

Spin Polarization in the Electron Gas by a Magnetic Impurity: Theory of the Excess Knight Shift

Burke Ritchie*

Laboratory for Theoretical Studies, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 1 April 1970)

In the absence of an applied magnetic field, a process which will permit the existence of a Fermi contact hyperfine interaction at the Cu^{63} nucleus, which is not zero when summed over the randomly oriented spins of N conduction electrons, is the scattering of s -wave electrons from the exchange potential of an open-shell impurity atom located at a distance R from the Cu nucleus, and then the subsequent Fermi contact interaction at the Cu nucleus. This is a two-center scattering analog of the virtual process which is responsible for most of the Fermi contact hyperfine structure of open-shell atoms (polarization of the closed s core). The first-order energy due to the Fermi contact interaction with the conduction electrons at the Cu nucleus, which have first scattered from Mn impurity atoms, is calculated as a function of R . It is found to change sign before $R=4.8299$ (nearest-neighbor distance), between $R=4.8299$ and $R=8$, and between $R=8$ and $R=10$ a.u., suggesting experiments in which compression or expansion can change the lattice distances and studies of the dependence on impurity concentration. The exchange potential is presented as a function of electron velocity and R . For completeness, the Ruderman-Kittel-Kasuya-Yosida-type spin-density waves are presented as a function of the distance from the impurity for several values of R . Also, for $R=0$, an estimate is made of the exchange polarization potential due to the adiabatic polarization of the impurity by the scattering electrons; it is found to be significant.

INTRODUCTION

A number of years ago, Sugawara¹ found a small temperature-dependent excess Knight shift in dilute Cu-Mn, Cu-Fe, and Cu-Cr alloys. According to Yoshida,² the polarization of the conduction-electron spin is localized in the vicinity of the solute atom and the shift should not differ from that of the solvent metal. Sugawara finds this conclusion inconsistent with the experimental results and attributes the extra shift to the uniform polarization of s electrons due to s - d exchange. In this paper we will attempt to establish the range of the polarization as a function of host-atom-impurity-atom distance in an effort to explain Sugawara's findings. No satisfactory explanation of the extra shift has yet been proposed, although HWJG,³ using a theory based on the Kondo-Applebaum many-body singlet ground state of the magnetic-impurity problem, derived a contribution with a $1/r^2$ dependence (where r is the distance from the impurity) to the spin polarization near the impurity (due to the s - d exchange interaction⁴ of the form $J\vec{s}\cdot\vec{S}$, where \vec{s} and \vec{S} are the conduction-electron and impurity-atom spins, respectively, and J is a constant proportional to the magnitude of the exchange potential). The ordinary Ruderman-Kittel-Kasuya-Yosida⁵ (RKKY) spin-density oscillations fall off as $1/r^3$. Since the HWJG polarization has a fixed sign (in fact, it is negative definite and predicts an excess Knight shift in agreement with experiment) and will shift the center of mass of the NMR line, it is

interpreted as an extra-long-range spin polarization in the vicinity of the impurity atom, which is a measure of the extra Knight shift at the host nucleus. In this paper we interpret the additional shift as a zero-applied magnetic-field Fermi contact coupling of the conduction-electron spins with the spin of a particular Cu nucleus, whose strength is a function of the exchange potential of the impurity conduction-electron scattering system. The impurity atom has an open shell with unpaired spins. Thus, if we take a given impurity to be in a particular free-atom ground state $|LSM_L = LM_S = S\rangle$, then the spin-up electrons will exchange with the atomic d electrons while the spin-down electrons will not exchange with the atomic d electrons. This is analogous to the virtual process ("core polarization" discussed by Watson and Freeman⁶) which gives the major contribution to the Fermi contact hyperfine structure in atoms with open p or d shells due to the exchange of a closed-shell s electron with an open-shell electron, its scattering into an s excited state, then the contact interaction and the scattering back into the original state.^{7,8}

