

tributable to differences in, or the absence of, corrections for absorption by free radicals.

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## A Limit Function for Long-Range Ferromagnetic and Antiferromagnetic Superexchange<sup>†</sup>

R. E. Coffman\* and G. R. Buettner<sup>‡</sup>

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242 (Received April 20, 1979)

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An experimentally determined limit function for long-range ferromagnetic and antiferromagnetic superexchange is proposed, the form of which comprises a quantitative statement of present knowledge of the "range" of superexchange effects in insulating solids. A possible functional form for this limit function, as well as for the general distance dependence of long-range superexchange, is also proposed. The fitting of this general function to experimental data for superexchange coupling vs. distance requires the fitting of three independent parameters. The possibility is considered that one of the parameters so obtained may be sensitive to the degree of extended character of the orbitals which mediate the superexchange effect. The superexchange limit function is shown to be important for characterizing the assignments of alternative paths of exchange interaction. It also serves to point out the need for improved theoretical methods for the analysis of the relative strength of competing paths of interaction in exchange coupled cluster complexes, and shows that there is a need for studies of superexchange interactions acting over distances greater than 6 Å.

### I. Introduction

The scalar, bilinear superexchange interaction between two paramagnetic transition metal ions, or between a paramagnetic transition metal and a nearby free radical, depends on the localized vs. delocalized nature of the electronic states which mediate the spin-exchange process,

as well as other internal variables. The electronic states which transfer the superexchange may be tightly bound and localized, as in the case of superexchange between two ions in an insulator. At the other extreme, the states which transfer the superexchange may be delocalized in a solid with an electronic band structure, having wide bands and narrow band gaps so that there may be measurable electrical conduction. The appropriate case for comparison here is superexchange in a semiconductor (metals and superconductors are not here considered), in which spin-spin exchange coupling is transferred via delocalized electronic states of the valence band. Now, it has been

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<sup>‡</sup>Department of Chemistry, Wabash College, Crawfordsville, Ind. 47933.

suggested<sup>1</sup> (from band theory perturbation calculations based on the second-quantization formalism) that the range of superexchange coupling in semiconductors may be greater than in insulators. If this is true, then a demonstration of this difference in superexchange mechanism might be accomplished by arriving at a useful operational definition of the term "range".

It is well known that superexchange interactions decay rapidly vs. distance. The question we raise here is whether there exists a distance-dependent limit to superexchange, measured between paramagnetic clusters in insulating solids? Such a function would then define the "range" for the superexchange interaction by giving a limiting magnitude for the superexchange interaction for a given distance. This function would be useful for various theoretical exercises, and comparisons with experiment. It may also help to delineate the true long-range (i.e., that part of the superexchange isotropic coefficient due to mixing with band states delocalized over an entire crystal) character of superexchange in semiconductors, as compared to insulators.

The superexchange interaction in a cluster compound is a complicated function of orbital symmetry and electron occupation numbers both of the metal atoms and of the intervening ligands.<sup>2</sup> The bridging angles are clearly recognized pertinent variables,<sup>3</sup> as well as the overall distance over which the superexchange acts. Now, superexchange interactions are observed over a wide range of compounds studied in physics and physical chemistry: metals, semiconductors, and insulating inorganic and organic complexes, as well as in biomacromolecules. So, the question we have asked is whether there exists a distance-dependent limit to superexchange which may be useful for studies of superexchange magnetic effects in "insulating" compounds. We find that the present body of data supports the existence of such a limit property. The question of theoretical justification is more difficult, and will be taken up at a later date.

