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On the Theory of Direct Exchage in Ferromagnets

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We are reporting on calculations of J as predicted by the Heisenberg model starting with its simple form and as developed in several ways for two cases for which (as Löwdin has shown) J is rigorously defined. (1) A pair of atoms with a single electron per atom (the hydrogenic case). J is calculated for the unrealistic but historically interesting case of hydrogen $3d$ functions and the computationally more difficult case of the exchange between $3d$ orbitals for the iron series elements. The fact that the iron series $3d$ orbitals are not eigenfunctions of the free atom (hydrogenic) hamiltonian is shown to profoundly affect the results. Calculations for all pairs of $3d$ orbitals show that J is sensitive to the angular dependence of the wave functions (and to the precise radial shape as well). (2) Two atoms with a single hole each in otherwise closed shells (such as a pair of iron series atoms in the $3d^9$ configuration). The effect on J of "clothing" the atoms with the remaining electrons is discussed first with regard to the effect of the core electrons on the one-electron potentials and secondly with respect to the effect of the overlap of the core electrons. We find that the direct exchange parameter J is large and *negative* for the two electron case [case (1)] and negative, but smaller, for the "clothed" $3d^9$ case [case (2)], whereas for ferromagnetism it should be positive. From this one may conclude that either the direct exchange mechanism is not the dominant source of the ferromagnetism of the transition metals or that the direct exchange model is an inappropriate description of their magnetic behavior.

1. Introduction

Since Heisenberg first used the exchange concept in order to explain the origin of ferromagnetism a number of approaches have been developed, all of which invoke as their dominant mechanism a particular exchange interaction from among the various types which are possible.

Central to the Heitler-London approach of Heisenberg is the "direct exchange" parameter, J, which has been a subject of considerable speculation and controversy. Quantitative estimates of direct exchange have been made by Wohlfarth[1] (J negative) and Kaplan[2] (J positive) but computational difficulties limited these investigations to internuclear distances and/or wave functions of symmetry inappropriate to the iron series metals. Because of this their results have been regarded as inconclusive. Recently Stuart and Marshall[3] made detailed calculations of J over a wide range of internuclear distances for a pair of free atom iron $3d_\sigma$ orbitals (i.e., $m_l=0$ along the internuclear axis). They found that J was always positive (the correct sign for ferromagnetism) but too small to account for the experimentally observed exchange effects. (We shall show that a different, and we believe, more appropriate definition of J changes their results.)

In this paper we are reporting on calculations of J as predicted by the Heisenberg model starting with its simple form and as developed in several ways for two cases (as Löwdin[4] has shown) for which J is rigorously defined. We find that the direct exchange parameter J is large and *negative* for the case of a pair of atoms with a single electron per atom (the hydrogenic case), [case (1)], and negative, but smaller, for the "clothed" $3d^9$ case, two atoms with a single hole each in otherwise closed shells (such as a pair of iron series atoms in the $3d^9$ configuration), case (2), whereas for ferromagnetism it should be positive. From this one may conclude that either the direct exchange mechanism is not the dominant source of the ferromagnetism of the transition metals or that the direct exchange model is an inappropriate description of their magnetic behavior.

2. Two-Electron Direct Exchange

Löwdin[4)] has shown that if one considers a two-electron system (or a two-electron-like system such as a pair of $3d^9$ atoms) and defines J by one-half the difference of the singlet and triplet state energies that the familiar Dirac-Van Vleck vector-model equation follows immediately in an almost trivial way. This definition provides a particularly convenient starting point for obtaining J; it also gives an exact form of the vector-model formula which, as Löwdin points out, is independent of any assumptions about correlation, non-orthogonality, polar states, relativistic effects, and the like.

For a two-atom system and with a two-electron Hamiltonian consisting of kinetic energy and coulomb potential energy terms the appropriate definition of J is

$$\begin{aligned} J=(1-S_{ab}^4)^{-1}\Bigg\{&\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|b(1)a(2)\right\rangle \\ &-S_{ab}^2\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|a(1)b(2)\right\rangle \\ &+S_{ab}\left[\left\langle b\left|-\frac{1}{2}\nabla^2-\frac{Z_b}{r_b}\right|a\right\rangle+\left\langle a\left|-\frac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|b\right\rangle\right] \\ &-S_{ab}^2\left[\left\langle b\left|-\frac{1}{2}\nabla^2-\frac{Z_b}{r_b}\right|b\right\rangle+\left\langle a\left|-\frac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a\right\rangle\right]\Bigg\}, \qquad (1) \end{aligned}$$

where S_{ab} equals the overlap integral between the $3d$ functions on centers a and b, Z_a and Z_b are effective nuclear charges (taken to be equal). The $\langle\ \rangle$ brackets denote the usual integrations over coordinates 1 and 2. Note that J, of course, does not depend on the internuclear repulsion term, Z_aZ_b/r_{ab}, but that if one wishes to include it (it must appear in both lines 1 *and* 2 of Eq. 1) the value of J will not be changed.