Therefore, many conduction electrons with randomly oriented spins will experience a net non-zero Fermi interaction with a Cu nucleus in the vicinity of an open-shell impurity atom, in the absence of an applied magnetic field. The strength of this interaction will depend on the magnitude of the exchange potential and thus on the distance between the Cu and impurity atoms. The interaction energy can be of either sign and thus does not have

to be in excess of the no-impurity shift. The connection with the HWJG and other theories now becomes more apparent. The above describes the microsystem of a single Cu-impurity pair. Since the other impurities of the system can be distributed among $2S+1$ degenerate states, the Fermi interactions over the entire system will still sum to zero unless there is an applied field or short-ranged magnetic order among the impurity atoms (known to exist for Mn).⁹ This paper will be concerned with a given pair for which the impurity has a particular spin projection M_s ($M_s = S$ is the case chosen), and thus with the zero-field shift localized in the region of this pair. It is clear what happens when the field is turned on. At zero temperature all of the Mn atoms occupy the lowest of the $2S+1$ Zeeman-split states, and the local shifts due to the Fermi contact interaction of N electrons with a particular Mn-Cu pair are of the same sign and add when summed over the entire system. As the temperature increases the levels become equally populated, and the local shifts sum to zero over the entire system. This is in agreement with the observations of Sugawara, in which the excess Knight shift (with one exception showing a more complicated behavior near zero temperature) decreases monotonically from a maximum in the zero-temperature limit and appears to converge with the no-impurity line at about 100°K .

THEORY

The first-order energy due to the Fermi contact interaction at the Cu nucleus is given by

$$\Delta E = \sum_{\vec{k}} \sum_{\sigma} \langle \psi_{\vec{k}\sigma}(\vec{r}) | 2\mu_e \mu_N \left(\frac{g}{2}\right) \pi \delta(\vec{r}) \vec{S} \cdot \vec{I} | \psi_{\vec{k}\sigma}(\vec{r}) \rangle, \quad (1)$$

where \vec{k} represents the set of quantum numbers klm [only $l=m=0$ contribute to this integral by the operation of the δ function $\delta(r)$], and σ is an index over the spin states of N conduction electrons, each of which has a wave function (dropping the spin indices),

$$\psi_{\vec{k}}(\vec{r}) = L^{-3/2} \sum_i a_i i^l (2l+1) e^{i\delta_l} u_{k,i}(r) P_l(\hat{r} \cdot \hat{k}), \quad (2)$$

where the radial waves are normalized by the condition that they vanish at the boundary of a box of dimension L . Hence, in Eq. (1) we may put

$$\sum_{\vec{k}} = \frac{L^3}{(2\pi)^3} \int k^2 dk d\Omega. \quad (3)$$

δ_l is the phase shift, defined as usual by the condition

$$\lim_{r \rightarrow \infty} u_{k,i}(r) = \sin(kr - \frac{1}{2}\pi l + \delta_l)/kr \quad (4)$$

and a are defined such that $a_i^* a_i$ is the Fermi distribution function which at zero temperature (assumed throughout) is 1 for electrons whose energies are below ϵ_F and 0 for electrons whose energies are

above, where ϵ_F is the Fermi energy, taken to be 7 eV for the free-electron model of Cu.¹⁰ \vec{s} and \vec{I} are the electron and nuclear spin angular momenta, respectively, μ_e and μ_N are $e\hbar/2m_e c$ and $2.22617 e\hbar/2m_p c$, respectively, and

$$\delta(\vec{r}) = \frac{1}{4\pi} \sum_l \frac{\delta(r)}{r^2} (2l+1) P_l(\cos\theta). \quad (5)$$

The particle wave function is given in the first-Born iteration by

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} - \int d\vec{r}' G(\vec{r}, \vec{r}') V(\vec{r}') e^{i\vec{k} \cdot \vec{r}'}, \quad (6a)$$

$$G(\vec{r}, \vec{r}') = \frac{1}{4\pi} \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}. \quad (6b)$$