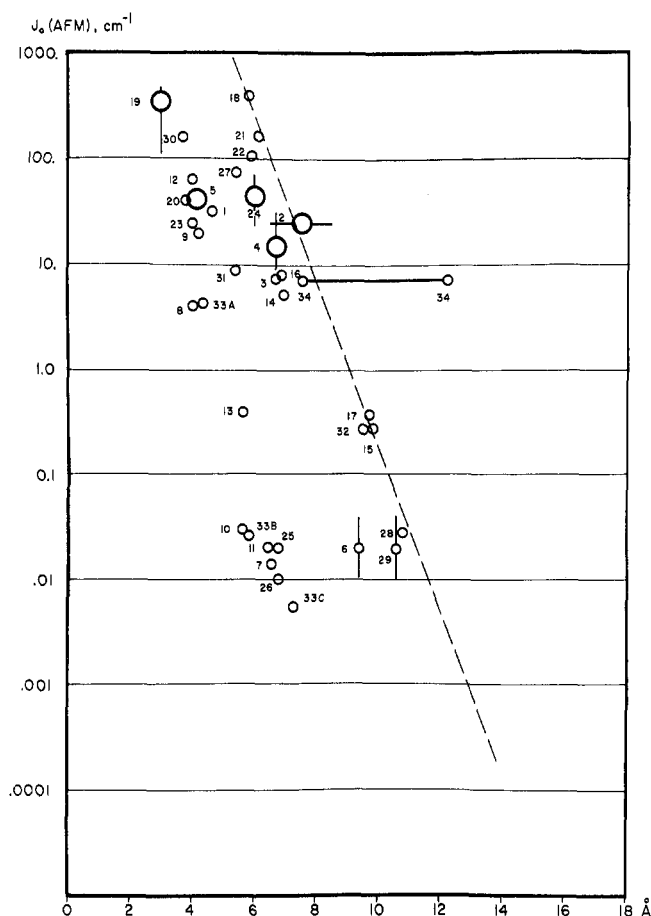
## II. Long-Range Behavior of Isotropic Superexchange

The superexchange interaction between two molecules, each with unpaired electronic spin, is a complicated function of the electronic and nuclear coordinates. We wish here to consider the limiting behavior related to the following separation of coordinates: if an explicit general function for the isotropic superexchange coefficient *could* be found, then we could arbitrarily group the internal coordinates as follows:

$$J_0^{\text{Ex}} = J_0(R_{12}, \zeta, \eta, \alpha, \beta, \gamma; \vec{R}_1, \vec{n}_1; \vec{R}_2, \vec{n}_2) \quad (1)$$

The first six coordinates, here, are the same six as for the dipole-dipole interaction. The nuclear coordinates  $\vec{R}_{1,2}$  of molecules 1 (or 2) determine the shape of each molecular fragment, and  $\vec{n}_{1,2}$  represents the pertinent set of quantum numbers describing (for example) the basis functions for both molecular fragments. The resulting function for the isotropic superexchange coefficient  $J_0^{\text{Ex}}$  must certainly fluctuate considerably as one varies the chemical nature of the two interacting species, their distance apart, and their relative orientations.

We here define the isotropic exchange operator in the form  $\mathcal{H}_{\text{ex}} = J_0^{\text{Ex}} \vec{S}_1 \cdot \vec{S}_2$ , so that positive values of  $J_0^{\text{Ex}}$  represent antiferromagnetic coupling of the two electronic spins, and the negative values represent ferromagnetic exchange coupling. Now, let us define the scalar quantity  $R \equiv R_{12}$  as a suitably chosen difference function  $f(\vec{R}_1) - f(\vec{R}_2)$  which represents the distance between centers of unpaired spin density. If, now, the nuclear coordinates and internal



**Figure 1.** Plot of antiferromagnetic values of superexchange  $J_0$ , defined by  $\mathcal{H}_{\text{ex}} = J_0 \vec{S}_1 \cdot \vec{S}_2$ , vs.  $R_{12}$  in angstroms. The units of  $J_0$  are  $\text{cm}^{-1}$ , and were originally accurately plotted as  $\log(J_0)$  vs.  $R_{12}$  (all literature data were converted to  $+J_0 \vec{S}_1 \cdot \vec{S}_2$  with multiplication by 2 or  $1/2$ , sign changes, and unit conversions as appropriate). Uncertainties in  $J_0$  and/or  $R_{12}$  are indicated, where known. Original data and references are given in Appendix I. The dotted "outer-limit" line was drawn by visual inspection.

