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Theory of Direct Exchange in Ferromagnetism

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An extensive investigation is presented on the role of direct exchange as the mechanism responsible for ferromagnetism. The direct exchange integral J which arises in Heisenberg's theory of ferromagnetism and which has been a subject of considerable speculation and controversy (particularly concerning its sign behavior as a function of internuclear separation) is considered for several 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 the precise radial shape as well). (2) A single hole 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. (From an analysis of these 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.) 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. Finally, a more exact model of direct exchange is discussed, as are some of the problems inherent in carrying it out.

I. INTRODUCTION

IT was not long after the discovery of the phenomenon of exchange by Heisenberg[1] and Dirac[2] as a characteristically quantum effect that Heisenberg[3] first used the exchange concept in order to explain the origin of ferromagnetism. Since then a number of approaches[4-8] to a theory of magnetism for the ferromagnetic metals have been developed, all of which invoke as their dominant mechanism a particular exchange interaction from among the various types which are possible. To date no approach has succeeded in providing satisfactory *quantitative ab initio* predictions and thus a detailed understanding of the phenomena. The refinements necessary to make any one theory "realistic" have made the computation associated with it intractable. Two of these approaches should be mentioned here: first, there is the "collective" or "itinerant" electron model[5,7] whose starting point is the energy band-molecular orbital formalism; secondly, there is the atomic orbital–Heitler-London model originally proposed by Heisenberg and more recently refined by Van Vleck[8] in the minimum polarity model. The collective electron model emphasizes the "free" nature of electrons in the solid and includes in the wave function the periodicity of the lattice, whereas the Heisenberg model stresses the "bound" or highly localized nature of the electrons by treating the solid as a collection of atoms. The relative merits and shortcomings of each model have been discussed often and at length in earlier papers.[4] The collective model is currently the more popular approach[5,9] but we must re-emphasize the difficulties associated with obtaining quantiative predictions with either scheme.

Central to the Heitler-London approach of Heisenberg is the "direct exchange" parameter. Starting from the model of the solid as a collection of atoms, the simple Heisenberg approach regards each pair of atoms as behaving like a hydrogen molecule, i.e., each atom is thought to have a single $3d$ electron which interacts with its neighbor and the dominant interaction for producing ferromagnetism in the solid is considered to arise from a superposition of this two-electron interaction. Despite the fact that the obvious naiveté of the model precludes a realistic description of the phenomenon, the Heisenberg approach has had many adherents and the model is still frequently invoked as an explanation of ferromagnetism. Until now, accurate calculations to check the prediction of the theory with

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[1] W. Heisenberg, Z. Physik **38**, 411 (1926).

[2] P. A. M. Dirac, Proc. Roy. Soc. **A112**, 661 (1926).

[3] W. Heisenberg, Z. Physik **49**, 619 (1928).

[4] For a good compilation reviewing the different viewpoints see the Proceedings of the Conference on Magnetism published in Revs. Modern Phys. **25**, 1 (1953) particularly the articles listed as references 5 through 8 inclusive. We shall refer to these papers, where extensive references may be found, rather than try to cite the complete literature.

[5] J. C. Slater, Revs. Modern Phys. **25**, 199 (1953).

[6] C. Zener and R. R. Heikes, Revs. Modern Phys. **25**, 191 (1953).

[7] E. P. Wohlfarth, Revs. Modern Phys. **25**, 211 (1953).

[8] J. H. Van Vleck, Revs. Modern Phys. **25**, 220 (1953).

[9] C. Herring, J. Appl. Phys. **31**, 31S (1960).

experiment have not been possible, although it is now more commonly believed that such investigations would give negative values for the direct exchange parameter.

In this paper we are reporting results of calculations of the direct exchange interaction as predicted by the Heisenberg model starting with its simple form and as developed in several ways. We find in all these cases that the Heisenberg exchange integral is *negative* 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.

In the Heitler-London[10] picture the energy of the molecule for the triplet and the singlet can be simply written as

$$E_{\pm}=2\epsilon+\frac{C_{ab}\pm J_{ab}}{1\pm S_{ab}^2}, \tag{1}$$

where the plus sign is associated with the singlet state and the minus sign with the triplet. For two atoms A and B, separated by a distance r_{ab} having one-electron wave functions ϕ_a and ϕ_b each with an atomic one-electron energy ϵ, we denote the interaction potential in atomic units as

$$V_{ab}=\frac{1}{r_{ab}}+\frac{1}{r_{12}}-\frac{1}{r_{1b}}-\frac{1}{r_{2a}}, \tag{2}$$

and the overlap integral between the one-electron functions as

$$S_{ab}=\int\phi_a{}^*(1)\phi_b(1)dv_1=\langle a|b\rangle; \tag{3}$$

then

$$C_{ab}=\int\phi_a{}^*(1)\phi_b{}^*(2)V_{ab}\phi_a(1)\phi_b(2)dv_1dv_2 =\langle a(1)b(2)|V_{ab}|a(1)b(2)\rangle \tag{4}$$

is the Coulomb energy and

$$J_{ab}=\int\phi_a{}^*(1)\phi_b{}^*(2)V_{ab}\phi_b(1)\phi_a(2)dv_1dv_2 =\langle a(1)b(2)|V_{ab}|b(1)a(2)\rangle \tag{5}$$

is the exchange energy. Equations (3) to (5) serve also to define the notation. Since J_{ab} produces the electrostatic energy difference between the triplet and singlet states it was considered by Heisenberg to be responsible for ferromagnetism and is called the Heisenberg direct exchange integral. It is J_{ab} as defined in Eq. (5) which has been used in the familiar Dirac-Van Vleck vector coupling formula for the spin-dependent interaction energy between two spins associated with the electrons on the two atoms,

$$E=E_0-2J_{ab}\mathbf{S}_a\cdot\mathbf{S}_b. \tag{6}$$

The generalization of Eq. (6) to many-electron systems by means of the spin Hamiltonian

$$H=-2\sum_{i>j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{7}$$

has been the basis of numerous discussions of both ferromagnetism and antiferromagnetism but usually with the assumption of a constant exchange integral J between nearest neighbors only. With J treated as an empirical parameter, a wide variety of experimental data can be understood.

As is well known, Heisenberg postulated that the direct exchange integral, J_{ab}, was positive for ferromagnets, whereas for the hydrogen molecule and indeed for almost all molecules, J is in fact negative. This change in sign Heisenberg explained as being a consequence of the use of functions with a high principal quantum number. It remained for Slater[11] to improve upon this rather unsatisfactory interpretation by stressing the overlap of the $3d$ functions as a function of internuclear separation. Slater argued that for small overlaps J was positive but changed sign as the overlap increased. Since the overlap depends on the ratio of the internuclear distance to the radius of the d shell Slater's simple postulate explained why just a few elements are observed to be ferromagnetic, i.e., for these the calculated ratio is such as to make J positive. Bethe[12] subsequently amplified Slater's arguments and stressed the dependence of J on the angular part of the wave functions.

Since then there has been considerable controversy regarding the validity of these arguments and disagreement as to the sign and magnitude of the direct exchange parameter. This has in part been due to an ambiguity in rigorously defining the term and in part to difficulties in carrying out accurate computations. Details of the role it does play in the magnetic properties of the metals and other magnetic materials should be understood before going on to more refined treatments. In the light of the above-mentioned controversy, its behavior is also a matter of some historical interest.

Several quantitative estimates of direct exchange have been made by Wohlfarth[13] (J_{ab} negative) and Kaplan[14] (J_{ab} 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[15] made detailed calculations of J over a wide range of internuclear distances for a pair of free atom iron[16] $3d_\sigma$ orbitals (i.e., $m_l=0$ along the inter-

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[10] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

[11] J. C. Slater, Phys. Rev. **35**, 509 (1930); **36**, 57 (1930).

[12] A. Sommerfeld and H. Bethe, *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part II, p. 595.

[13] E. P. Wohlfarth, Nature **163**, 57 (1949).

[14] H. Kaplan, Phys. Rev. **85**, 1038 (1952).

[15] R. Stuart and W. Marshall, Phys. Rev. **120**, 353 (1960).

[16] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).

nuclear axis). They found that J was always positive (the correct sign for ferromagnetism) but too small to account for the experimentally observed exchange effects. The magnitude of J found by these authors has disturbed those who felt that direct exchange was responsible for ferromagnetism while the sign they obtained convinced others that the result was anomalous.[17] We shall show that the problem lies in the question of defining direct exchange properly. Löwdin[18] has shown that if one starts by asking for the J that appears in the vector coupling model [Eq. (6)] there is one case where J can be uniquely defined; this is the case of a pair of atoms with one unpaired electron per atom. As we will show in the next section, the familiar Heisenberg parameter [Eq. (5)] can be derived as the direct exchange parameter appropriate to the two-electron Heitler-London formalism *only if* the orbitals used are hydrogen atom eigenfunctions and if S_{ab}^2 in Eq. (1) is neglected. Otherwise Eq. (5) should be "extended" to include additional terms. Since Stuart and Marshall[15] considered some, but not all of these terms, their results were not obtained from an appropriate definition of J and so are not conclusive. One purpose of the present work is to consider the form and effect of these additional terms and also to consider direct exchange for pairs of $3d_\pi$ ($m_l=1$) and $3d_\delta$ ($m_l=2$) orbitals, cases not previously considered, but which must play an important role in a more exact treatment of the problem.

We shall follow Löwdin's[18] approach for those cases for which J is rigorously defined. Examples of these are a pair of atoms with a single electron per atom (the hydrogenic case), with a single electron outside of closed shells (e.g., a pair of alkali atoms) and with a single hole in otherwise closed shells (such as a pair of iron series atoms in the $3d^9$ configuration). The principal objectives of this investigation are to resolve some of the earlier controversies concerning the Heisenberg parameter and to further our understanding by a study of concrete examples of the role actually played by direct exchange.

