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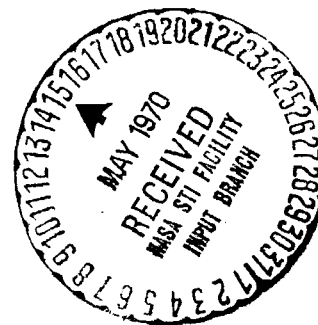
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SPIN POLARIZATION IN THE ELECTRON GAS BY A MAGNETIC IMPURITY: THEORY OF THE EXCESS KNIGHT SHIFT

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GSFC —— GODDARD SPACE FLIGHT CENTER ——

GREENBELT, MARYLAND

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Theory of the Excess Knight Shift

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Abstract

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 does not average to zero when summed
over the randomly oriented spins of N conduction electrons is the
scattering of s-wave electrons from the long-ranged exchange poten-
tial of an open-shell impurity atom located at a distance R from
the Cu nucleus and then the Fermi contact interaction at the Cu
nucleus. This is a two-center 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 of the conduction
electrons at the Cu nucleus which have first exchange scattered
from the 3d electrons of Mn is calculated as a function of R.
It is found to change sign between R=4.8299 (nearest neighbor
distance), R=4.8299 and R=8, and R=8 and R=10 au, suggesting
dependence on impurity concentration experiments and experiments
in which compression or expansion can change the lattice distances.
The exchange potential is presented as a function of electron
velocity and R. For completeness the RKKY 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 and found to be signi-
ficant.

for the spin up electron and the <u>absence</u> of these potentials
for the spin down electron. This is analogous to the virtual
process which gives the major contribution to the Fermi contact
hyperfine structure in open shell atoms due to the exchange of
an 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.[5,6] This process is represented
diagrammatically by,
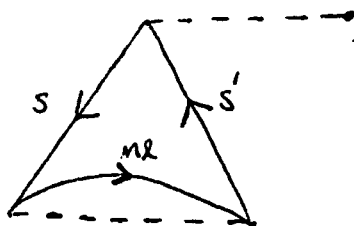
Therefore many conduction electrons with randomly oriented spins
will experience a net nonzero Fermi interaction with a Cu nucleus
in the vicinity of an open shell impurity atom, in the absence of
an applied magnetic field. The strength of this interaction will
depend on the magnitude of the exchange 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 micro-
system 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 average
to zero unless there is an applied field or short ranged magnetic
order among the impurity atoms (known to exist for Mn[7]). 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.

(after page 4)

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
Interaction are of the same sign and add. As the temperature
increases the levels become equally populated, and the local
shifts average to zero over the entire system. This is in
agreement with the observations of Sugawara.

Theory

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

$$\sum_{\underline{k}}\sum_{\sigma} < \psi_{\underline{k}\sigma}(\underline{r}) \mid 2\mu_e\mu_N 8\pi/3\delta(\underline{r})\underline{s}\cdot\underline{1} \mid \psi_{\underline{k}\sigma}(\underline{r}) > \qquad 1$$

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

$$\psi_{\underline{k}}(\underline{r}) = (2/R_0)^{\frac{1}{2}}k\sum_{\ell}a_{\ell}(i)^{\ell}(2\ell+1)^{\frac{1}{2}}e^{i\delta_{\ell}}u_{k,\ell}(r)P_{\ell}(\cos\theta)/(4\pi)^{\frac{1}{2}} \qquad 2$$

where the radial waves are normalized by the condition that they vanish at the boundary of a sphere of radius R_0; hence,

$$\sum_{\underline{k}} = R_0/\pi\int dk\sum_{\ell m} \qquad 3$$

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

$$\lim_{r \to \infty} u_{k,\ell}(r) = \sin(kr - \pi/2\ell + \delta_\ell)/kr \qquad 4$$

and a_ℓ are defined such that $a_\ell^* a_\ell$ is the Fermi distribution function which at zero temperature (assumed throughout) if 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 7ev for the free electron model of Cu[8]. $\underline{s}$ and $\underline{I}$ 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

$$\delta(\underline{r}) = \sum_\ell \delta(r)/r^2 (2\ell+1) P_\ell(\cos\theta)/4\pi \qquad 5$$

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

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

$$G(\underline{r},\underline{r}') = 1/4\pi e^{ik|\underline{r}-\underline{r}'|} \Big/ |\underline{r}-\underline{r}'| \qquad 6$$