quantum numbers are varied over all possible types of interacting molecular fragments, and also over all relative orientations, then this process defines two limit functions (which may not be smooth, but which are certainly definable):

$$J_0^{\text{EX}}(R_{12}; \text{AFM}) = \max(J_0^{\text{EX}}(R_{12}; \text{all coordinates})) \quad (2a)$$

$$J_0^{\text{EX}}(R_{12}; \text{FM}) = \min(J_0^{\text{EX}}(R_{12}; \text{all coordinates})) \quad (2b)$$

These equations may be viewed as the upper and lower boundary curves (envelopes) obtained as a result of plotting all  $J_0^{\text{EX}}$  values (of either sign) vs.  $R_{12}$ . Now, it may be possible to evaluate such limit functions analytically, but at present there would be a clear "model" dependence. We have found what we believe to be a reasonable approximation to one of these limit functions by making use of the considerable body of experimental data presently available on both accurate magnetic measurements and interpretation, and crystallographic structural data of compounds generally classified as insulators.

For this purpose, experimental data were collected from the literature of studies satisfying these three criteria: reliable structural data (or, in a few cases, a good estimate) must exist, the value of  $J_0^{\text{EX}}$  must have been determined by magnetic resonance or magnetic susceptibility with an isotropic exchange operator of the form  $\pm n J_0 \vec{S}_1 \cdot \vec{S}_2$  ( $n = 1$  or  $2$ ; Ising model determinations were excluded), and the sign of  $J_0^{\text{EX}}$  must have been determined. The experimental data found in this search are presented in Figures 1 and

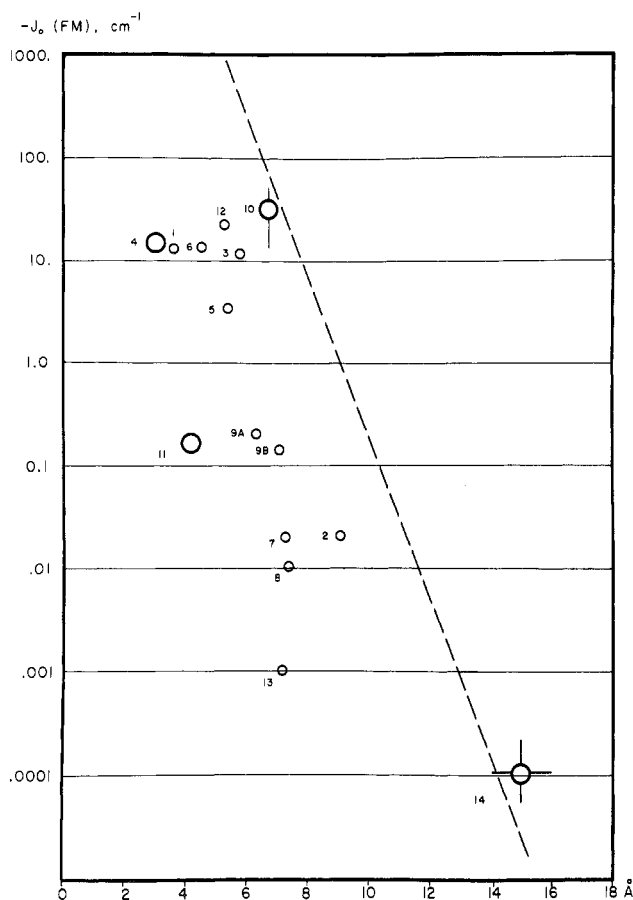


Figure 2. Plot of ferromagnetic superexchange values of  $J_0$  vs.  $R_{12}$ , with  $\mathcal{H}_{\text{ex}}$  defined as in Figure 1. Original data and references are given in Appendix I. The dotted "outer-limit" is traced from Figure 1.

2, plotted as  $\log(J_0^{\text{Ex}})$  vs.  $R$ .