In Sec. II we consider the form of direct exchange for the case of a two-electron two-atom system. We first derive the formula for J and after carrying out calculations for the unrealistic but historically interesting case of hydrogen $3d$ functions we discuss the case of exchange between $3d$ orbitals for the iron series elements. We then consider, in Sec. III, J for a pair of iron series atoms in the $3d^9$ configuration which permits us to retain the uniqueness in the definition of J while discussing a more realistic case than a simple two-electron system. This involves a "clothing" of the two atoms with the remaining electrons, thus abandoning the point charge model of Sec. II. The discussion is presented in two parts, considering first the effect of the "core" electrons on the one-electron potentials and then the effect of the overlap of the "core" electrons on the determination of J. Section IV discusses a more exact model of direct exchange and some of the problems inherent in carrying out calculations with it. Finally, Sec. V states some conclusions.

II. TWO-ELECTRON DIRECT EXCHANGE

A. Derivation and Definition of J

In a recent discussion, Löwdin[18] 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

$$J=\tfrac{1}{2}({}^1E-{}^3E), \tag{8}$$

where ${}^1E$ and ${}^3E$ are the singlet and triplet state energies, that the familiar vector-model equation, Eq. (6), follows immediately in an almost trivial way. E_0 of Eq. (6) has a simple definition; it is the weighted average energy of all possible spin states. Equation (8) is 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, nonorthogonality, polar states, relativistic effects, and the like.

Consider for the two-atom system a two-electron Hamiltonian consisting of kinetic energy and Coulomb energy terms, i.e.,

$$H=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2+\frac{Z_aZ_b}{r_{ab}}+\frac{1}{r_{12}}-\frac{Z_a}{r_{1a}}-\frac{Z_b}{r_{1b}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{2b}}, \tag{9}$$

where subscripts 1 and 2 denote electron coordinates and Z_a and Z_b (which are taken to be equal) are effective nuclear charges on centers A and B, respectively. Using the notation introduced in Sec. I, the Heitler-London ground configuration energies are then

$$\begin{aligned}{}^1E&=(1+S_{ab}^2)^{-1}[\langle a(1)b(2)|H|a(1)b(2)\rangle\\&\qquad+\langle a(1)b(2)|H|b(1)a(2)\rangle],\\{}^3E&=(1-S_{ab}^2)^{-1}[\langle a(1)b(2)|H|a(1)b(2)\rangle\\&\qquad-\langle a(1)b(2)|H|b(1)a(2)\rangle].\end{aligned}\tag{10}$$

These equations can be specialized to yield Eq. (1) by assuming $Z_a=Z_b=1$ *provided* that ϕ_a and ϕ_b are hydro-

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[17] See W. J. Carr, Jr. (to be published) for a discussion of direct exchange based on some calculations similar to those we are reporting here.

[18] P. O. Löwdin, *International Symposium on Magnetism and Transition Metals*, Oxford University, September, 1959; Technical Note No. 46, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished); and P. O. Löwdin, Revs. Modern Phys. (to be published).

gen atom eigenfunctions. Using Eq. (8) one finds

$$J=(1-S_{ab}^4)^{-1}\left\{\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|b(1)a(2)\right\rangle\right.$$

$$-S_{ab}^2\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|a(1)b(2)\right\rangle$$

$$+S_{ab}\left[\left\langle b\left|-\tfrac{1}{2}\nabla^2-\frac{Z_b}{r_b}\right|a\right\rangle+\left\langle a\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|b\right\rangle\right]$$

$$-S_{ab}\left[\left\langle b\left|-\tfrac{1}{2}\nabla^2-\frac{Z_b}{r_b}\right|b\right\rangle\right.$$

$$\left.\left.+\left\langle a\left|-\tfrac{1}{2}\nabla^2-\frac{Z_a}{r_a}\right|a\right\rangle\right]\right\}. \tag{11}$$

We take Eq. (11) to be the appropriate definition of J for the two-electron direct exchange. Now if the ϕ's are eigenfunctions of the one-electron one-center problem, i.e., if

$$(-\tfrac{1}{2}\nabla^2-Z_a/r_a)\phi_a(r)=\epsilon\phi_a(r), \tag{12}$$

then

$$\begin{aligned}{}_b\langle a|-\tfrac{1}{2}\nabla^2-Z_a/r_a|b\rangle&=S_{ab}\langle b|-\tfrac{1}{2}\nabla^2-Z_a/r_a|a\rangle\\&=\epsilon S_{ab}^2=S_{ab}^2\langle a|-\tfrac{1}{2}\nabla^2-Z_a/r_a|a\rangle,\end{aligned} \tag{13}$$

and thus the last two lines of Eq. (11) cancel, resulting in

$$J=(1-S_{ab}^4)^{-1}\left\{\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|b(1)a(2)\right\rangle\right.$$

$$\left.-S_{ab}^2\left\langle a(1)b(2)\left|\frac{1}{r_{12}}-\frac{Z_a}{r_{2a}}-\frac{Z_b}{r_{1b}}\right|a(1)b(2)\right\rangle\right\}. \tag{14}$$

Note that J, of course, does not depend on the internuclear repulsion term, Z_aZ_b/r_{ab}, in contrast with Eq. (5), but that if one wishes to include it [it must appear in both lines 1 *and* 2 of Eq. (14)] the value of J will not be changed.[19]

Further, if one introduces Z_aZ_b/r_{ab} terms into Eq. (14), neglects all terms with overlap integrals of order two or greater, and sets $Z_a=Z_b=1$ then one obtains the familiar, and often used, Heisenberg integral [Eq. (5)]. Note that Eqs. (5) and (14) are derived *if and only if* the ϕ's are hydrogen atom eigenfunctions. 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 $Z=1$, neither Eq. (5) (the Wohlfarth[13] and Kaplan[14] case) nor Eq. (14) (the Stuart and Marshall[15] case) are altogether appropriate expressions for J.

As an instructive comparison here and because it is pertinent in what follows, we show in Fig. 1 the one-electron $3d$ radial charge densities for hydrogen and for[20] Co^{++}. The difference between them is very striking. We shall report results of calculations for the hydrogenic case [for which Eq. (14) is exact] and for iron series $3d$ orbitals using Eqs. (11) and (14) with $Z=1$. We shall see that the additional terms in Eq. (11) profoundly affect the computed J.

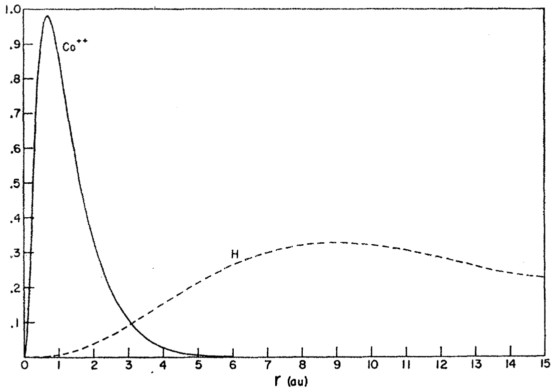

FIG. 1. Co^{++} $3d$ wave function compared with the hydrogen atom $3d$ wave function.

Alternatively, one could choose an "effective" nuclear charge (Z) with a value other than $+1$ so that the last two lines of Eq. (11) cancel, in which case Eq. (14) would be exact. [With a hydrogenic $3d$ orbital defined for that Z, the two radial densities in Fig. 1 are brought into closer (but still poor) coincidence. But since the iron series $3d$ orbitals are not hydrogenic in *shape* (quite apart from scaling) the choice of Z is not unique but is dependent on the angular behavior of the orbitals and on the A-B internuclear distance.] On doing this, as we shall see, the new Z (typically of a value of $+8$ to $+10$) must be inserted into the nuclear potential terms of Eq. (14) and one is no longer approximating the remainder of each iron series atom by a charge of $+1$ as has been done in all previous investigations. Values of Z such that the last two lines of Eq. (11) cancel and the resulting J's will also be given later in this section when we report our numerical results.

B. Evaluation of Integrals

Two-center integrals are, of course, necessary for the evaluation of the equations given in the previous section. To do this we have used the Coolidge-Löwdin-Barnett-Coulson method[21] as developed by Switendick and Corbató[22] for the IBM 704 and 709. A few comments should be made concerning the method and the resultant integrals. First, the Barnett-Coulson ex-

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[19] Stuart and Marshall (reference 15) chose to include this term in their counterpart to Eq. (14).

[20] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

[21] A. S. Coolidge, Phys. Rev. **42**, 189 (1932); P. O. Löwdin and S. O. Lundqvist, Arkiv Fysik **3**, 147 (1951); M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. (London) **A243**, 221 (1951).

[22] A. C. Switendick and F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1959 (unpublished), p. 70.

pansions break down for very small internuclear distances and therefore J was not calculated and hence will not be reported for such distances. This is not too serious since the Heitler-London approach to direct exchange is inappropriate at these distances anyway. For large internuclear distances there are also some difficulties in obtaining accurate "Coulomb" integrals.[23] This problem could be remedied with finer integration meshes—meshes beyond the scope, however, of computer and program size. This has not been a serious problem for the evaluation of the J's of Eqs. (11) and (14) but it can produce difficulties when we "clothe" the iron series atoms, a matter to be discussed later (see Sec. III). Integral accuracy can be a serious problem when evaluating a quantity like J which involves terms of differing sign. We have endeavored to have terms accurate to the digits reported in this paper and while we believe that we have been generally successful in this, it is not impossible that errors have crept in which affect some of the details, but not the substance, of the results to be reported here.

C. Direct Exchange Integral for Hydrogen 3*d* Wave Functions

We have previously noted that Eq. (14) was the appropriate expression for J for the case of a two-electron system *if and only if* the expression was evaluated with hydrogenic orbitals. Otherwise Eq. (11) was the appropriate definition of J. Before discussing the case of exchange between 3*d* orbitals for the iron series elements it is instructive to calculate J for the unrealistic but historic case of exchange between hydrogen atom 3*d* wave functions. This is done to end speculation about the sign of J for this simple case and to fix ideas for what follows.