The potential is defined,

$$V(\underline{r}) = 2(-Z_1/r_{Mn} - Z_2/r_{Cu} + \sum_{j=1}^{N_1+(N_2-1)} \int d\underline{r}' \frac{\{\psi_j^*(\underline{r}')(1 \pm \delta(m_s,m_s'))P_{ij}\psi_j(\underline{r}')}{|\underline{r} - \underline{r}'|}$$

$$\pm \psi_j^*(\underline{r}')\delta(m_s,m_s')P_{ij}\psi_j(\underline{r}')(\epsilon_j - k^2/2)\}) \qquad 7$$

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
and numbers of electrons of Mn and Cu respectively, ϵ_j are the
orbital energies of the bound states $\psi_j(\underline{r})$ on Cu and Mn, and P_{ij}
permutes the coordinates of the bound and scattering electrons,
giving exchange potentials for (+) singlet and (-) triplet
scattering respectively. 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 <u>except</u> those products which involve exchange
with the Mn d electrons.

Rigorously we should consider the scattering as modified
by the residual $1/r_{Cu}$ (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 un-
distorted plane waves), and the neglect of band effects is at least
qualitatively correct for the long-ranged exchange process considered

here. Further there is an additional potential[9], $V_{pol} \pm V_{pol,exch}$, which results from the 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 $V_{pol,exch}$ 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 the appendix)

We specialize eq. 6 to r=0 (the only contribution to the delta function interaction in 1), leaving only the leading term in the expansion of G,

$$\lim_{r \to 0} \psi_{\underline{k}}(\underline{r}) = (1 - 1/4\pi \int d\underline{r}' e^{ikr'}/r' \underline{V}(\underline{r}') e^{i\underline{k} \cdot \underline{r}'}) \times (2/R_0)^{\frac{1}{2}} ka_0 e^{i\delta}0/(4\pi)^{\frac{1}{2}}$$

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where $\underline{V}$ is obtained by keeping only the s-d exchange terms in 7, since all others cancel when 1 is evaluated. We then define,

$$J(k,R)/k = -1/4\pi \int d\underline{r}' \cos(kr')/r' \underline{V}(\underline{r}) j_0(kr')$$

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where we have kept the leading term in the plane wave expansion of $e^{i\underline{k} \cdot \underline{r}'}$. This is equivalent to spherically averaging the potential so that the $\ell=0$ partial wave, which is the only wave which contributes to 1, is uncoupled to other partial waves.

If the spin up states are given by 8, then the spin down states are given by,

$$\lim_{r \to 0} \psi_{\underline{k}}(\underline{r}) = 1 \times (2/R_0)^{\frac{1}{2}} ka_0 e^{i\delta}0/(4\pi)^{\frac{1}{2}}$$

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which is a consequence of the choice $M_s=S$ for the ^6S ground
state of Mn.   Thus to first order in J eq. 1 becomes,

$$\Delta E^s/\mu_e \mu_N = 4/\pi \int_0^{k_F} dk \ k \ J(k,R) \qquad\qquad 11$$

when the exchange potentials take the upper sign (singlet
scattering).   The total shift is given by,

$$\Delta E = 1/4 \Delta E^s + 3/4 \Delta E^t \qquad\qquad 12$$

where ΔE^t results when the potentials take the upper sign
(triplet scattering).

RKKY Spin Density

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

$$\rho{\uparrow}{\downarrow} = |\psi_{\underline{k}}{\uparrow}{\downarrow}|^2$$

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\,\underline{r}} - e^{ikr}/4\pi r \int d\underline{r}' e^{-i\underline{k}'\,\underline{r}'}(\underline{V}(\underline{r}') + 2\,(8\pi/3\mu_e\mu_N2\delta(\underline{r}')m_s m_I)$$

$$\psi_{\underline{k}}(\underline{r}') \qquad\qquad 13$$

for large distances from the Cu nucleus. For close distances we can write,

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\,\underline{r}} - e^{-i\underline{k}\,\underline{r}}/4\pi \int d\underline{r}' e^{ikr'}/r'(\underline{V}(\underline{r}') + 2\,(8\pi/3\mu_e\mu_N2\delta(\underline{r}')m_s m_I)$$

$$\psi_{\underline{k}}(\underline{r}') \qquad\qquad 14$$

Now substitute 14 into the right hand side of 13 and keep only cross products of the Fermi and <u>V</u> interactions. When the modulus is taken and the difference of spin down and spin up densities summed over k, the result to first order in J is,

$$\sigma(r) = 4/\pi \int_0^{k_F} dk \ \sin(2kr)/r^2 J(k,R) \times 4/3\mu_e\mu_N m_s m_I \times 1/4\pi$$

$$r = (r_{Mn}^2 + R^2 - 2r_{Mn}R\cos\theta_{Mn})^{\frac{1}{2}} \qquad\qquad 15$$

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,

$$\rho(r) = 1/4\pi \int d\phi d\theta \sin\theta \sigma(r') \qquad\qquad 16$$

This function is plotted in Figs. 1, 2 and 3 for several values of R.