The potential is defined by

$$V(\vec{r}) = 2 \left\{ -\frac{Z_1}{r_{\text{Mn}}} - \frac{Z_2}{r_{\text{Cu}}} + \sum_{j=1}^{N_1+N_2-1} \int d\vec{r}' \left[\psi_j^*(\vec{r}') \times \left(\frac{1 - \delta(m_s, m'_s) P_{ij}}{|\vec{r}-\vec{r}'|} \right) \psi_j(\vec{r}') - \psi_j^*(\vec{r}') \delta(m_s, m'_s) P_{ij} \psi_j(\vec{r}') (\epsilon_j - \frac{1}{2}k^2) \right] \right\}, \quad (7)$$

where m_s and m'_s are the spin projections of the scattering and atomic electrons, respectively; $Z_1(N_1)$ and $Z_2(N_2)$ are the charges (numbers of electrons) of Mn and Cu, respectively; ϵ_j are the orbital energies of the bound states $\psi_j(\vec{r})$ on Cu and Mn; and P_{ij} permutes the coordinates of the bound and scattering electrons. The key point of the potential is the fact that when the summation over spin states is performed in (1) there is cancellation of the products of the Fermi interaction and the Coulomb (direct) interaction and cancellation of the products of the Fermi interaction and the exchange interaction for all interactions *except those products which involve exchange with the Mn d electrons*.

Equations of motion for N independent spin orbitals in this potential are derivable from the *unrestricted* Hartree-Fock theory, in which orbitals of different spin are permitted to have different spatial parts.¹¹

Rigorously we should consider the scattering as modified by the residual $1/r_{\text{Cu}}$ (Coulomb tail) potential left when the 4s electron is removed and the band structure (resulting from use of Bloch waves) which the less completely screened potential can support at close distances. The first consideration is not relevant in the first-Born method of solution used here (iteration with undistorted plane waves), and the neglect of band effects is at least qualitatively correct for the localized exchange process considered here. Further, there is an additional potential,¹² $V_{\text{pol}} \pm V_{\text{pol, exch}}$, which results from the

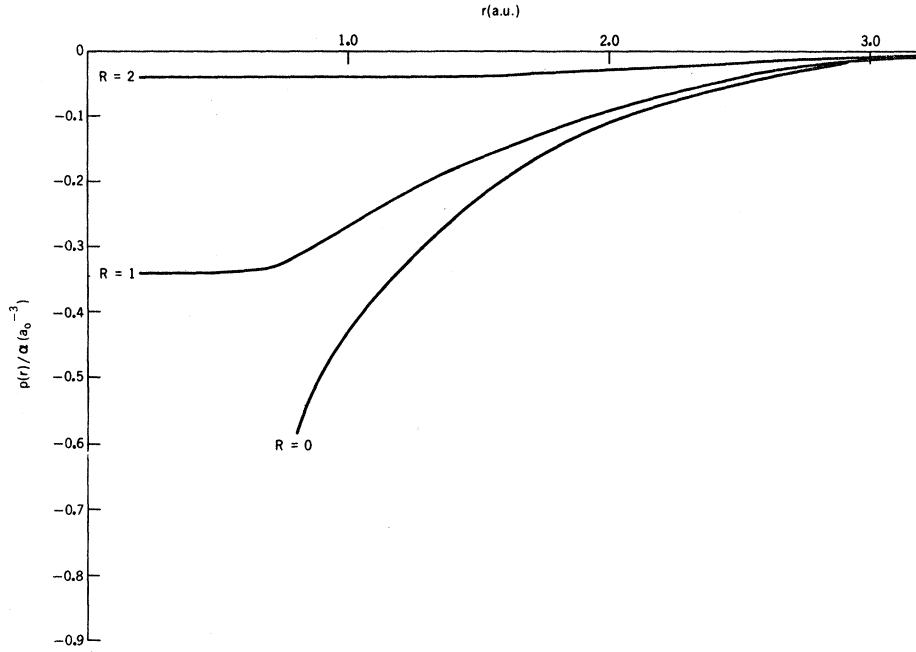


FIG. 1. $p(r)/\alpha$, where $\alpha = \frac{3}{5}[(1/4\pi)\mu_e\mu_N]$ as a function of r , the distance from Mn, averaged over the angles of Mn, for several values of R . Calculated using J values converged through $j=2$.

long-ranged polarization of the target by the scattering electron and is known to affect the phase shift by about 10% in the low-energy elastic scattering from hydrogen atoms. We have estimated the contribution of $V_{\text{pol,exch}}$ for the fictitious case ($R=0$) when the Cu and Mn atoms are united and found the exchange potential changed by about 10%. A careful study of this potential at nonzero R is therefore indicated (see Appendix).