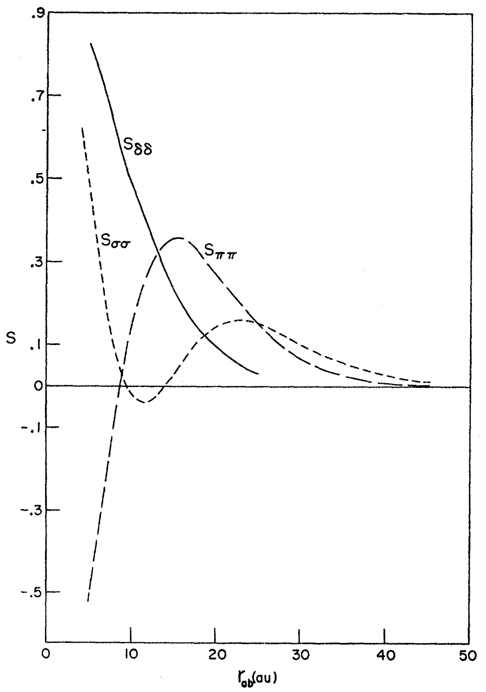

FIG. 2. Overlap integrals, S_{ab}, for the hydrogenic 3*d* wave functions as a function of internuclear distance, r_{ab} (in au).

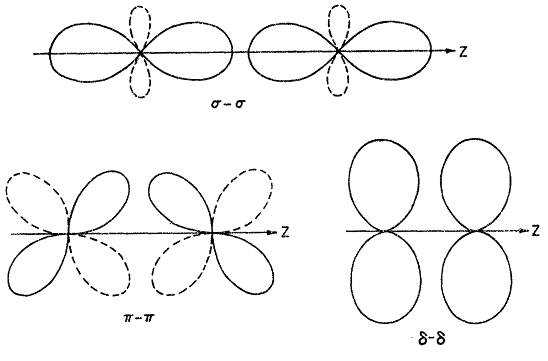

FIG. 3. Angular dependence of the 3*d* wave functions. The *z* (internuclear) axis is included in the plane of the drawings; dashed lines denote regions 180° out of phase with solid-line regions.

The J of Eq. (14) (with $Z_a = Z_b = 1$) was calculated as a function of the internuclear separation for pairs of hydrogen 3*d* orbitals of like m_l value. We have not considered J for pairs of differing m_l for which both Eqs. (14) and (5) reduce to the simple exchange integral

$$J_{12} = \langle a(1)b(2)|1/r_{12}|b(1)a(2)\rangle, \qquad (15)$$

because the overlap integral S_{ab} is zero. As is well known the exchange integral J_{12} is always positive.

When viewing the results of this section it should be borne in mind that the hydrogen 3*d* radial function is very diffuse with a maximum at $r=9$ a.u. (atomic units). (See Fig. 1.) If one scaled this function to bring it into rough agreement with the iron series orbitals one would find that an internuclear distance, ~40 to 50 a.u. corresponds to observed internuclear distances in the Fe, Co, and Ni metals.

Before considering J let us inspect the important overlap integrals (S_{ab}'s); these have been graphed as a function of internuclear distance r_{ab} in Fig. 2. Their behavior is easily understood if one considers the angular dependence of the wave functions. The reader may remind himself of this dependence[24] by inspecting Fig. 3. Note that the z (internuclear) axis is included in the plane of the drawings and that dashed lines denote regions 180° out of phase with solid line regions. The phase of one atom with respect to the other as

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[23] Two-center integrals of the form $\langle a|1/r_b|a\rangle$ and $\langle a(1)b(2)|1/r_{12}|a(1)b(2)\rangle$.

[24] We shall be discussing the calculation of J for 3*d* orbitals in the m_l (spherical harmonic) representation. Equivalently, one can consider J's defined for the cubic e_g ($3z^2-r^2$ and x^2-y^2) and t_{2g} (xy, yz and xz) orbitals. The two representations are related by a simple transformation; for convenience we have chosen to work in the m_l representation. The results are not very different for the two representations, the center of gravity for the sum of all the J's being shifted by very small additional integrals.

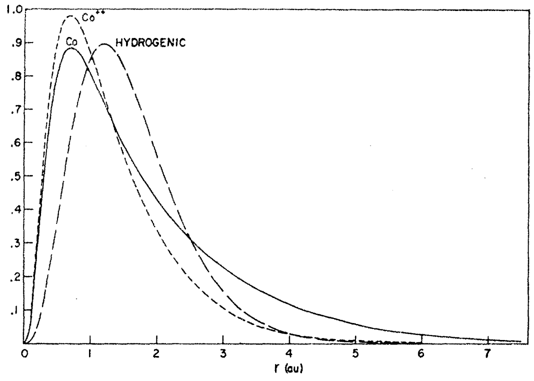

FIG. 4. Several $3d$ functions, for Co^{++} ($3d^7$), Co ($3d^9$), and a hydrogenic (single exponential) $3d$ orbital which would yield approximately the same multiplet structure as the neutral Co function.

shown in Fig. 3 is that also used in the calculations. The negative $S_{\sigma\sigma}$'s occur when one atom's loop of one phase has its principle overlap with the loop of opposite phase on the other atom. Although the angular dependence of the orbitals dominates, the behavior of the S's is also a function of the ***shape*** of the radial functions, a feature not indicated in Fig. 2. The $S_{\sigma\sigma}$'s obtained for iron series $3d$ orbitals by Stuart and Marshall[15] and by ourselves (to be reported later) do not go negative. This difference in shape can be seen in Fig. 4 where several $3d$ functions, for Co and Co^{++}, are plotted along with a hydrogenic (single exponential) $3d$ orbital which would yield approximately the same multiplet structure as the neutral Co function.

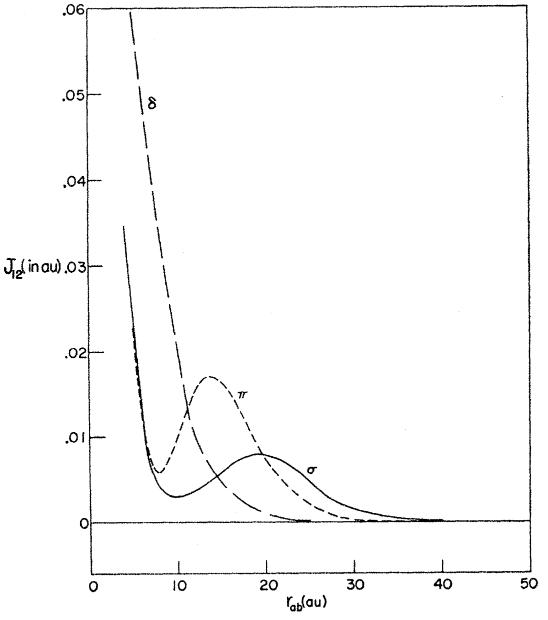

FIG. 5. The simple exchange integral, J_{12}, of Eq. (15) calculated for hydrogen $3d$ wave functions as a function of internuclear separation.

Let us now consider the Heisenberg direct exchange parameter, J, of Eq. (14) and also the simple exchange integral, J_{12}, of Eq. (15). The latter is included (as Fig. 5) because it has been a common (but *incorrect*) practice to neglect all overlaps in the definition of the exchange parameter. Our calculated values for J are plotted in Fig. 6 also as a function of r_{ab}, the internuclear distance (note the differences in scale of the two figures). We see that only $J_{\sigma\sigma}$ resembles the simple J_{12} integral. This is in large part due to the small magnitude of $S_{\sigma\sigma}$ over much of the range of investigated internuclear distance. Of greater interest is the sign behavior of the J's—a behavior which has been found to be strongly dependent on the angular behavior of the orbitals. $J_{\sigma\sigma}$ is positive over the region studied (smaller internuclear distances were not studied for the reasons given earlier), $J_{\pi\pi}$ is positive for smaller internuclear distances and becomes negative for larger distances and $J_{\delta\delta}$ is everywhere negative. Although the Heitler-London approach is completely inappropriate for small r_{ab}, the behavior of J is a matter of curiosity for such distances. A study of the individual integrals (not tabulated here) which contribute to J suggests that $J_{\delta\delta}$ very likely reverses itself and becomes positive at some very small distance and also that it is not impossible that $J_{\sigma\sigma}$ and $J_{\pi\pi}$ reverse their behavior, becoming smaller in magnitude and perhaps even negative at some extremely small internuclear distance.

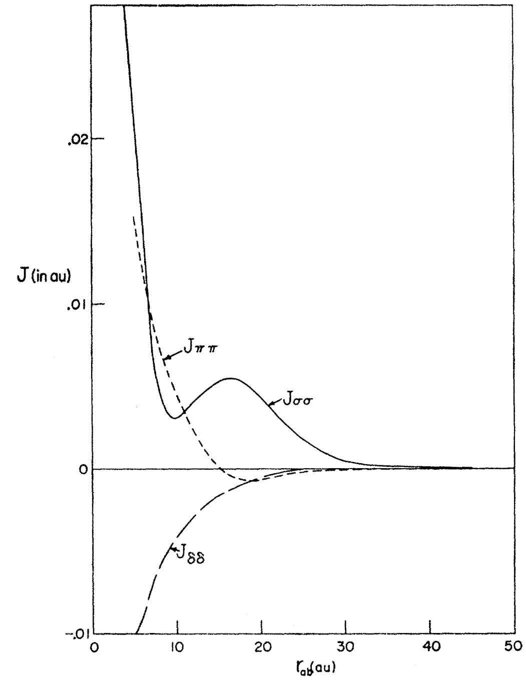

FIG. 6. The Heisenberg direct exchange parameter, J, of Eq. (14) calculated for hydrogen $3d$ wave functions as a function of r_{ab}, the internuclear separation. Note that the scale differs from that in Fig. 5.

It should be noted that for the internuclear distances of 40 to 50 a.u., 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.

The results of Fig. 6 contrast with the two schools of argument concerning the behavior of J, one of which said that J is always negative and the other which said that J is negative for small internuclear distances, becomes positive, goes through a maximum and decays to zero. The computed J's are strongly dependent on the angular behavior of the orbitals and as a result are in general disagreement with either of the above points of view.

D. Direct Exchange Integral for Iron Series 3*d* Functions

The simple but totally unrealistic case of hydrogen 3*d* functions provided us with a case for which Eq. (14) was an exact definition of J. We shall now consider the more realistic and computationally more difficult case of direct exchange between iron series 3*d* wave functions. First we discuss our choice of the iron series element and the specific orbitals to be used and then present the numerical results.