It is important to note that even though eq. 13 results from the large r expansion of the Green's function (6), it is the only surviving term in the limit r'=0 when the Fermi interaction in 13 is evaluated, and likewise for the small r expansion of the Green's function to give 14. Thus the result (15) is not asymtotic for large 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,

$$\xi = (r_{Mn} + r_{Cu})/R$$

$$\eta = (r_{Mn} - r_{Cu})/R \qquad\qquad 17$$

where R is along the polar axis of the reference frame. The inverse distance $|\underline{r}-\underline{r}'|$ are given in spheroidal coordinates by the Neumann expansion[10],

$$2/R \sum_{j} \sum_{m} (2j+1)\,((j-|m|)!\,/(j+|m|)!\,)^2 P_j^{|m|}(\xi_<) Q_j^{|m|}(\xi_>) P_j^{|m|}(\eta_1) P_j^{|m|}(\eta_2)$$

$$e^{im(\phi_1 - \phi_2)} \times (-1)^m \qquad\qquad 18$$

where P and Q are the associated Legendre functions of the first and second kind respectively. The results were checked by taking R=.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 and s and d pair. For R≠0, however, the expansion must be carried

to convergence , and the contribution for each term through
j=8 is tabulated in Table 2. 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 2 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.[11]

Results and Discussion

Values of $J(k,R)$ and ΔE^S are tabulated in Tables 1 and 2. Two interesting features of these results are the very long range 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[5,6] in which better than 90% of the contribution to the core polarization exchange diagram (see the Introduction) comes from the continuum excited states of the atom. This is due, of course, to the unboundedness of the continuum functions; thus the boundedness of the integrals is governed by how tightly the d electrons are bound. The oscillatory behavior of ΔE^S can be inferred from the oscillatory dependence of $J(k,R)$ on k for larger R by inspection of Table 1, and is to be expected when the interaction 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, from the point of view of the absolute numerical accuracy but especially from the point of view 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, the consideration of band effects, the adiabatic polarization of the target (see the appendix), electron correlation, and the deviation of the d orbitals from those of the free atom. Also in Cu-Mn it is very important to consider the short ranged magnetic order (clustering) of the solute atoms.

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Table 1. $-J(k,R)/2$ for selected R (a.u.) and k (a.u.)

R \ k	.179555	.359110	.538666	.718221
0	.138979	.234850	.271143	.257822
1	.123648	.201331	.233198	.206854
2	.083067	.115420	.099597	.080544
3	.053684	.056676	.028384	.017862
4	.034861	.015703	.007004	-.003130
6	.013852	-.009138	.000178	.000995
8	.002826	-.003457	.003119	-.002141

Table 2. $-\Delta E^s/\mu_e\mu_N$ for selected R(a.u.). j is the index in the expansion of r_{12}^{-1}.

| R\j	0	1	2	3	4	5	6	7	8	Sum
1	.009955	.043161	.066580	.011081	.000653	.0000185	.0000028			.131451
2	.013052	.030241	.012339	.005532	.000922	.0000793	.0000036			.061247
3	.008619	.010647	.001418	.000760	-.000646	-.000234	-.0000543			.020510
4	.004264	.001441	-.000549	-.001280	-.000822	-.000318	-.0000857			.003198
4.8299	.001848	-.000725	-.000716	-.000356	-.000141	-.000024	.000012	.000011	.000008	-.000082
6	.000156	-.000545	-.000191	.000372	.000442	.000311	.000161	.000076	.000044	.000614
8	.000068	.000202	.000235	.000152	.000090	.000050	.000021	.000005	-.000001	.000676
10	.000018	.000050	.000009	-.000083	-.000154	-.000166	-.000137	-.000098	-.000067	-.000474