Only if the one-electron wave functions are eigenfunctions of the one-center problem do the last two (square bracketed) terms of Eq. 1 cancel. Therefore, for discussions of the exchange interaction between a pair of iron series $3d$ orbitals, in which the nucleus and the other electrons of each atom are approximated by a point charge with $Z=1$, Eq. 1, without the "correction" terms (the Stuart and Marshall case) is not an altogether appropriate expression for J.

We have evaluated J using Eq. 1 for : (1) the historically interesting but unrealistic case of free atom hydrogen $3d$ wave functions, the only case for which J consists of only the first two terms of Eq. 1; and (2) with Hartree-Fock $3d$ wave functions for Co ($3d^9$) and Co^{2+} ($3d^7$).

Fig. 1 shows J's for hydrogen $3d$ functions for various m_l values as a function of internuclear separation. Note that none of these follows the familiar Slater-Bethe Curve, and that for the internuclear distances of 40 to 50 au, which bear some corresponding relation to the iron series metals, $J_{\sigma\sigma}$ is small and positive and $J_{\pi\pi}$ and $J_{\delta\delta}$ are smaller in magnitude and negative.

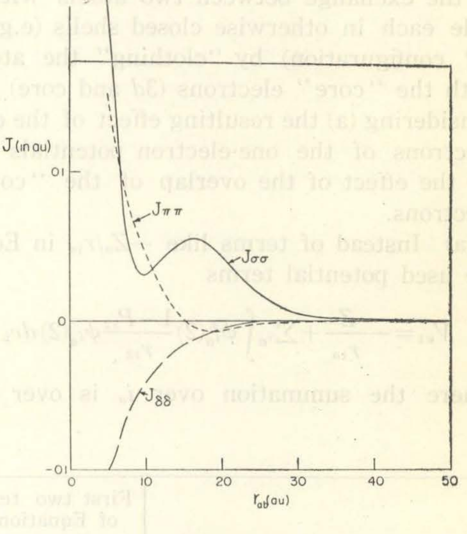

Fig. 1.

For the iron series functions, J is found to depend strongly on the precise shape of the radial functions as well as on the angular portion of the wave function. In Table I we give our calculated J's for two internuclear separations without (column 1) and with (column 2) the "correction terms" (i.e., the last two lines of Eq. 1). The correction terms *dominate*, changing J's which might otherwise be positive (as found by Stuart and Marshall, who evaluated $J_{\sigma\sigma}$ with iron $3d$ wave functions) to large and *negative*[5]. That J is sensitive to orbital choice is shown by the large increase in the magnitude of the J's on going from the Co^{2+} to the Co $3d$ orbitals. One also sees that $J_{\sigma\sigma}$ (and $S_{\sigma\sigma}$) can be smaller than $J_{\pi\pi}$ (and $S_{\pi\pi}$), a fact that runs counter to prevailing estimates. Also listed is an "average" J, computed with the assumption (made previously by Stuart and Marshall) that each orbital has equal probability of being occupied. J's for pairs of orbitals of differing m_l (the "non-diagonal" terms) are included in the J_{av}'s but (for lack of space) are not listed in the Table.

3. Direct Exchange for a Pair of "Clothed" $3d^9$ Atoms

We also considered the more realistic case of the exchange between two atoms with a hole each in otherwise closed shells (e.g., a $3d^9$ configuration) by "clothing" the atoms with the "core" electrons ($3d$ and core) and considering (a) the resulting effect of the core electrons of the one-electron potentials and (b) the effect of the overlap of the "core" electrons.

(a) Instead of terms like $-Z_a/r_{1a}$ in Eq. 1 we used potential terms

$$V_{a1}=-\frac{Z}{r_{1a}}+\sum\nolimits_{i_a}\int\psi^*_{i_a}(2)\frac{1-P_{12}}{r_{12}}\psi_{i_a}(2)\,dv_2\,,$$

where the summation over i_a is over the twenty-six "paired" electrons (the ψ's) on the A atom, Z is the actual nuclear charge, and P_{12} is a permutation operator (of coordinates 1 and 2) so that exchange interactions are included along with the coulomb interactions. If this change is made in Eq. 1 then there are many more integrals to be computed.