Choice of Iron Series 3d Functions

The choice of the element is simplified by our intention to evaluate J for "clothed" ions in Sec. III as a less naive model of the interaction between the two atoms. Experimental neutron form factor data[25] and energy band calculations[26] can assist us in our choice of orbitals.

For the "clothed" atom, we will consider the case of a hole in an otherwise closed shell neutral atom. Co $3d^9$ falls in this category and will be our choice. The metal, of course, is better described as being in the $3d^84s$ configuration.

Neutron form-factor measurements[25] and energy band calculations[26] (for Fe) tell us that the unpaired 3*d*-band electrons have a radial distribution which is contracted relative to the average behavior for the band. The energy band results suggest that the neutral free atom Co $3d^9$ Hartree-Fock 3*d* functions[20] provide a reasonable description of the average radial behavior of the band. Such a choice would be advantageous because it would allow a cancellation of terms similar to that used on going from Eq. (11) to Eq. (14). On the other hand we are interested in the exchange coupling of the unpaired 3*d* band electrons. Comparison of experimental[25] and computed[27] neutron form factors suggests that the Hartree-Fock Co^{++} $3d^7$ orbitals better approximate the unpaired *d*-band radial behavior. The choice of the 3*d* orbital from the $3d^7$ configuration calculation would be analogous to that of Stuart and Marshall.[15] They used an Fe 3*d* orbital obtained in a neutral Fe $3d^64s^2$ calculation[16] and due to the fact that 4*s* electrons have little or no effect on the 3*d* orbitals their choice is equivalent to a divalent ion solution. Calculations with Co^{++} $3d^7$ orbitals would provide a more meaningful comparison with the Stuart and Marshall results.

The one-electron charge densities for the two Co orbitals appear in Fig. 4 along with that of the hydrogenic (single exponential) 3*d* orbital previously described. It is clear that there is an important difference in shape between the latter function and the Hartree-Fock Co orbitals.

Below, we report J values for both the Co and Co^{++} orbitals; this will also give some indication of the important question of the sensitivity of J to orbital choice. Equations (11) and (14) are evaluated with $Z_a=Z_b=1$, i.e., a model in which the rest of the atom is replaced by a point charge. A more realistic treatment is given in Sec. III.

Numerical Results for Co

The observed internuclear distance for fcc Co is approximately 4.75 a.u. and so we have evaluated J with the Co and Co^{++} 3*d* orbitals at this distance using Eqs. (11) and (14) (with $Z_a=Z_b=1$). J's have also been evaluated with the Co^{++} orbitals for a number of other distances and we will report the results for a distance of 2.25 a.u. This gives some idea of the variation of J with r_{ab} over a reasonable range of internuclear separation.

Before inspecting values for J, let us consider the $S_{\sigma\sigma}$ overlap which behaved so strikingly as a function of r_{ab} for the hydrogen 3*d* orbital. $S_{\sigma\sigma}$'s, evaluated for the Co^{++} and Co 3*d* orbitals, are plotted in Fig. 7. The

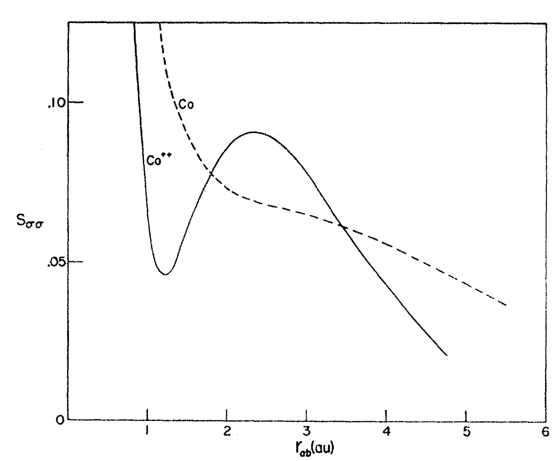

FIG. 7. The overlap integral between $3d_\sigma$ functions, $S_{\sigma\sigma}$, for Co^{++} and Co as a function of internuclear separation.

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[25] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids **10**, 147 (1959); R. Nathans, C. G. Shull, A. Andreson, and G. Shirane, *ibid.* **10**, 138 (1959); R. Nathans and A. Paoletti, Phys. Rev. Letters **2**, 254 (1959).

[26] J. H. Wood, Phys. Rev. **117**, 714 (1960) and further work (to be published); F. Stern, *ibid.* **116**, 1399 (1959).

[27] R. E. Watson and A. J. Freeman, Acta Cryst. **14**, 27 (1961).

TABLE I. Integrals[a] necessary for the evaluation of Eqs. (11) and (14) for pairs of $3d$ orbitals of like m_l value. These were obtained for Co^{++} $3d$ orbitals at 4.75 and 2.25 au and for Co $3d$ orbitals at a 4.75-au separation. Energies are in au (1 au = 27.07 ev).

	S_{ab}	P	Q	R	T	U	V	W
				$3d$ of Co^{++} at 4.75 au				
$\sigma\sigma$	0.02128	0.1504	0.1471	0.00972	0.0004297	1.3264	8.3470	0.00503
$\pi\pi$	0.01132	0.2134	0.2121	0.00453	0.0000671	1.3264	8.3470	−0.00063
$\delta\delta$	0.00169	0.2049	0.2078	0.00061	0.0000011	1.3264	8.3470	−0.00044
				$3d$ of Co^{++} at 2.25 au				
$\sigma\sigma$	0.09054	0.4983	0.4809	0.09682	0.03604	1.3264	8.3470	0.3548
$\pi\pi$	0.17538	0.4510	0.4491	0.12975	0.02960	1.3264	8.3470	0.3118
$\delta\delta$	0.07797	0.3959	0.4160	0.04572	0.00340	1.3264	8.3470	0.0713
				$3d$ of Co at 4.75 au				
$\sigma\sigma$	0.04640	0.1701	0.1649	0.02250	0.00314	1.1647	6.7779	0.0307
$\pi\pi$	0.05563	0.2168	0.2151	0.02078	0.00144	1.1647	6.7779	0.0191
$\delta\delta$	0.01672	0.2017	0.2064	0.00523	0.000085	1.1647	6.7779	0.0028

[a] $P = \langle a(1)b(2)|1/r_{12}|a(1)b(2)\rangle$; $Q = \langle a|1/r_b|a\rangle$; $T = \langle a(1)b(2)|1/r_{12}|b(1)a(2)\rangle$; $R = \langle a|1/r_b|b\rangle$; $U = \langle a|1/r_a|a\rangle$; $V = \langle a|-\frac{1}{2}\nabla^2|a\rangle$; $W = \langle a|-\frac{1}{2}\nabla^2|b\rangle$.

Co^{++} case shows a trough, as did the hydrogen orbital $S_{\sigma\sigma}$, but it nowhere goes negative. The Co $S_{\sigma\sigma}$ shows no trough but a slight flattening out in the region of 2.5 to 3 a.u. The difference in $S_{\sigma\sigma}$ behavior is, as noted earlier, due to the important difference in shape of the radial orbitals.

The integrals necessary for evaluating Eqs. (11) and (14) appear in Table I. When viewing these, comparison should be made with the experimental exchange parameters of 0.0006 au from spin-wave dispersion measurements[28] and 0.0009 au from low temperature magnetization data.[29] The J's for pairs of orbitals of differing m_l values appear in Table II; these are the simple exchange integrals, J_{12} [Eq. (15)], in the two-electron Heisenberg approximation to J. They are small but not negligible. Table III shows J's evaluated for orbitals of common m_l using both Eqs. (11) and (14). It is clear that Eqs. (11) and (14) yield very different J's for orbitals of like m_l value. Equation (14) was evaluated by Stuart and Marshall for $J_{\sigma\sigma}$ but with Fe $3d$ functions; our values for this case are in substantial agreement with theirs. The Eq. (14) values are similar to what has been seen for the hydrogen orbitals, i.e., $J_{\sigma\sigma}$ is positive and $J_{\pi\pi}$ and $J_{\delta\delta}$ are smaller in magnitude and negative. Equation (11), which is, however, the appropriate definition of J, yields J's which are *large* and *negative*. As one might suspect, and indeed is found, J is sensitive to orbital choice. There is a large increase in the magnitude of the J's on going from the Co^{++} 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.

For comparison with experiment one wishes an average J. This in turn requires an assumption concerning the probability that a pair of "unpaired" orbitals have any one assignment of m_l values. Let us assume (as did Stuart and Marshall) that any one of the twenty-five possible assignments is equally possible.[30] For $r_{ab}=4.75$, one obtains average J's of -0.00041 au for the Co^{++} orbitals and -0.00380 for

TABLE II. Direct exchange [i.e., Eq. (15)] for pairs of $3d$ orbitals of unlike m_l value obtained for Co^{++} $3d$ orbitals at internuclear separations of 4.75 and 2.25 a.u. and for Co $3d$ orbitals at 4.75 a.u. Energy units are in a.u. (1 au = 27.07 ev).

Center A	Center B	J for Co^{++} orbitals at 4.75 au	J for Co^{++} orbitals at 2.25 au	J for Co orbitals at 4.75 au
σ	π	0.0000371	0.00815	0.000561
σ	δ	0.0000040	0.00266	0.000160
π	$\bar{\pi}$	0.0000072	0.00399	0.000169
π	δ	0.0000027	0.00393	0.000127
π	$\bar{\delta}$	0.0000007	0.00098	0.000028
δ	$\bar{\delta}$	0.0000000_4	0.00014	0.000003

TABLE III. J (in au) evaluated using Eqs. (11) and (14) (and the integrals of Table I), the effective nuclear charge (Z) such that the last two lines of Eq. (14) cancel and the value, $J(Z)$, obtained by inserting that Z into Eq. (11) or (14). Values are reported for the Co^{++} $3d$ orbitals at internuclear distances of 2.25 and at 4.75 au and for the Co $3d$ orbitals at 4.75 au.