The data, experimental methods, and references used in the plots of Figures 1 and 2 are given in tabular form in Appendix I. (See paragraph at end of text regarding supplementary material.) The experimental methods used in the papers covered in this survey cover a wide ground: EPR line shape, EPR intensity, magnetic susceptibility, NMR shifts, analysis of the Curie-Weiss constant, optical spectroscopy, spin-wave plus effective field theory, specific heat, magnetic relaxation, and parallel microwave pumping. Note that all exchange coupling data have been converted so that the tabulated  $J_0$  is that of the effective isotropic operator  $\mathcal{H}_{\text{ex}} = J_0 \mathbf{S}_1 \cdot \mathbf{S}_2$ . The exchange coupling data in the plots are observed to vary over at least five orders of magnitude, and the values of  $R$ , in either figure, vary over a range of 6 to about 11 Å, so the total range over which the behavior of  $J_0^{\text{Ex}}$  vs.  $R$  is observed is considerably larger than in previous studies.

Fewer ferromagnetic than antiferromagnetic data points were found, a situation predicted by the Kanamori-Goodenough rules, since ferromagnetic superexchange coupling generally depends on a special ( $90^\circ$ ) geometry.<sup>2,4,5</sup> In addition, the plot of  $\log J_0$  vs.  $R$  presents a well-defined linear "outer-boundary", a situation not found when the data are plotted as  $\log J_0$  vs.  $\log R$ . The significant observation is that there is a well-defined outer boundary (drawn, in the figure, by visual inspection; see section IV for a discussion of exceptions) to the antiferromagnetic data, being given approximately by (see the dashed line in Figure 1)

$$J_0(R; \text{AFM}) = 1.35 \times 10^7 \exp(-1.80R) \text{ cm}^{-1} \quad (3)$$

where the distance  $R$  is measured in angstrom units. A

similar outer-limit function could not be derived for the ferromagnetic data, but it was observed that the following inequality appears to hold:

$$|J_0(R; \text{FM})| \leq |J_0(R; \text{AFM})| \quad (4)$$

so the limit function for the antiferromagnetic data appears to apply to the ferromagnetic data as well.

The physically significant conclusion which we deduce from this study of experimental superexchange is this: the isotropic superexchange parameter is *bounded* (in absolute value), and for large  $R$  the bound is *small*. Moreover, the bound decreases as  $R$  ( $\geq 6$  Å) increases. Equation 3 is an approximation to this bound, for which we would like both to find theoretical justification, as well as to subject it to experimental tests.

### III. Long-Range Distance Dependence of Superexchange

The empirical dependence of the isotropic exchange coefficient  $J_0$  on  $R_{12}$  has been the subject of a number of careful experimental and theoretical studies. An empirical dependence of  $J_0(R)$  on a power of  $R$  is referred to as a "magnetic Grüneisen law"

$$J_0(R) = AR^{-n} \quad (5)$$

after a study by Bloch<sup>6</sup> who found that  $\gamma_m = -d \ln J_0 / d \ln V$  is approximately equal to  $10/3$  for a number of magnetic solids. This is equivalent to  $n = 10$  in the equation above, the factor of  $1/3$  being a dimensionality factor. The other simple empirical form of  $J_0(R)$  is to assume that it follows an exponential law

$$J_0(R) = J_{00} \exp(-\epsilon R) \quad (6)$$

where  $J_{00}$  is an appropriate exchange "constant". This is the form assumed by Harris in a study of the nearest neighbor exchange between  $\text{Mn}^{2+}$  ions in  $\text{MgO}$ ,  $\text{MnO}$ , and  $\text{CaO}$ . The dependence of  $J_0$  on  $R$  was found to be well described by an exponential law, of the form of eq 6. One might expect (from the nature of quantum-mechanical two-electron, multicenter integrals) an exponential dependence as the limiting form for the superexchange  $J_0$  dependence on  $R$ , but an explicit calculation, using the four-electron model for superexchange by Shrivastava and Jaccarino,<sup>8</sup> shows that the singlet-triplet splitting simply depends on too many integrals for one to make such a deduction by direct inspection of the equations. An earlier calculation by Johnson and Sievers on the scalar superexchange interaction in  $\text{MnO}$ ,  $\text{MnF}_2$ , and  $\text{MnF}_2 \cdot \text{Fe}^{2+}$  gave satisfactory values of  $\gamma_m$  near to the  $10/3$  value (but somewhat higher) and led to the suggestion that the approximate value of  $\gamma_m \approx 3.0$ - $3.4$  may be a result of the dominance of  $\sigma$  bonding in the superexchange process.

