B_{12})_{\mathrm{ECP}}^{\mathrm{cont}}/(B_{12})_{\mathrm{NR}}$, where $(B_{12})_{\mathrm{NR}}$ is the direct contribution to the pseudodipolar interaction, can be obtained from the second and the third terms of Eq. (9). The form of this expression is similar to Eq. (23). $|\psi_{\vec{k}}(0)|^2$ in the numerator and one of the $|\psi_{\vec{k}}(0)|^4$ $[|\psi_{\vec{k}}(0)|^2 \times |\psi_{\vec{k}}(0)|^2]$ in the denominator are replaced by the matrix element of the operator $(1/r^3)Y_{20}(\hat{r})$. The phase factor (in both the numerator and the denominator) $\chi\sin 2\chi$ $(\chi = kR_{12})$ is also changed to $(\cos\chi - \chi\sin\chi)(\sin\chi - \chi\cos\chi)/\chi$ [see Eqs. (50e) and (51) of Ref. 5]. The important contribution to the matrix element in the above case has been assumed to come from the p part of the conduction-electron wave function.

III. RESULTS AND DISCUSSION

The results of our ECP calculation using Eqs. (20)–(22) are presented in Table I under the one-OPW column. Different contributions to A_{12} from conduction electrons alone are also listed in the same table. All the entries have been calculated using properly normalized single-OPW functions. These were constructed by orthogonalizing plane waves to available Hartree-Fock core states.[11] We find that the contribution to $(A_{12})_{\mathrm{ECP}}$ from the s part of the conduction-electron wave function is dominant and nearly two orders of magnitude larger than that from p and d parts. $(A_{12})_{\mathrm{ECP},s}$ is nearly 38.0% of the direct contribution $(A_{12})_{\mathrm{NR}}^{\mathrm{cont}}$ for cesium and 45.0% for rubidium. The ECP contributions to the Knight shift for these two metals were 20.0 and 23.0% of the respective direct contributions.[9] The percentagewise contribution of ECP to A_{12} is roughly twice that to K_s. This is a consequence of the fact that $(A_{12})_{\mathrm{ECP}}$ involves two orders of hyperfine interaction, whereas $K_{s,\mathrm{ECP}}$ only involves one.

The relativistic contribution to A_{12}, $(A_{12})_{\mathrm{Rel}}^{\mathrm{cont}}$ has been obtained by subtracting the nonrelativistic contact contribution $(A_{12})_{\mathrm{NR}}^{\mathrm{cont}}$ from the results of Ref. 6. Among several relativistic effects, the most dominant ones in the study of hyperfine properties are the mass velocity[6,12] and Darwin corrections.[6,12] Spin-orbit effects do not affect the spin density associated with the s electrons. $(A_{12})^{\mathrm{cont}}_{\mathrm{Rel}}$ refers to the relativistic contribution to A_{12} from the s part of the conduction electrons alone. The contribution to A_{12} from p and d parts and relativistic corrections to these are quite negligible.[6] For cesium, it is seen that the relativistic effects are more significant compared to ECP. For rubidium, a relatively light metal, the ECP effects are more important. The results of ECP and relativistic calculations clearly point out the necessity of including both these effects in the analysis of indirect spin-spin interactions in metals.