We specialize Eqs. (6) to $r \rightarrow 0$ [the only contribution to the δ -function interaction in (1)], leaving only the leading term in the expansion of G :

$$\lim_{r \rightarrow 0} \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} - \frac{e^{-i\vec{k} \cdot \vec{r}}}{4\pi} \int d\vec{r}' \frac{e^{i\vec{k} \cdot \vec{r}'}}{r'} V(\vec{r}') e^{i\vec{k} \cdot \vec{r}'} \quad (8)$$

\hat{V} is obtained by keeping only the s - d exchange terms in (7); all others cancel when (1) is evaluated. We then define

$$\frac{J(k, R)}{k} = -\frac{1}{4\pi} \int d\vec{r}' \frac{\cos kr'}{r'} \hat{V}(\vec{r}') j_0(kr') \quad (9)$$

as the strength of the spin polarization by the Mn d electrons, where we have kept only the zeroth-order term in the plane-wave expansion of $e^{i\vec{k} \cdot \vec{r}'}$. Thus, to first order in J , Eq. (1) yields

$$\frac{\Delta E}{\mu_e \mu_N} = \frac{4}{\pi} \int_0^{k_F} dk k J(k, R). \quad (10)$$

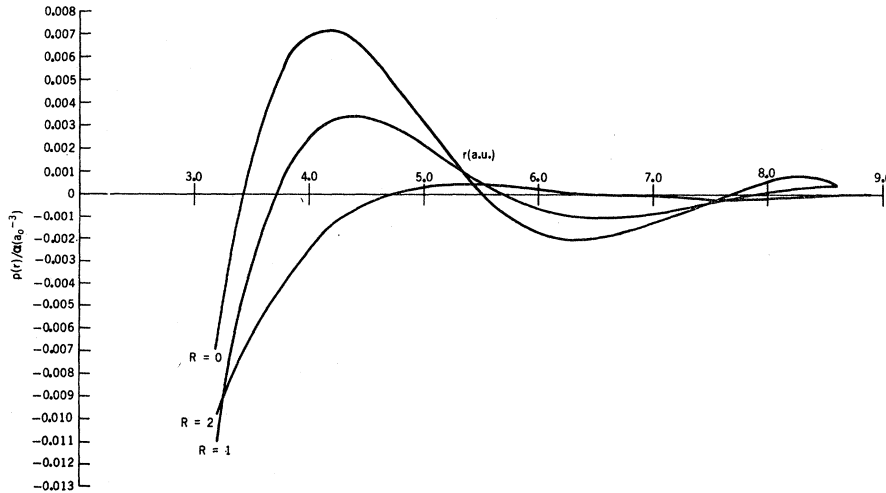


FIG. 2. $p(r)/\alpha$, where $\alpha = \frac{3}{5}[(1/4\pi)\mu_e\mu_N]$ as a function of r , the distance from Mn, averaged over the angles of Mn, for several values of R . Calculated using J values converged through $j=2$.