	J of Eq. (14)	J of Eq. (11)	Z	$J(Z)$
		$3d$ of Co^{++} at 4.75 au		
$\sigma\sigma$	+0.000081	−0.00648	9.33	−0.00225
$\pi\pi$	−0.000008	−0.00192	9.07	−0.00040
$\delta\delta$	−0.0000004	−0.000044	8.91	−0.000007
		$3d$ of Co^{++} at 2.25 au		
$\sigma\sigma$	+0.0223	−0.0461	17.21	−0.134
$\pi\pi$	−0.0022	−0.3702	11.20	−0.185
$\delta\delta$	−0.0011	−0.0824	10.04	−0.0198
		$3d$ of Co at 4.75 au		
$\sigma\sigma$	+0.00140	−0.0220	9.01	−0.0097
$\pi\pi$	−0.00021	−0.0351	8.14	−0.0072
$\delta\delta$	−0.000031	−0.0033	7.78	−0.00043

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[28] R. N. Sinclair and B. N. Brockhouse, Phys. Rev. **120**, 1638 (1960).

[29] P. Weiss and M. Forrer, Ann. phys. **12**, 359 (1929) discussed in ref. 28.

[30] Stuart and Marshall's averaging only included their calculated value for $J_{\sigma\sigma}$ whereas we use all twenty-five contributions from Tables II and III.

Co as compared with the observed[28] spin-wave exchange parameter of +0.0006 to +0.0009 au. The calculated value of J may be changed by a more refined assumption regarding orbital occupancy but this will in no case change the sign. Thus, if one assumes that the two-atom two-electron Heisenberg exchange parameter is relevant to the "direct exchange" of the metal one concludes that, because of its sign, direct exchange is not the source of the metal's ferromagnetism but that it is a large effect and cannot be neglected in a more sophisticated treatment of the problem.

If one is willing to insert Z's of other than +1 into Eqs. (11) and (14) one can ask what nuclear charge would cause the last two lines of Eq. (11) to cancel, making the two equations yield identical results. This charge is given by

$$Z=\frac{-\frac{1}{2}S_{ab}\langle a|\nabla^2|a\rangle+\frac{1}{2}\langle a|\nabla^2|b\rangle}{S_{ab}\langle a|1/r_a|a\rangle-\langle a|1/r_a|b\rangle}. \tag{16}$$

Calculated values for such Z's are given in Table III along with the $J(Z)$'s which are obtained by inserting these Z's into Eq. (11) or Eq. (14). The Z's for the Co^{++} (or Co) $3d$ orbitals do not have a common value; their value is dependent on both m_l and the internuclear separation. This variation is another indication of the nonhydrogenic behavior of the iron series orbitals. The $J(Z)$'s differ with the other J's of the table but they are substantial and negative, behaving much like the Eq. (11) values. One should note that the Z's and $J(Z)$'s represent an abandonment of the basis for going to the two-electron Heisenberg parameter, i.e., abandoning a description of the remaining electrons and the nucleus of the iron series atom by a point charge of +1.

III. DIRECT EXCHANGE FOR A PAIR OF $3d^9$ ATOMS

The one-electron per atom case discussed in the previous section showed that for this simple model J was negative and, therefore, that "direct" exchange was not responsible for ferromagnetic coupling. One might argue that this was not a realistic case and that, since the $3d$ electrons are part of an atom having many other electrons, a more "realistic" calculation of the direct exchange parameter would result in totally different results. In order to test this let us consider J for the case where a pair of iron series atoms is "clothed" with the remaining electrons and in this way abandon the point-charge model (with either $Z=1$ or effective Z_a's and Z_b's) of the previous section. We shall divide our discussion into two parts considering first the effect of the "core" electrons on the one-electron potentials and then the effect of the overlap of the "core" electrons on the determination of J.

A. J for "Clothed" Potentials

Consider the case of two $3d^9$ ions for which ${}^3E-{}^1E$ argument of the last section holds. The most obvious effect of going to the new model is to replace the simple nuclear attraction terms in the Hamiltonian by the more realistic multi-electron potential, e.g.,

$$-\frac{Z_a}{r_{1a}}\longrightarrow V_{1a}\equiv-\frac{Z}{r_{1a}}+\sum_{i_a}\int\psi_{i_a}^*(2)\frac{1-P_{12}}{r_{12}}\psi_{i_a}(2)dv_2, \tag{17}$$

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. We shall continue to denote the unpaired $3d$ electrons involved in the "direct" exchange by ϕ [and by $a(1)$ or $b(1)$ when brackets are used to denote integrations] and the other paired electrons by ψ. With this change, Eq. (14) (for example) becomes

$$\begin{aligned}J=(1-S_{ab}{}^4)^{-1}\Big\{&\Big\langle a(1)b(2)\Big|\frac{1}{r_{12}}\Big|b(1)a(2)\Big\rangle-S_{ab}{}^2\Big\langle a(1)b(2)\Big|\frac{1}{r_{12}}\Big|a(1)b(2)\Big\rangle\\&+2S_{ab}\Big\langle b(1)\Big|-\frac{Z}{r_{2a}}+\sum_{i_a}\int\psi_{i_a}^*(2)\frac{1}{r_{12}}\psi_{i_a}(2)dv_2\Big|a(1)\Big\rangle-2S_{ab}{}^2\Big\langle b(1)\Big|-\frac{Z}{r_{2a}}+\sum_{i_a}\int\psi_{i_a}^*(2)\frac{1}{r_{12}}\psi_{i_a}(2)dv_2\Big|b(1)\Big\rangle\\&-S_{ab}\sum_{i_a}\Big\langle b(1)\psi_{i_a}(2)\Big|\frac{1}{r_{12}}\Big|\psi_{i_a}(1)a(2)\Big\rangle+S_{ab}{}^2\sum_{i_a}\Big\langle b(1)\psi_{i_a}(2)\Big|\frac{1}{r_{12}}\Big|\psi_{i_a}(1)b(2)\Big\rangle\Big\}.\end{aligned} \tag{18}$$

Here we have assumed a common radial behavior for ϕ_a and ϕ_b. Several simplifications were made in writing Eq. (18). This equation should of course be symmetrical in summations over i_a and i_b but we have chosen to write out only one of the summations and to combine terms. The differing coefficients (2 and 1, respectively) arise from spin orthogonality and the last two terms were written as a summation over all the other electrons on the A site instead of as two times (once for each site) a summation over all the other electrons having spins parallel to the "exchanging" electrons (i.e., a summation over one-half the other electrons).

Similarly, if one uses Eq. (17) for the one-electron nuclear attraction potentials then the last two lines of Eq. (11) become

$$\begin{aligned}\Omega=(1-S_{ab}{}^4)^{-1}\Bigg\{&S_{ab}\Bigg[\Bigg\langle b(1)\Bigg|-\tfrac{1}{2}\nabla_1{}^2-\frac{Z}{r_{1a}}+\sum_{ia}\int\psi_{ia}{}^*(2)\frac{1-P_{12}}{r_{12}}\psi_{ia}(2)dv_2\Bigg|a(1)\Bigg\rangle\Bigg]\\&+S_{ab}\Bigg[\Bigg\langle a(2)\Bigg|-\tfrac{1}{2}\nabla_2{}^2-\frac{Z}{r_{2b}}+\sum_{ib}\int\psi_{ib}{}^*(1)\frac{1-P_{12}}{r_{12}}\psi_{ib}(1)dv_1\Bigg|b(2)\Bigg\rangle\Bigg]\\&-S_{ab}{}^2\Bigg[\Bigg\langle a(1)\Bigg|-\tfrac{1}{2}\nabla_1{}^2-\frac{Z}{r_{1a}}+\sum_{ia}\int\psi_{ia}{}^*(2)\frac{1-P_{12}}{r_{12}}\psi_{ia}(2)dv_2\Bigg|a(1)\Bigg\rangle\Bigg]\\&-S_{ab}{}^2\Bigg[\Bigg\langle b(2)\Bigg|-\tfrac{1}{2}\nabla_2{}^2-\frac{Z}{r_{2b}}+\sum_{ib}\int\psi_{ib}{}^*(1)\frac{1-P_{12}}{r_{12}}\psi_{ib}(1)dv_1\Bigg|b(2)\Bigg\rangle\Bigg]\Bigg\}.\qquad(19)\end{aligned}$$

These terms together with Eq. (18) form the new counterpart of Eq. (11) as the definition of J for two interacting but "clothed" holes ($3d^9$ atoms).

It is clear that the possibility of exact cancellations among these terms in the manner expressed by Eqs. (12) and (13) is here *extremely desirable* since it avoids taking differences between a large number of terms (of equal magnitude) and the resulting loss of significant figures. Before discussing the numerical results obtained for J for this case let us first consider one feature of this problem in the light of the conventional Hartree-Fock formalism.

The one-center Hartree-Fock equations have the form

$$(-\tfrac{1}{2}\nabla_1{}^2+V_{1a})\psi_i(r_1)=\epsilon_i\psi_i(r_1),\qquad(20)$$

when defined for an individual one-electron wave function $\psi_i(r)$, and when $\sum_{ia}$ in V_{1a}, the multi-electron potential operator given in Eq. (17), includes all the *other* electrons on center A. If the ψ_i's (which include the ψ_{ia}'s and ϕ's) were obtained by the solution of such equations defined for the $3d^9$ configuration then the sum of all terms of Eq. (19) (i.e., the quantity labeled Ω) equals zero. As was seen for the case discussed in Sec. II, this makes the computation much easier and reduces the possible sources of numerical error.

Unfortunately, the Hartree-Fock equations solved by the conventional method *do not* take on the form of Eq. (20). One restriction associated with the conventional method is that there be a single radial function per shell (we have in fact made use of this restriction by having "paired" orbitals which make no contribution to the spin symmetry of the system). For an open shell ion, the solution of equations of the form of Eq. (20) will in general yield different radial functions for different orbitals. In order to meet this restriction, what is generally solved for is an *average*[31] equation, per shell, of the equations which can be individually derived. The cancellation of terms in Eq. (19) becomes considerably complicated by this, a matter discussed at greater length in the Appendix. In practice we will ignore the fact that the $3d$ orbitals are the solution of *averaged* Hartree-Fock equations. We expect that the errors associated with doing this are small (see the Appendix); they are, in fact, smaller than the numerical errors which would accumulate if these terms were included. When effecting the cancellations in Eq. (19) it should be noted that when the $3d^7$ Co^{++} orbitals are used we must account for the fact that Eq. (19) was written for the $3d^9$ configuration. Terms involving the two extra electrons are not involved in the cancellation and their contribution to J must be evaluated. As we shall see, these terms are of substantial magnitude.