Figure Captions

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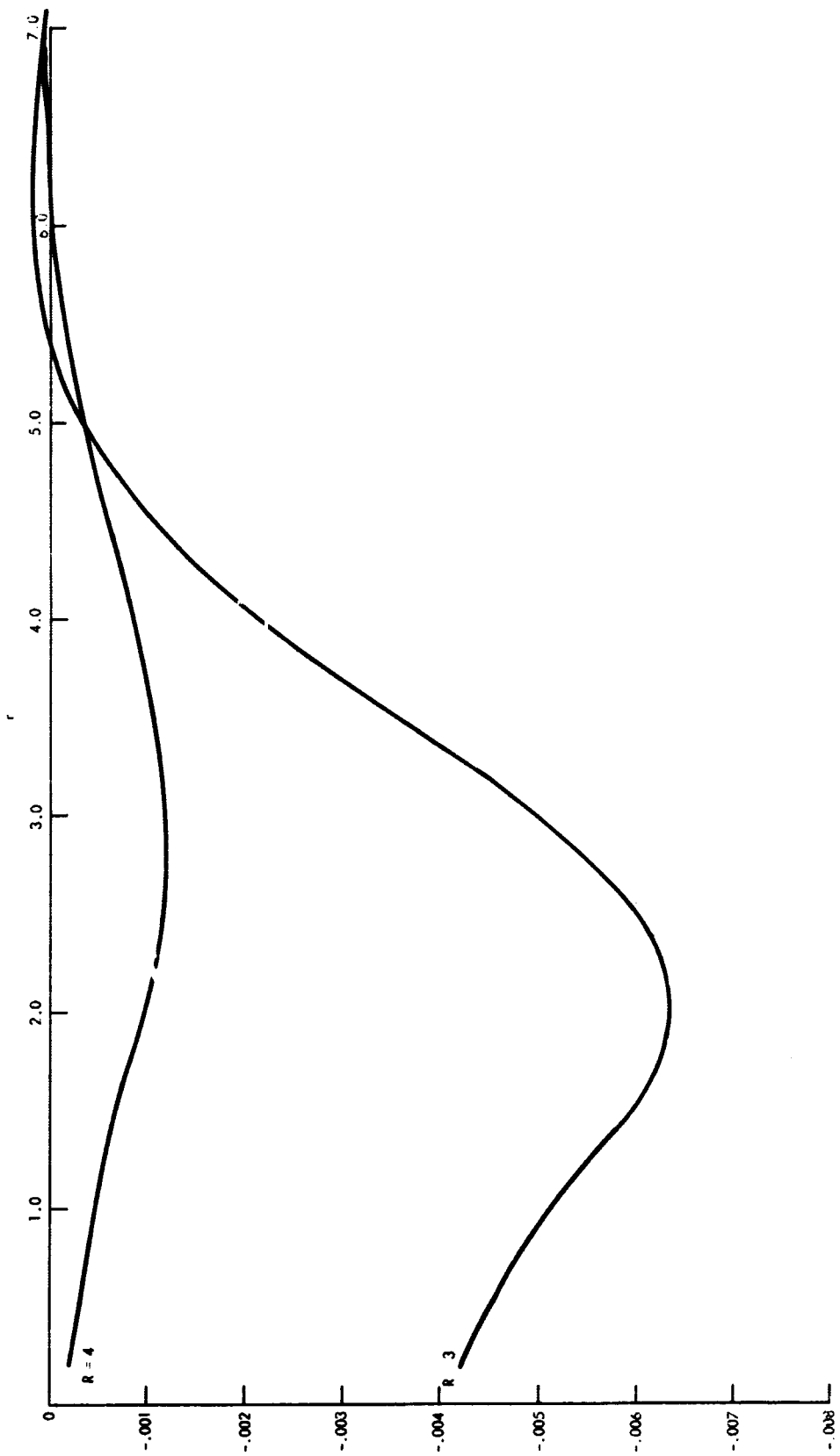
Fig. 2. $p(r)/\alpha$ where $\alpha = \frac{1}{4\pi}\mu_e\mu_N \times 3/5$ as a function of r, the distance from Mn, averaged over the angles of Mn, for several values of R. Calculated using J values converged through j=2.