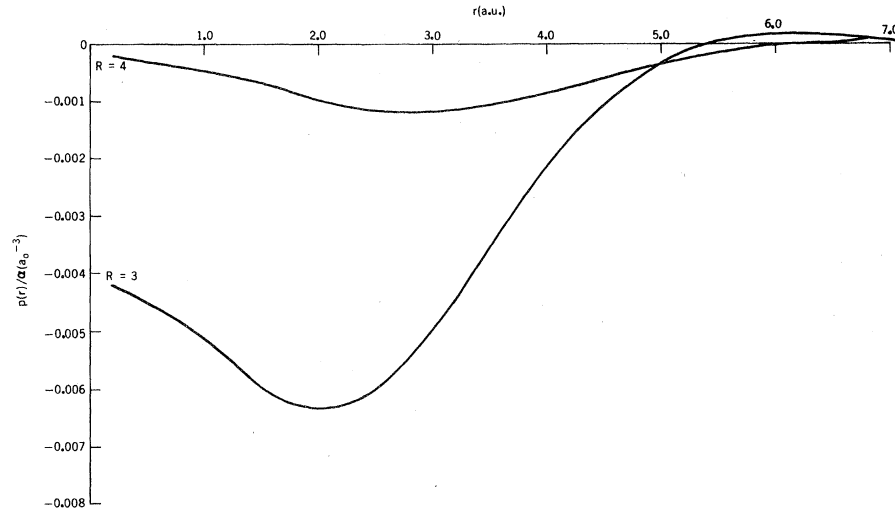


FIG. 3. $p(r)/\alpha$, where $\alpha = \frac{3}{8}[(1/4\pi)\mu_e\mu_N]$ as a function of r , the distance from Mn, averaged over the angles of Mn, for several values of R . Calculated using J values converged through $j=2$.

RKKY SPIN DENSITY

The spin-density function is defined here as $\rho\uparrow - \rho\downarrow$, where

$$\rho\uparrow\downarrow = |\psi_{\vec{k}}\uparrow\downarrow|^2, \quad (11a)$$

$$\begin{aligned} \psi_{\vec{k}}(\vec{r})' &= \{e^{i\vec{k}\cdot\vec{r}} - (e^{i\vec{k}\cdot\vec{r}}/4\pi r) \int d\vec{r}' e^{-i\vec{k}\cdot\vec{r}'} \\ &\times [V(\vec{r}') + 2(\frac{3}{8}\pi)\mu_e\mu_N 2\delta(\vec{r}')m_s m_I] \psi_{\vec{k}}(\vec{r}')\} |\uparrow\rangle \end{aligned} \quad (11b)$$

for large distances from the Cu nucleus. In general we can write

$$\begin{aligned} \psi_{\vec{k}}' &= \{e^{i\vec{k}\cdot\vec{r}} - \int d\vec{r}' G(\vec{r}, \vec{r}') \\ &\times [V(\vec{r}') + 2(\frac{3}{8}\pi)\mu_e\mu_N 2\delta(\vec{r}')m_s m_I] e^{i\vec{k}\cdot\vec{r}'}\} |\uparrow\rangle. \end{aligned} \quad (12)$$

Now substitute (12) into the right-hand side of (11b) and keep only cross products of the Fermi and V interactions. When the modulus squared is taken, the difference of spin-down and spin-up densities summed over \vec{k} and integrations over spin states performed, the result to first order in J is

$$\sigma(r) = \frac{4}{3\pi^2} \mu_e \mu_N m_s m_I \int_0^{k_F} \frac{\sin 2kr}{r^2} J(k, R) dk, \quad (13a)$$

$$r = (r_{Mn}^2 + R^2 - 2r_{Mn}R \cos\theta_{Mn})^{1/2}. \quad (13b)$$

We average this expression over the angles of Mn in the usual way and define the perturbation to the electron density resulting from the two-center scattering process as a function of the distance from the impurity atom as

$$p(r_{Mn}) = (1/4\pi) \int d\phi d\theta \sin\theta \sigma(r). \quad (14)$$

This function is plotted in Figs. 1–3 for several values of R .

NUMERICAL PROCEDURES

The exchange integrals defined by $J(k, R)$ are the two-electron two-center type, and the integrations are performed numerically in prolate spheroidal coordinates defined by

$$\xi = (r_{Mn} + r_{Cu})/R, \quad (15a)$$

$$\eta = (r_{Mn} - r_{Cu})/R, \quad (15b)$$

where R is along the polar axis of the reference frame. The inverse distance $|\vec{r} - \vec{r}'|$ is given in spheroidal coordinates by the Neumann expansion¹³

$$\begin{aligned} \frac{2}{R} \sum_{jm} (-1)^m (2j+1) ([j-|m|]!/[j+|m|]!)^2 P_j^{1m} \\ \times (\xi) Q_j^{1m}(\xi) P_j^{1m}(\eta_1) P_j^{1m}(\eta_2) e^{im(\phi_1 - \phi_2)}, \end{aligned} \quad (16)$$

where P and Q are the associated Legendre functions of the first and second kind, respectively. The results were checked by taking $R=0.01$ in the spheroidal coordinates and checking against the $R=0$ integrals in spherical polar coordinates. Note that in the $R=0$ limit only the $j=2$ term of the Neumann series is nonvanishing in the integral defined by (9) owing to the angular integrations over the s and d pair. For $R \neq 0$, however, the