TABLE IV. J's (in au) for "clothed" potentials with Co^{++} $3d$ wave functions at $r_{ab}=4.75$ au and 2.25 au and Co $3d$ wave functions at $r_{ab}=4.75$ au. [See Eqs. (18) and (19).]

	Co at $r_{ab}=4.75$ au	Co^{++} at $r_{ab}=4.75$ au	Co^{++} at $r_{ab}=2.25$ au
$J_{\sigma\sigma}$	−0.00050	−0.001073	−0.00774
$J_{\pi\pi}$	−0.00151	−0.000295	−0.09158
$J_{\delta\delta}$	−0.00011	−0.000007	−0.01716

Numerical values of J, for the "clothed" atoms, appear in Table IV. Again we see that J is large and negative although smaller in magnitude than the two-electron results quoted earlier in Table III. The results of Table II hold here as well for pairs of orbitals of unlike m_l. Two approximations were made in the calculations. First, as indicated above, the Ω contribution [Eq. (19)] was set equal to zero (with the exception of the terms associated with the two extra $3d$ orbitals when the Co^{++} $3d$ functions were used). Secondly, the "clothing" was limited to the $3s$, $3p$, and $3d$ electrons, i.e., the ten $1s$, $2s$ and $2p$ orbitals were neglected and Z was replaced by $Z-10$ in Eq. (18). Serious numerical errors were encountered when the necessary integrals involving the $1s$, $2s$, and $2p$ orbitals were obtained. Being the most localized, they contribute the least to the effect of the "clothed" potentials and in view of this they were neglected. Accurate inclusion of these terms

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[31] D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957).

(and the parallel adjustment of the Z used) would produce very small quantitative changes in the J's reported in Table IV. Their inclusion would not effect the qualitative behavior of the results appearing there. Because of the accumulated numerical errors associated with the terms [of Eq. (18)] included in the J's, the results of Table IV should be viewed only qualitatively anyway. The numerical uncertainty of these results is greater than that of the preceding sections. Evaluation of the second and third terms of Eq. (18) is the primary source of the errors. These terms involve a differencing of terms of almost equal magnitude which is most serious for term three. These terms are made up of two-center "Coulomb" integrals,[23] the type of integral which has given us the greatest difficulty with numerical accuracy.

In the face of the numerical uncertainty associated with the J's of Table IV, it does not seem appropriate to supply a detailed listing of the various terms [of Eqs. (18) and (19)] contributing to them. Inspection of one case may, however, be instructive. Let us consider $J_{\sigma\sigma}$ for Co^{++} at 4.75 au. For this case the five terms of Eq. (18) make contributions of $+0.000362$, -0.000628 (of which the "clothing" contributes -0.000214), $+0.000137$ (of which the "clothing" contributes $+0.000004$), -0.000062 and $+0.000000$ au, respectively; the fact that our orbitals are eigenfunctions for the $3d^7$ provides an Ω contribution of -0.000882 au. We see that the Ω contribution is substantial; it drives the negative J's determined for Co^{++} orbitals more negative than those evaluated for neutral Co. This effect is similar to that seen in the preceding section. One should also note the small magnitude (zero to the number of digits quoted) of the last term of Eq. (18). This term is the one term which we have considered which is proportional to the fourth,[32] rather than the second, order in S_{ab}. It is substantially smaller for $J_{\pi\pi}$ and $J_{\delta\delta}$. Its small size is important to the discussion which follows, and so has been included here.

If now we compute an average J, as we did earlier for the two-electron problem (Sec. II D), we find some different (and surprising) answers (if one considers only Table IV). Assuming that each $3d$ orbital has an equal probability of being occupied by a hole, J_{av} for Co^{++} $3d$ orbitals at $r_{ab}=4.75$ is -0.000059 au whereas for Co $3d$ orbitals, at the same r_{ab}, it is $+0.00000_5$ 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. It should be noted that the assumption of equal probability of hole occupancy by each of the orbitals is about the most restrictive one that can be made. Therefore for any other assumption which correlates the holes on the two centers the value of J will be more negative than the J_{av} values quoted above. However, in view of the simplicity of the model, the tenuousness of the arguments, and the fact that so far we have only treated half of the question of clothing we shall not dwell on this matter any longer.

B. Effect of Core Electron Overlap

We have seen the effect of "clothing" the free atom potentials with the "core" electrons on the calculation of J. Having allowed these electrons to play a role in the interaction we must now recognize that some of these paired electrons, the ψ_i's, have the same radial extent as the exchanging $3d$'s (i.e., the ϕ'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.

If we let

$$\mathrm{I}=\det\{a(1)\alpha(1)b(2)\beta(2)\psi_1(3)\alpha(3)\psi_1(4)\beta(4)\cdots\},$$

and

$$\mathrm{II}=\det\{b(1)\alpha(1)a(2)\beta(2)\psi_1(3)\alpha(3)\psi_1(4)\beta(4)\cdots\},$$

then with

$$^1\psi=\mathrm{I}+\mathrm{II} \quad \text{and} \quad {}^3\psi=\mathrm{I}-\mathrm{II},$$

$$J=\tfrac{1}{2}(^1E-{}^3E)=\frac{1}{2}\left\{\frac{H_{\mathrm{I,I}}+H_{\mathrm{I,II}}}{S_{\mathrm{I,I}}+S_{\mathrm{I,II}}}-\frac{H_{\mathrm{I,I}}-H_{\mathrm{I,II}}}{S_{\mathrm{I,I}}-S_{\mathrm{I,II}}}\right\}$$

$$=\frac{S_{\mathrm{I,I}}H_{\mathrm{I,II}}-S_{\mathrm{I,II}}H_{\mathrm{I,I}}}{S_{\mathrm{I,I}}^2-S_{\mathrm{I,II}}^2}. \qquad (21)$$

Here $H_{\mathrm{I,II}}$ is the matrix element of energy between determinants I and II and $S_{\mathrm{I,II}}$ is the corresponding overlap determinant. The terms in Eq. (21), which can be grouped in ascending powers of overlap integrals present all the elements of the well-known "overlap catastrophe" for a solid, only on a more modest scale. If we account for the fact that the integrals which are multiplied by products of overlap integrals are themselves proportional to the (zero, first and second powers of) overlaps, then one observes that the individual contributions to Eq. (21) are of the order of (ascending) even powers of overlaps. With the sole exception of the last term in Eq. (18) (which is of the fourth order) all the terms considered so far have been second-order terms. If the overlap of the one-electron functions is sufficiently small (as it is for our case of two Co atoms at the observed internuclear distance of 4.75 au) there

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[32] It is made up of two-center "exchange" integrals which are of the order S^2 multiplied with a coefficient S_{ab}^2.

is no overlap problem and we can limit our attention to those additional terms which are of the second order in the overlaps. $S_{\mathrm{I,I}}$ is of the order 1 whereas $S_{\mathrm{I,II}}$ is of the order $S_{ab}{}^2$. With these approximations these terms are easy to find. One of these is:

$$\Delta_{\mathrm{I}}=-2S_{ab}\sum_{ia}{}'' S_{ia,b}\Big\langle a(1)\Big|-\tfrac{1}{2}\nabla_1{}^2-\frac{Z}{r_{1a}}-\frac{Z}{r_{1b}}+\sum_{j}{}'\int dv_2\,\psi_j{}^*(r_2)\frac{1-P_{12}}{r_{12}}\psi_j(r_2)\Big|\psi_{ia}(1)\Big\rangle$$

+a similar term for center B. (22)

The $\sum'$ is over all the ψ's of *both* centers *except* for ψ_{ia} and $\sum''$ indicates that this sum should be limited to one orbital of each pair of paired ψ's for the center in question. Note that one can carry over the discussion of the one-center eigenvalue equation of the previous subsection [cf. Eq. (20)] and a similar cancellation of terms can be affected here. In this case, however, the cancellation follows from the orthogonality of ϕ's and ψ's associated with the same nucleus. In general the same features apply here as discussed above for the cancellation of terms in Eq. (19) and the same care must be observed.

Other contributions to J of the second order in overlaps are

$$\Delta_{\mathrm{II}}=+\sum_{ia}{}'' S_{ia,b}{}^2\Big\langle a(1)\psi_{ia}(2)\Big|\frac{1}{r_{12}}\Big|\psi_{ia}(1)a(2)\Big\rangle$$

+a similar sum for center B, (23)

$$\Delta_{\mathrm{III}}=-2\sum_{ia}{}'' S_{ia,b}\Big\langle a(1)b(2)\Big|\frac{1}{r_{12}}\Big|\psi_{ia}(1)a(2)\Big\rangle$$

+a similar sum for center B, (24)

$$\Delta_{\mathrm{IV}}=+2\sum_{ia}{}''\sum_{jb}{}''\left[S_{ia,jb}S_{ab}+S_{ia,b}S_{jb,a}\right]\times\Big\langle a(1)\psi_{jb}(2)\Big|\frac{1}{r_{12}}\Big|\psi_{ia}(1)b(2)\Big\rangle, \quad (25)$$

and finally

$$\Delta_{\mathrm{V}}=+2\sum_{ia<ja}{}''\sum{}'' S_{ia,b}S_{ja,b}\times\Big\langle\psi_{ia}(1)a(2)\Big|\frac{1}{r_{12}}\Big|a(1)\psi_{ja}(2)\Big\rangle$$

+a similar sum for center B. (26)

Up to this point in our treatment J for a pair of ϕ's differing in m_l was simply given by J_{12} of Eq. (15) (due to S_{ab} being zero by symmetry). However, Δ_{II} through Δ_{V} make nonzero contributions to J for this case and our calculations show that their individual contributions can be larger in magnitude than the J_{12} of Eq. (15). A second feature of the Δ terms is that the symmetry requirements for nonzero S's reduces the individual integrals which must be considered to a manageable number. Finally with exception of Δ_{I} and Δ_{IV} (which happen to make the smallest nonzero contributions to J), the necessary two-electron integrals are either easily obtainable one-center integrals or are those which have already been obtained in the process of evaluating Eq. (18).