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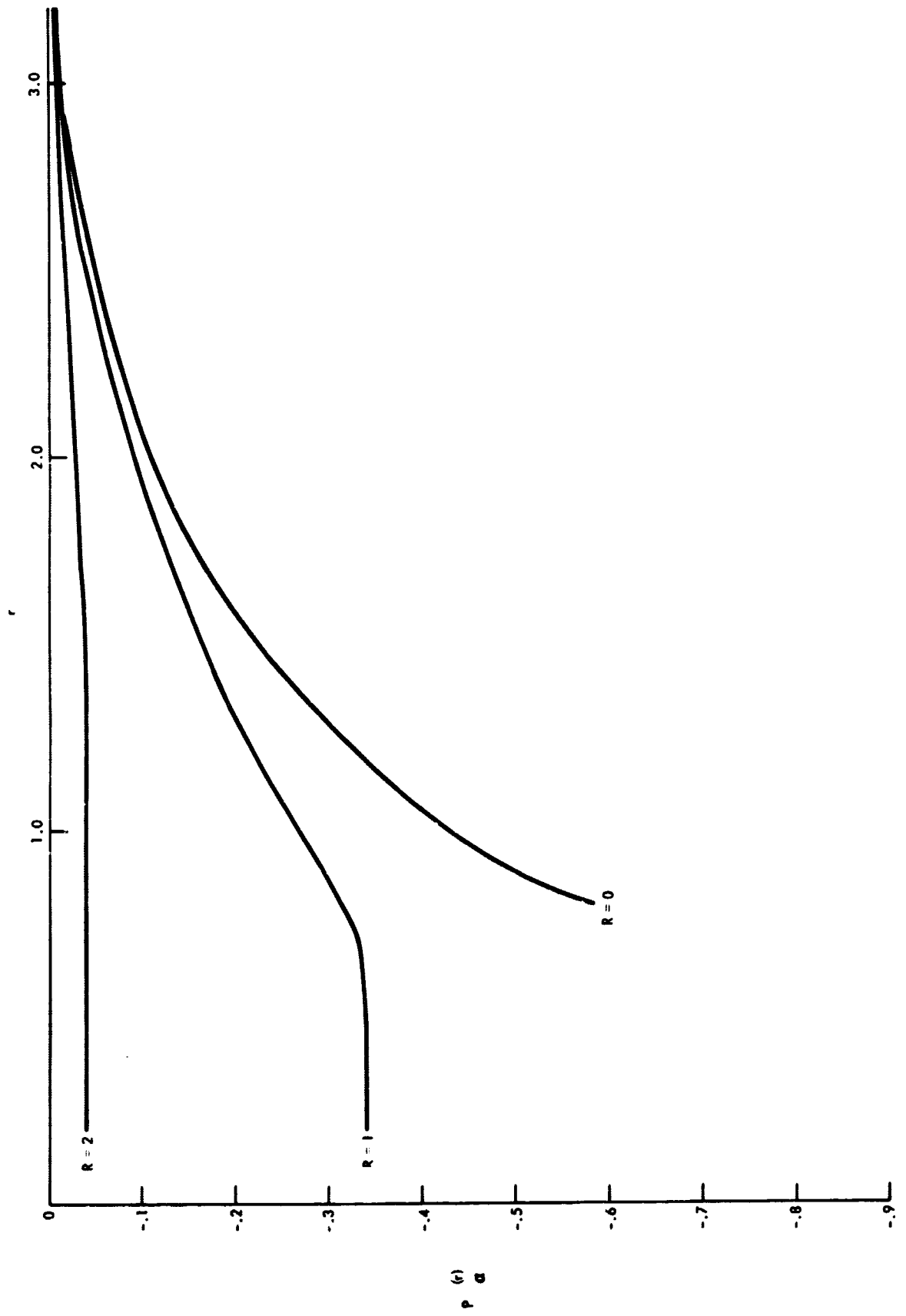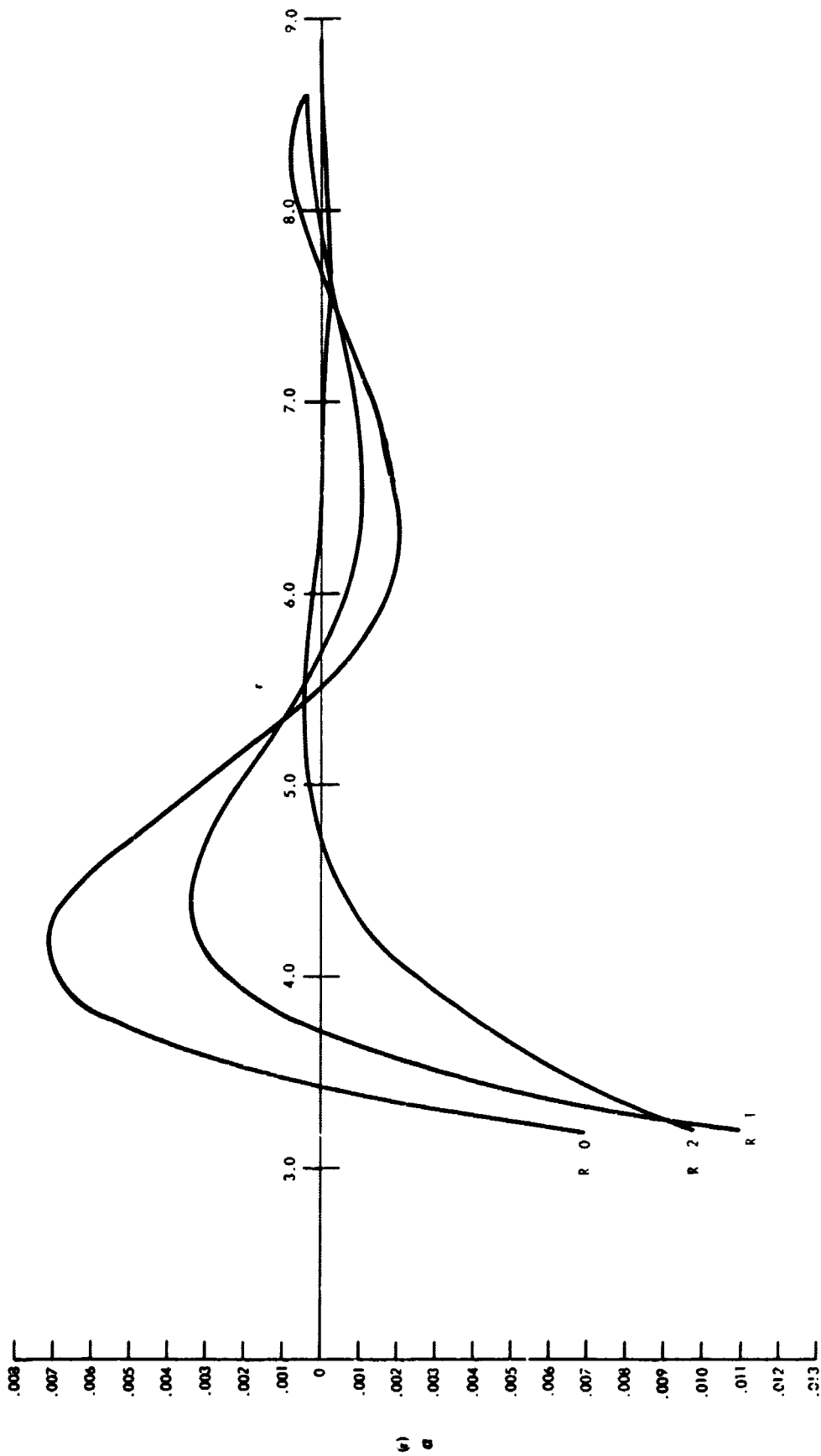
Appendix. Adiabatic exchange polarization potential.