TABLE I. $-J(k, R)/2$ for selected R (a.u.) and k (a.u.).

k	0.179 555	0.359 110	0.538 666	0.718 221
R				
0	0.138 979	0.234 850	0.271 143	0.257 822
1	0.123 648	0.201 331	0.233 198	0.206 854
2	0.083 067	0.115 420	0.099 597	0.080 544
3	0.053 684	0.056 676	0.028 384	0.017 862
4	0.034 861	0.015 703	0.007 004	-0.003 130
6	0.013 852	-0.009 138	0.000 178	0.000 995
8	0.002 826	-0.003 457	0.003 119	-0.002 141

expansion must be carried to convergence, and the contribution for each term through $j=8$ is tabulated in Table II. The overlap terms in Eq. (7) were estimated to contribute about 1% at $R=1$ to the energy shift and were neglected (note that only the $m=0$ d electron has an overlap with the s waves).

Inspection of Table II shows that for R greater than about 4, the convergence is very slow. The numbers for the higher R 's are not fully converged, but are adequate to establish that the oscillatory variation of the shift with R is not an artifact of a nonconverged series. Also, it is felt that this convergence is adequate given the set of physical approximations used in this calculation.

All integrals were evaluated using the analytic Hartree-Fock d orbitals of Mn calculated by Clementi.¹⁴

RESULTS AND DISCUSSION

Values of $J(k, R)$ and ΔE are tabulated in Tables I and II. Two interesting features of these results are the long range with R of the exchange potential and the oscillatory dependence of the energy shift on R . The long range is familiar in the evaluation of atomic hyperfine structure by perturbation theory^{6,7} in which better than 90% of the contribution to the core polarization exchange interaction (see the Introduction) comes from the continuum-excited states of the atom. This due, of course, to the boundary conditions of the continuum functions; thus, the convergence of the integrals is governed by how tightly the d electrons are bound. The oscillatory behavior of ΔE can be inferred from the oscillatory dependence of $J(k, R)$ on k for larger R by inspection of Table I, and is to be expected when the interactions is small at large R , leaving a kind of distorted overlap of d orbitals with continuum orbitals. This means that there will be a complicated dependence of the shift on impurity concentration and suggests dependence on concentration experiments and/or experiments in which compression or expansion of the metal can change the lattice distances. Note that the interaction is almost at a node for the nearest-neighbor distance $R=4.8299$ and is larger and of opposite sign at the next-nearest-neighbor distance $R=6.8305$.

In the interpretation of the results for larger R it is important to appreciate the smallness of the interaction and thus the tentativeness of the numbers of this calculation, not only from the point of view of the absolute numerical accuracy, but especially in that better approximations to the physics need to be considered. Some of these include the exact numerical solution of the relevant equations to obtain scattering wave functions more accurate than the first-Born iteration used here, as well as the consideration of band effects, the adiabatic

TABLE II. $-\Delta E/\mu_B \mu_N$ for selected R (a.u.). j is the index in the expansion of γ_{12}^1 .

j	0	1	2	3	4	5	6	7	8	Sum
R										
1	0.009955	0.043161	0.066580	0.011081	0.000653	0.000185	0.0000028			0.131451
2	0.013052	0.030241	0.012339	0.005532	0.000922	0.0000793	0.0000036			0.061247
3	0.008619	0.010647	0.001418	0.000760	-0.000646	-0.000234	-0.0000543			0.020510
4	0.004264	0.001441	-0.000549	-0.001280	-0.000822	-0.000318	-0.0000857			0.003198
4.8299	0.001848	-0.000725	-0.000716	-0.000356	-0.000141	-0.000024	0.000012	0.000011	0.000008	-0.000082
6	0.000156	-0.000545	-0.000191	0.000372	0.000442	0.000311	0.000161	0.000076	0.000044	0.000614
8	-0.000068	0.000202	0.000235	0.000152	0.000090	0.000050	0.000021	0.000005	-0.000001	0.000676
10	0.000018	0.000050	0.000009	-0.000083	-0.000154	-0.000166	-0.000137	-0.000098	-0.000067	-0.000474

polarization of the target (see Appendix), electron correlation, electron screening in the gas, and the deviation of the d orbitals from those of the free atom. Also, in Cu-Mn it is important to consider the short-ranged magnetic order (clustering) of the solute atoms.