In Table V we give the results of our calculations for the correction terms to J due to the overlap of the "core" electrons for the Co^{++} and Co $3d$ orbitals at $r_{ab}=4.75$ au. The first column gives the previous J values (see Table II for the off-diagonal terms and Table IV for the diagonal terms), the next five are the various Δ terms of Eqs. (22) through (25), and the last is the final J which is the sum of all the previous terms. Only Δ_{I} provides any difficulty with accuracy (although Δ_{IV}, which is made up of two-center Coulomb integrals,[28] would if it were not so small). The "averaged" Hartree-Fock correction to Δ_{I} has been neglected, as has been done previously, whereas the $3d^7\rightarrow 3d^9$ correction for the Co^{++} orbitals was included. We see that individual Δ contributions can be appreciable. Again the separate diagonal J's are negative, much smaller than was found for the two-electron case, but of the same magnitude as the observed values. The core overlaps have not made drastic changes in the J's (due to the differing signs of the Δ terms) but the relative values of the terms has been shifted about. This is particularly true of the nondiagonal terms which, for the first time in our discussion, are now no longer just the simple electrostatic exchange integrals of Eq. (15). Again if we invoke an occupancy argument, assigning equal probability for a hole to have any specific m_l value on any center, we find J_{av}'s of -0.00006 au for the Co $3d$ orbital and -0.000076 au for the Co^{++} function. We see that here too the nondiagonal terms play an important role and will also be important in any more exact treatment (such as discussed in the next section). Occupancy arguments will again affect the J_{av}'s, making them more *negative* than the values just quoted. These results bring our conclusion (but not our values) into agreement with that of Stuart and Marshall[15] (but for different reasons). J is small and of the wrong sign to account for the observed ferromagnetism of the transition metals.

IV. DISCUSSION OF DIRECT EXCHANGE AND A MORE EXACT MODEL

We have been studying the predictions of a model of exchange interaction which has, as we have noted, serious deficiencies. In this section we will consider some aspects of what would be involved in a more rigorous treatment which uses the two-atom localized orbital picture as its basis. It is beyond the scope of the present paper, however, to either report such an investigation or to give a detailed description of how it

TABLE V. Δ_i's [see Eqs. (22) through (25)] and the resultant J's (in au) for Co and Co^{++} $3d$ orbitals at $r_{ab}=4.75$ au. The J's to which the Δ_i's are added are also included.

	J of Table II or IV	Δ_{I}	Δ_{II}	Δ_{III}	Δ_{IV}	Δ_{V}	J=sum of preceding terms
				Co^{++} at $r_{ab}=4.75$ au			
$\sigma\sigma$	−0.001073	0.000053	0.000045	−0.000120	0.000002	0	−0.001093
$\sigma\pi$	0.000037	0	0.000034	−0.000042	0	−0.000018	0.000011
$\sigma\delta$	0.000004	0	0.000027	0.000003	0	−0.000036	−0.000002
$\pi\pi$	−0.000295	0.000001	0.000001	−0.000005	0	0	−0.000298
$\pi\bar{\pi}$	0.000007	0	0.000020	−0.000007	0	0	0.000020
$\delta\delta$	−0.000007	0	0	0	0	0	−0.000007
$\delta\bar{\delta}$	0	0	0	0	0	0	0
$\delta\pi$	0.000003	0	0.000009	−0.000004	0	0	0.000008
$\delta\bar{\pi}$	0.000001	0	0.000003	−0.000001	0	0	0.000003
				Co at $r_{ab}=4.75$ au			
$\sigma\sigma$	−0.00050	0.00013	0.00049	−0.00131	0.00002	0	−0.00117
$\sigma\pi$	0.00056	0	0.00032	−0.00061	0.00001	−0.00016	0.00012
$\sigma\delta$	0.00016	0	0.00020	−0.00005	0	−0.00031	0
$\pi\pi$	−0.00151	0.00004	0.00003	−0.00012	0.00002	0	−0.00154
$\pi\bar{\pi}$	0.00017	0	0.00038	−0.00002	0	0	0.00053
$\delta\delta$	−0.00011	0	0	0	0	0	−0.00011
$\delta\bar{\delta}$	0	0	0.00002	0	0	0	0.00002
$\delta\pi$	0.00013	0	0.00018	−0.00012	0	0	0.00019
$\delta\bar{\pi}$	0.00003	0	0.00006	−0.00003	0	0	0.00006

should be carried out. The approach utilizes configuration mixing, some aspects of which have also been used in Van Vleck's "minimum polarity" model[8] of exchange. Before discussing what the approach would involve and what some of its limitations might be, let us consider several investigations which shed light on some phases of how the problem could be handled and in what way the results should be viewed.

The hydrogen chain problem, which is amenable to solution, has been the subject of considerable investigation.[33] Mattheiss[30] has recently reported a detailed configuration interaction study for the six atom case where, using H $1s$ orbitals, all configurations were considered and all multi-center integrals[34] were evaluated and used. Configuration interaction calculations were done for wave functions of common symmetry *and then* the resulting energy spectrum was fitted to see how well it matched a vector coupling equation [Eq. (7)]. The chain was studied as a function of internuclear separation and at the stable internuclear distance of ~2 au (i.e., where the ground-state total energy is a minimum) it was observed that neither a single configuration atomic (localized) orbital nor a single configuration molecular (itinerant) orbital description satisfactorily yields the energy spectrum, i.e., configuration interaction or perturbation theory is necessary. In addition, using perturbation theory, Mattheiss obtained an analytic expression for an effective nearest-neighbor exchange integral J. While there are many interesting features[35] of Mattheiss's results, the technique of inspecting the spectrum after configuration interaction, the perturbation theory analysis and the observation that a single configuration description is inadequate are of greatest interest to us here. The model of the preceding sections is, after all, a single configuration description.

The hydrogen s orbital, one-electron (or pair of electrons) per atom case just discussed differs in many ways from the problem of interest here. Diatomic molecular calculations such as that of Nesbet[36] for N_2 are more akin to the case at hand. Nesbet's investigation is of particular interest because he related the various types of configurations, which appeared in the calculation, to several mechanisms of superexchange theory. In addition he showed which configurations would contribute to a $J\mathbf{S}_i\cdot\mathbf{S}_j$ term and which would yield terms of a higher order in S. This relied on an observation[37] of a property of spin projected functions. In N_2 the unfilled shells are the atomic $2p$ and for some internuclear distances of interest Nesbet observed that the lowest energy single configuration was one in which some of the $2p$ orbitals were treated as atomic orbitals and some as molecular orbitals. This observation is of interest because the recent work of Anderson,[38] Clogston,[39] and Wolff[40] on magnetic moments in alloys have emphasized the localized behavior of the orbitals

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[33] L. F. Mattheiss, Phys. Rev. **123**, 1209, 1219 (1961) and references therein.

[34] The three- and four-center integrals, which are normally just estimated, were calculated using programs of M. P. Barnett (unpublished).

[35] See reference 30 and J. C. Slater, Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, October 15, 1960, (unpublished), p. 4.

[36] R. K. Nesbet, Phys. Rev. **122**, 1497 (1961).

[37] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

[38] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[39] A. M. Clogston (to be published).

[40] P. A. Wolff (to be published).

contributing to the moment. The one-electron energies of these orbitals overlap the conduction bands for which the itinerant orbital description is most appropriate. These observations suggest that the most successful single configuration or limited multiconfiguration description of a pair of iron series ions is one in which some of the $3d$ orbitals are molecular orbitals and some are atomic orbitals. Nesbet discusses an approach similar to this for the metal; we will consider a much more limited investigation.

We are interested in the magnetic interaction of an iron series ion with its neighbors in the crystal. We would like to treat a case such as the interaction of that ion with the cluster of its nearest neighbors. Unfortunately such an investigation is formidable and we will instead limit ourselves to the interaction between a pair of neighbors.

Above, we have surveyed several investigations which help illustrate how one might treat the problem. Let us now briefly consider what would be involved in such an investigation. This will be followed by a discussion of two shortcomings associated with such a treatment.

For our example let us consider the problem for a pair of Ni atoms. If one considers all functions belonging to a particular set of configurations the resulting configuration interaction calculation is on a smaller scale, hence simpler, than investigations with similar sets for Fe or Co. This does not necessarily mean that in practice the Ni_2 case converges more rapidly to a "final" result.

As already observed, energy band results tell us that configurations involving $4s$ as well as $3d$ orbitals should be included in the investigation. In addition there is also "$4p$" behavior in both the "$3d$" and "$4s$" bands and therefore configurations involving $4p$ orbitals cannot be ignored. Eqs. (22) to (26), above, suggest that the presence of $4s$ and $4p$ orbital behavior in the many-electron function will play an important role in the spin dependent terms of the energy. Perhaps the $4p$ character can be introduced with some "hybridized" orbitals[41] in such a way as to minimize the complications (i.e., the number of additional configurations) associated with the $4p$ orbitals.

Let us consider the scale of the configuration interaction problem where neutral, singly, and doubly ionized (one ion positively and at the same time, the other negatively) ion configurations are included. If one restricts oneself to configurations involving just $3d$ and $4s$ orbitals one has a problem involving over eleven thousand different molecular functions. If one adds atomic configurations of the form $3d^{n-2}4p^2$ to those already considered, the number of molecular functions increases by a factor of one hundred. Other types of "$4p$ configurations" would further increase the scale of the problem.

The problem is not as formidable as the numbers above suggest. First, we could be selective in the "$4p$ configurations" and secondly the problem factorizes since the many-electron Hamiltonian has zero-valued matrix elements between molecular functions of differing spacial and/or spin symmetry. Secondly, a number of the molecular symmetries will be associated with states of high energy and so can be ignored. Finally, judicious use of molecular many-electron functions constructed from sets of atomic and molecular orbitals could reduce the number of important configurations.