In comparing the theoretical value of A_{12} with experiment, we still have another important factor to consider. This has to do with the use of single-OPW functions for the conduction-electron wave function. The actual wave function for the electrons has a many-OPW character.[12,13] An excessive amount of computational effort would be required if one were to carry out a complete band-structure analysis for the entire occupied $\vec{k}$ space (not just the Fermi surface) that one needs in the calculation of A_{12}. However, from the results on K_s obtained by using many-OPW functions[13] we can arrive at some reasonable conclusions regarding the change in A_{12} from its one-OPW value when a more realistic wave function is used. It was found for cesium[13] that the spin density at the nucleus associated with electrons at the Fermi surface decreased by 18% in going from a single- to many-OPW functions. One therefore overestimates the s content of the wave function in a single-OPW approximation. However, as one moves from the Fermi surface to the Brillouin zone center, the s character of the occupied band increases (for the alkali metals). Consequently, single-OPW functions give increasingly better representations of the conduction-electron wave functions as one approaches the zone center. Remembering that A_{12} involves the second power of the spin density at the nucleus and that the region of $\vec{k}$ space contributing to A_{12} is not confined solely to the Fermi surface (as in K_s), it is reasonable to expect that the decrease in $(A_{12})^{\mathrm{cont}}_{\mathrm{NR}}$ in going from a single- to many-OPW representation would be about 30% for cesium. For rubidium, no many-OPW calculation of K_s is available. We have therefore utilized for this metal the same reduction factor as for cesium to obtain a many-OPW estimate of $(A_{12})^{\mathrm{cont}}_{\mathrm{NR}}$. The many-OPW estimates of $(A_{12})^{\mathrm{cont}}_{\mathrm{NR}}$ for both metals are included in Table I.

Next we consider the effect of using many-OPW functions on the relativistic contribution to A_{12}, i.e., $(A_{12})^{\mathrm{cont}}_{\mathrm{Rel}}$. A complete band calculation using Dirac OPW's[6] is extremely complicated. It is reasonable to assume that the reduction in the s content of the conduction-electron wave function in going from a single- to many-OPW representation is the same in both nonrelativistic and relativistic cases, the only difference between these two cases being in the strength of the hyperfine matrix elements (spin density). Thus we reduce $(A_{12})^{\mathrm{cont}}_{\mathrm{Rel}}$ by 30% for both cesium and rubidium and enter these reduced values in Table I. This approximation,[14] we believe, gives a lower limit to the s content of the conduction-electron wave function.

TABLE II. One-OPW results for B_{12} (in cps units).

	Cs	Rb
$(B_{12})_d$	2.07	0.36
$(B_{12})_{\mathrm{ECP}}$	0.44	0.09
$(B_{12})_{\mathrm{tot}}$	2.51	0.45
$(B_{12})_{\mathrm{expt}}$	35.00 ± 5	11.00 ± 2

It is relatively difficult to assess the change in $(A_{12})_{\mathrm{ECP},s}$ in going to a many-OPW representation. In an earlier paper[9] we have seen that the scaling down of the s part of the ECP contribution to spin density by the same factor as the direct spin density works extremely well for K_s. This is, however, not true for the non-s ECP contributions. But since the contribution to $(A_{12})_{\mathrm{ECP}}$ from the s part is at least an order of magnitude larger than from the non-s parts, the scaling down procedure is expected to be a good approximation for obtaining a many-OPW estimate of $(A_{12})_{\mathrm{ECP},s}$. Thus the entries of Table I for $(A_{12})_{\mathrm{ECP},s}$ are reduced by 30% to obtain the corresponding many-OPW entries in Table I.

The most difficult question of all is the evaluation of relativistic effects on $(A_{12})_{\mathrm{ECP},s}$. It is not possible to make a semiquantitative assessment of this effect from simple physical arguments. But most likely, the incorporation of relativistic effects will increase $(A_{12})_{\mathrm{ECP},s}$ appreciably since the inner core states, which are more relativistic, are involved. However, we do not attempt to make any estimate of this change in $(A_{12})_{\mathrm{ECP},s}$ in the present paper.

For the sake of completeness, we have included in Table I the contributions to A_{12} arising from orbital and dipolar effects. These constitute only a small part (8% for Cs and 10% for Rb) of the total contribution to A_{12}. Therefore, no attempt has been made to estimate the change in these contributions in going to a many-OPW representation.