ACKNOWLEDGMENTS

The author wishes to thank Dr. F. H. M. Faisal and Dr. R. Drachman for helpful discussion, Dr. Merle Riley for the use of his integrater Difsys, and A. Silver for able computing assistance.

APPENDIX: ADIABATIC EXCHANGE POLARIZATION POTENTIAL

The contribution of the adiabatic exchange polarization potential is estimated as follows. When the Mn target is polarized by a static electron at \vec{r}_2 , the solution to the first-order equation from Rayleigh-Schrödinger perturbation theory (for a perturbation on the $m=0$ orbital in particular, where nondegenerate perturbation theory can be used because the d orbitals are not split by the dipole potential of polarized orbital theory¹⁰) is

$$\Phi = - \left(\frac{[2]^{7/2}}{[720]^{1/2}} \right) \left(\frac{[5]}{[4\pi]} \right)^{1/2}$$

$$\times \left(\frac{u_1(r)}{r} \right) \frac{P_1(\vec{r} \cdot \vec{r}_2)}{r_2^2} P_2(\cos\theta) \epsilon(r < r_2), \quad (A1)$$

where ϵ is a step function 1 for $r < r_2$ and 0 for $r > r_2$, where the radial part of the $3d$ orbital (un-normalized) is taken to be $r^2 e^{-r}$ (based on a binding energy of about 0.6 a.u. as calculated by Clementi). We do not take Clementi's Hartree-Fock function for the unperturbed orbital because then we could not find an analytic solution to the first-order equation. The first-order radial solution is

$$u_1(r) = e^{-r} \left(r^2 + \frac{r^3}{2} + \frac{r^4}{5} + \frac{r^5}{15} + \frac{11r^6}{14 \times 15} + \frac{11r^7}{4 \times 14 \times 15} \right. \\ \left. + \frac{22r^8}{9 \times 4 \times 14 \times 15} + \frac{154r^9}{35 \times 9 \times 4 \times 14 \times 15} \right. \\ \left. + \frac{308r^{10}}{11 \times 35 \times 9 \times 4 \times 14 \times 15} + a_{11} r^{11} \right), \quad (A2)$$

where $a_{11} \sim 10^{-4}$. The exchange potential is generated by substituting 1 for *one* Ψ_j in Eq. (7) of the text. $J(k, R=0)$ is about 10% of $J(k, R=0)$ calculated with unpolarized orbitals. It is clear that this effect should be looked at more quantitatively.

*NRC-NAS-NASA Resident Research Associate.

¹T. Sugawara, J. Phys. Soc. Japan **14**, 643 (1959).

²K. Yoshida, Phys. Rev. **106**, 893 (1957).

³A. H. Heeger, L. B. Welsh, M. A. Jensen, and G. Gladstone, Phys. Rev. **172**, 302 (1968), referred to as HWJG.

⁴For a discussion see C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1961), p. 360.

⁵M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954); K. Yosida, *ibid.* **106**, 893 (1957); Ref. 3.

⁶R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967), p. 53.

⁷Hugh P. Kelly, Phys. Rev. **173**, 142 (1968).

⁸E. S. Chang, Robert T. Pu, and T. P. Das, Phys. Rev. **174**, 1 (1968).

⁹Reference 3, p. 309.

¹⁰Reference 3, p. 315.

¹¹For a brief history of different forms of Hartree-Fock theory which achieve closed-shell spin polarization in the atomic hyperfine-structure problem, and for appropriate references, see Uzi Kaldor and F. E. Harris, Phys. Rev. **183**, 1 (1969).

¹²A. Temkin, Phys. Rev. **116**, 358 (1959); A. Temkin, Phys. Rev. Letters **6**, 354 (1961).

¹³J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1963), p. 266.

¹⁴E. Clementi, J. Chem. Phys. **41**, 295 (1964).