The resultant J's are given in column 3 of Table I. Again they are fairly large and negative. If we compute a J_{av}, assuming each $3d$ orbital has an equal probability of being occupied by a hole, J_{av} for Co^{2+} $3d$ orbitals at $r_{ab}=4.75$ a.u. is -0.000059 a.u. whereas for Co $3d$ orbitals, at the same r_{ab}, it is $+0.000005$ au (which is at the limit of accuracy of our calculations). Thus, while an examination of the $J_{\sigma\sigma}$ term only (or of the other diagonal terms as well) would lead to the conclusion that J was *negative* (and substantial), the off-diagonal positive terms have a large enough magnitude to greatly reduce the diagonal estimate and in fact to change the sign of J for the Co case. These results point out the importance of the off-diagonal terms *and* the sensitivity of the result to the assumption concerning the probability of orbital occupancy. Since this is only one-half of the question of "clothing," the actual numerical results are not too meaningful at this point.

(b) Having seen the effect of "clothing" the free atom potentials with the "core" electrons on the calculation of J and having allowed these electrons to play a role in the interaction we must now recognize that some

Table I.

		First two terms of Equation 1	Complete Equation 1	$3d^9$ with "clothing"	"Clothed" $3d^9$ with core overlap
$3d$ of Co^{++} at 4.75 au	$\sigma\ \sigma$	+ .000081	− .00648	− .001073	− .001093
	$\pi\ \pi$	− .000008	− .00192	− .000295	− .000298
	$\delta\ \delta$	− .0000004	− .00004	− .000007	− .000007
	J_{av}	+ .000010	− .00041	− .000059	− .000076
$3d$ of Co^{++} at 2.25 au	$\sigma\ \sigma$	+ .0223	− .0461	− .00774	
	$\pi\ \pi$	− .0022	− .3702	− .09158	
	$\delta\ \delta$	− .0011	− .0824	− .01716	
$3d$ of Co at 4.75 au	$\sigma\ \sigma$	.00140	− .0220	− .00050	− .00117
	$\pi\ \pi$	− .00021	− .0351	− .00151	− .00154
	$\delta\ \delta$	− .00003	− .0033	− .00011	− .00011
	J_{av}	+ .00019	− .0038	.00000	− .0006

of these paired electrons, the ψ_i's, have the same radial extent as the exchanging $3d$'s and therefore one can expect other overlaps of the same order of magnitude as S_{ab} and in turn additional contributions to J. To obtain these contributions one can set up wave functions for the triplet and singlet states (of the 54 electron problem) and calculate one-half the singlet-triplet energy difference. Again there are many new integrals which must be included in the calculation. This we have done, to second order in the possible overlaps, and the results are given in column 4 of Table I. These terms do not affect the J's drastically, but serve to shift the relative values of the terms (see column 5 of the Table)—particularly for the non-diagonal terms, which are now for the first time other than the simple elecrostatic $1/r_{12}$ exchange intergrals. The values of J_{av} are sensitive to the occupancy argument used; other arguments would make J_{av} more negative. Further, from an analysis of these core overlap terms it is suggested that the paired "4s" conduction electrons of the metal can play an important role in "direct exchange," quite aside from a Zener type of effect.

These results, along with a discussion of a more exact model, are to appear in a forthcoming publication⁶⁾.

References

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2 H. Kaplan: Phys. Rev. **85** (1952) 1038.

3 R. Stuart and W. Marshall: Phys. Rev. **120** (1960) 353.

4 P. O. Löwdin: Revs. Mod. Phys. (1962) to appear; *International Symposium on "Magnetism and Transition Metals,"* Oxford University, September 1959; Technical Note No. 46, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished).

5 Similar conclusions were reached independently by W. J. Carr, Jr. (this Conference).

6 A. J. Freeman and R. E. Watson: Phys. Rev. **124** (1961) 1439.

DISCUSSION

W. MARSHALL: Stuart and Marshall did not attempt to calculate these correction terms because, whether or not they changed the sign of the effective exchange integral, the low statistical weight to be given to the important overlap pairs seemed certain to make the effect small compared to main exchange contribution which must come from elsewhere. However in other materials the orbitals might be occupied in such a way that a higher statistical weight was appropriate and for such cases direct exchange could be important.

W. J. CARR: I agree with Dr. Marshall that in Fe, Ni and Co the direct exchange is probably quite small compared with other exchange couplings present. However, direct exchange may be important in the magnetostriction and in the elastic constants of these materials. Also it may be an important coupling in the case of the antiferromagnetic metals, for example, Mn and Cr.