The scale of such a computation depends on the specific choice of many-electron functions which are included. A "reasonably" defined scope of the problem is likely to involve one with at least a few secular equations which are 50×50 to 100×100 in dimensions (as against the 8×8 treated by Nesbet). Such cases can be solved with current computational techniques. More serious is the question of accurately evaluating the matrix elements in the matrices to be diagonalized. The problems of numerical accuracy encountered by us in the present paper (such as matrix elements of the "clothed" potentials) are less serious than what would be involved here. Terms such as Eqs. (22) to (26) and others of similar form would have to be included. Reduction in the scope of the investigation and the use of perturbation theory for all but the most important configurations[42] would reduce the number of matrix elements to be evaluated but it will not resolve the problem of numerical accuracy. Greater accuracy than what we have obtained is necessary for such an investigation. Another, more easily resolved, difficulty is that of obtaining the properly symmetrized functions for which the matrix elements are to be evaluated. For an investigation of this scale it might be desirable to do the group theory on a digital computer as Mattheiss[33] did for his problem. Observations of the type made by Nesbet[42] would be more difficult because of the more complicated (due to several partially filled shells) spatial symmetry problem.

Assuming that such a Ni_2 configuration interaction investigation was carried out and that the resulting energy spectrum is scrutinized, there remains the question of what bearing the results have on the magnetic properties of the metal. First, do the symmetries built into the molecular calculation distort the relevance to the metal and secondly, how would the presence (if included) of the other neighboring ions in the metal perturb the results? Paired electrons associated with these neighbors would make nonzero contributions to total energies in a manner similar to the effects discussed in Sec. III. Except for new "clothed" Coulomb potential terms, the contributions would be proportional to the fourth and higher orders (note that our investi-

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[41] As suggested by J. C. Slater (private communication).

[42] Nesbet, reference 36, believes that perturbation theory can, in practice, be relied on for this. See his Table IV for a comparison of configuration interaction and perturbation theory results.

gation was limited to second-order terms) in overlap integrals. While these individual contributions are small, there are many of them and they greatly increase the possibility of the "overlap catastrophe." This is a problem which Carr[43] has investigated. Experiments using inert gas crystals[44] as hosts for near neighbor pairs of iron series ions would help resolve the importance of the symmetry and additional neighbor effects. Experimental data of this sort would provide an invaluable link between such a theoretical investigation and the observed magnetic properties of the metals—and in fact would indicate whether a two-interacting-atom description is relevant to the metal's ferromagnetic behavior.

V. SUMMARY AND CONCLUSION

We have been investigating the role of direct exchange as a mechanism responsible for ferromagnetism by carrying out accurate calculations with the Heisenberg model, but extended and refined in several ways. In this way we have been able to check the predictions of the theory with experiment. We have determined the sign and magnitude of the direct exchange integral, J, as a function of internuclear separation (about which there has been considerable speculation and controversy) for several cases for which, as Löwdin has shown, J is rigorously defined.

We first considered a pair of atoms with a single electron per atom, corresponding to the case of two hydrogenic atoms. J was 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. Calculations for all pairs of $3d$ orbitals showed that J is sensitive to the angular dependence of the wave functions—and to the precise radial shape as well. It was seen that $J_{\sigma\sigma}$ is not necessarily the dominant term and that other J's can in fact be larger. In our observations for the hydrogen orbitals [for which Eq. (14) holds exactly] we have seen that the behavior of the "diagonal" J's (i.e., between like $3d$ functions on each center) as a function of internuclear separation does not consistently follow any one of the forms suggested by past authors (an observation which relates to an historic and fascinating controversy[4]). The fact that the iron series $3d$ functions are not eigenfunctions of the hydrogenic Hamiltonian was found to markedly affect the results. The "correction" terms dominate, changing J's which might otherwise be positive (the Stuart and Marshall result) to large *negative* values (i.e., opposed to ferromagnetism).

We then discussed the more realistic case of a single hole in otherwise closed shells; our example was Co in the $3d^9$ configuration. Here the effect on J of "clothing" the atoms with the remaining electrons (both in the core and in the rest of the $3d$ shell) was considered, 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. From an analysis of these terms it was 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. We saw that the effect of clothing was to reduce the magnitude of J (i.e., make less negative) and that while the diagonal J's were themselves fairly large the positive nondiagonal terms greatly reduced the diagonal estimate and gave final J_{av}'s which were still *negative* but smaller in magnitude (by one order) than the observed values. While the core overlap terms, i.e., the Δ's of Eq. (22) through (26), do not appreciably affect the J_{av}'s they are sizeable and can greatly perturb the individual J's, thus making the results even more sensitive to the occupancy argument used. Finally, a more exact model of two-atom exchange was discussed as were some of the problems inherent in carrying out such calculations.

From these results 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. Our particular preference is for the latter point of view.

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APPENDIX

We consider here the form of the Hartree-Fock equations that are actually solved and the implications of this form on the evaluation of direct exchange terms. Let us rewrite Eq. (20) for Co $3d$ orbitals in the form:

$$\left\{\left[\int \sum_{j=1}^{n} \phi_j^*(r_2)\frac{(1-P_{12})}{r_{12}}\phi_j(r_2)dv_2\right]+R\right\}\phi_i(r_1) = \epsilon_i\phi_i(r_1), \quad \text{(A1)}$$

where ϕ_i is a $3d$ orbital. The sum ($j=1$ to n) is over all occupied $3d$ orbitals and R includes nuclear potential, kinetic energy and two-electron Coulomb and exchange terms involving the $1s$, $2s$, $2p$, $3s$, and $3p$ shells. For the case of an unfilled $3d$ shell, the effect of the term in square brackets is a function of the m_l and m_s values associated with ϕ_i while R is not. In practice we solve

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[43] W. J. Carr, Jr., Phys. Rev. **92**, 28 (1953).

[44] Work along these lines is underway at the Lawrence Radiation Laboratory at Livermore, California by E. Lee.

Hartree-Fock radial equations and the radial form of Eq. (A1) is:

$$\left[\int \Theta_{m_l}(\theta,\phi)\chi_{m_s}\{\quad\}\Theta_{m_l}(\theta,\phi)\chi_{m_s}\sin\theta d\theta d\phi ds\right]U_i(r)$$
$$=\epsilon_i U_i(r), \qquad \text{(A2)}$$

where U, Θ, and χ are the radial, angular, and spin parts of ϕ_i and the $\{\quad\}$ term is that of Eq. (A1). As already indicated, the operator in $[\quad]$ is dependent of m_l and m_s and as a result different U_i's would be obtained for ϕ_i's of differing m_l and m_s if such equations were solved. Now we want a single $U(r)$ per shell and the normal[31] way of obtaining this is to solve Eq. (A2) averaged over occupied m_l and m_s values, i.e.,

$$\left[\frac{1}{n}\sum_{i=1}^{n}\left(\int \Theta_i^*(\theta,\phi)\chi_i\{\quad\}\Theta_i(\theta,\phi)\chi_i\sin\theta d\theta d\phi ds\right)\right]$$
$$\times U_{3d}(r)=\epsilon_{\mathrm{av}}U_{3d}(r). \qquad \text{(A3)}$$

Here we have a radial equation with an averaged operator multiplying $U_{3d}(r)$. Unfortunately the parallel situation does not occur for an equation written for the ϕ_i's, i.e., one does not have an averaged operator operating on ϕ_i. The averaging involves the angular and spin behavior of the set of occupied ϕ_i's. In other words, the ϕ_i's are not strict eigenfunctions of an equation of the form

$$H_a\phi_i=\epsilon_i\phi_i \quad \text{or} \quad \epsilon_{\mathrm{av}}\phi_i, \qquad \text{(A4)}$$

where H_a includes terms or the average of terms of the type appearing in Eq. (20).

This considerably complicates effecting a cancellation of terms after the manner used in Sec. II. As already indicated, such a cancellation is extremely desirable since it appreciably reduces the accumulation of numerical errors in the evaluation of J. The cancellation is between the terms

$$S_{ab}\langle\phi_b|H|\phi_a\rangle-S_{ab}^2\langle\phi_a|H|\phi_a\rangle, \qquad \text{(A5)}$$

where H is defined for the nine $3d$-electron Co atom. If Eq. (A4) did hold one would merely have to evaluate

$$S_{ab}\langle\phi_b|H-H_a|\phi_a\rangle-S_{ab}^2\langle\phi_a|H-H_a|\phi_a\rangle. \qquad \text{(A6)}$$

The R terms of Eq. (A1) would drop out of each integral and terms of the type appearing in $\{\quad\}$ would undergo substantial cancellation within each integral separately. The second term can be easily evaluated for the case at hand separately. One simply multiplies equations similar to Eqs. (A2) (defined for H) and (A3) (defined for H_a) by $U_{3d}(r)$, integrates and takes the difference.[45] Since Eq. (A4) does not hold, the first term cannot be similarly handled and it is perhaps easier to evaluate Eq. (A5), abandoning the cancellations and accepting the accumulated errors.

Fortunately, U_{3d}'s which are eigenfunctions of Eq. (A3) are approximate eigenfunctions of Eq. (A2). This in turn implies that Eq. (A5) approximately equals zero if U_{3d} was obtained for the nine $3d$-electron ion. In turn it implies that if we are using the Co^{++} U_{3d} that we need only consider those terms involving the two $3d$ electrons which contribute to the H of Eq. (A5) (which we remind the reader, is defined for the neutral atom) but do not appear for the Co^{++} ion. We have done this in the work reported in Sec. III since the errors introduced in an attempt to evaluate either Ω [see Eq. (19)] or Δ_1 [Eq. (22)] with our integrals appear to be more serious than those associated with following such a policy. We expect that the errors will affect the last digit of the J's so reported (see Tables IV and V).

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[45] This is simply the difference between ϵ_{av} and ϵ_i. These quantities have been tabulated for the Co orbitals used here [see R. E. Watson, Tech. Rept. No. 12, Solid State and Molecular Theory Group, 1959 (unpublished)].