Adding all the contributions to A_{12} listed in Table I, we see that $(A_{12})_{\mathrm{tot}}$ for cesium is 171.0 cps and for rubidium it is 26.0 cps. The agreement with experiment[1] for cesium (200.0 cps) is reasonably good when we note that the relativistic effect on ECP is expected to increase its contribution to $(A_{12})_{\mathrm{tot}}$ in the direction of experiment. The agreement with experiment[1] for rubidium (50.0 cps) is not as good. It is difficult to think of any additional mechanism which will improve upon the present theoretical value considerably. We believe that a complete numerical calculation of various contributions will not alter $(A_{12})_{\text{tot}}$ by more than 10% for rubidium where relativistic effects are relatively unimportant. Since the experimental value itself is so small (50 cps), an improved experimental value of A_{12}, preferably by spin-echo techniques,[2] is desirable for rubidium.

The direct contributions to B_{12} associated with the second-order dipolar processes are[5] negligibly small, the reason being the weak p character of the conduction-electron wave function. The major contribution to B_{12} comes from a combination of the Fermi contact and dipolar interactions. The small contribution to B_{12} which we have denoted as $(B_{12})_{\text{NR}}$ in the Table II, can again be related to the weak p character of the conduction-electron wave function. An improved calculation of $(B_{12})_{\text{NR}}$ using many-OPW functions is not expected to alter its value appreciably. The reason for this is that the increase in the p character of the wave function associated with an improved wave-function calculation is compensated by a decrease in the s character.

The MP functions utilized in the calculation of $(A_{12})_{\text{ECP}}$ can be used to calculate $(B_{12})_{\text{ECP}}^{\text{cont}}$. The results are given in the Table II, and are found to be nearly 20–25% of $(B_{12})_{\text{NR}}$ [we can ignore the difference between $(B_{12})_{\text{NR}}$ and $(B_{12})_d$ which includes the relativistic correction]. The inclusion of $(B_{12})_{\text{ECP}}^{\text{cont}}$ does not improve the agreement between theory and experiment. The reason for the small values of $(B_{12})_{\text{ECP}}^{\text{cont}}$ can be traced back to the weak p character since the matrix element of $1/r^3 Y_{20}(\hat{r})$ occurs in the calculation. Due to the weak p character, the contributions to $(B_{12})_{\text{ECP}}$ from the terms in Eq. (10) are also expected to be negligible.

Since the conduction electrons have strong s character, it is likely that $(B_{12})_{\text{ECP}}^{\text{dip}}$ can be large as it requires the perturbation of the conduction electrons by the Fermi contact interaction. In addition, the outermost p ($5p$ for Cs and $4p$ for Rb) and d ($4d$ for Cs and $3d$ for Rb) cores are highly polarizable and can therefore make $(B_{12})_{\text{ECP}}^{\text{dip}}$ quite large. One has here a process similar to Sternheimer enhancement[15] of the electric field gradient excepting that it is the spin-dipolar field produced by the spin-polarized conduction electrons that gets enhanced. A quantitative estimate of this enhancement has not been attempted because of the associated numerical difficulties. If $(B_{12})_{\text{ECP}}^{\text{dip}}$ also comes out to be small, then one has to look more critically at the experimental values of B_{12}. The experimental values are extremely small and may not be quite reliable. Improved experimental values of B_{12}, preferably obtained by spin-echo techniques, will be helpful.

IV. CONCLUSION

In this paper we have made an attempt to analyze the relative importance of various contributing physical effects in the study of indirect nuclear spin-spin interactions in rubidium and cesium metals. We find that the ECP contributions to (A_{12}) are quite significant. For cesium, which is a heavy metal (large Z), the relativistic effects are more important than the ECP. As regards the pseudodipolar coupling parameter B_{12}, the situation is still unclear. There is a good possibility that the inclusion of the contribution $(B_{12})_{\text{ECP}}^{\text{dip}}$ can remove the existing order-of-magnitude discrepancy between the theory and the experiment. A detailed numerical calculation will make this point clear. Improved experimental values of this parameter are also needed to bridge the gap between the theory and the experiment.

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