The contribution of the adiabatic exchange polarization potential is estimated as follows. When the Mn target is polarized by a static electron at r_2, the solution to the first order equation from Rayleigh-Schrodinger 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 theory[9]) is,

$$\Phi = -(2)^{7/2}/(720)^{\frac{1}{2}} x (5/4\pi)^{\frac{1}{2}} u_1(r)/r P_1(\hat{r}\cdot\hat{r}_2)/r_2^2 P_2(\cos\theta) \epsilon(r<r_2) \quad 1$$

where ϵ is a step function 1 for $r<r_2$ and 0 for $r>r_2$ where the radial part of the 3 d orbital (unnormalized) is taken to be $r^2\exp(-r)$ (based on a binding energy of about .6 a.u. as calculated by Clementi). We do not take Clementi's HF 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,

$$u_1(r) = e^{-r}(r^2+r^3/2+r^4/5+r^5/15+11r^6/(14\times15)+11r^7/(4\times14\times15)$$

$$+22r^8/(9\times4\times14\times15)+154r^9/(35\times9\times4\times14\times15)+308r^{10}/(11\times35\times9\times4\times14\times15)$$

$$+ 0(10^{-4})r^{11}) \quad\quad\quad 2$$

The exchange polarization potential is generated by substituing 1 for <u>one</u> 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.