The only conclusion which we believe follows from the studies quoted above is that it is not known whether (5) or (6) is the correct form for the empirical dependence of  $J_0(R)$  on  $R$ . This is not surprising, since the range of  $J_0$  studied in any particular study is only an order of magnitude (a factor of 10), and the range of  $R$  is usually about 0.5 Å. Now, one may show that if  $J_0(R)$  is forced to be exponential in character and fit eq 6, then the value of  $n$  in eq 5 is given by  $n = 3\gamma_m = \epsilon R_{12}^0$  (this is easily shown by expanding eq 6 about the value of  $R^0$  in a Taylor's series expansion, and by using the relation  $n = -(\Delta J / \Delta R)(R/J)$ ). With these relations in hand, examination of the various references cited failed to produce a consistent set of values of  $\gamma_m$  from system to system. We have been able to show this by examining the available data for systems in which  $J_0^{\text{Ex}}(R)$  had been fitted to either an exponential or a power law over a small range of  $R$  values. The value of  $\epsilon$  (or  $n$ )

TABLE I: Grüneisen and Exponential Exchange Coefficients

$R_{1,2}^0, \text{Å}$	$\epsilon$	$n$	law	ref
3.0	6.38	(19.1) <sup>b</sup>	exponential	19
3.9-4.2	(2.4) <sup>b</sup>	10	Grüneisen	21
4.3	2.97 <sup>a</sup>	13	both	25
4.8	4.57 <sup>a</sup>	22	both	25
5.6	(1.94) <sup>b</sup>	10.9	Grüneisen	32, 33
6-10	1.8	(10-20) <sup>b</sup>	exponential	this work

<sup>a</sup> Obtained by least-squares fitting, to an exponential law, the data given in ref 10. <sup>b</sup> The numbers in parentheses are determined from the experimental value of  $\epsilon$  (or  $n$ ) with  $n = \epsilon R_{1,2}^0$ ; see text.

can be found from the experimentally determined  $n$  (or  $\epsilon$ ) from the relation  $n = \epsilon R^0$ , where  $R^0$  is the center of the region about which  $J_0(R)$  has been fitted (we were able to numerically verify this relation by using the data of Hutchings et al.<sup>10</sup>). The results are given in Table I. One can draw no conclusion from this table other than that  $J_0(R)$  can be reasonably well fitted to either a power law or an exponential law over a small region of  $R$ . The Grüneisen parameter " $n$ " apparently takes values in the range of 10-20, and  $\epsilon$  must decrease with increasing  $R^0$ .

While studies of the variation of  $J_0^{\text{Ex}}$  over small ranges of  $R$  have been inconclusive, the statistical data of Figures 1 and 2 show that the positive and negative limiting values of  $J_0^{\text{Ex}}$  vs.  $R$  must have exponential character. A power law of the form  $(R)^{-n}$  is definitely of the wrong type to fit the facts. In the next section, we take up this question: What is the simplest functional form for  $J_0^{\text{Ex}}(R)$  which is in agreement with present theoretical knowledge of superexchange?

#### IV. Discussion

There are two salient points about the limit function idea proposed here which we must discuss. These are: What does theory predict about the general functional form of long-range superexchange? When are exceptions to the limit function "range" (i.e., points lying far to the right of the limit curve in Figures 1 and 2) to be considered "new mechanisms" of superexchange (or extensions of the "range"), as distinguished from points which lie too far to the right due to misidentification of the exchange path? Investigation of these questions is useful and instructive, as we now show.

First, the general superexchange problem, using a cluster model, is too difficult to solve analytically, since it involves so many orbitals, electrons, and nuclei that any possibility of deriving a general analytic solution directly giving the dependence of  $J_0^{\text{Ex}}$  on  $R$  is completely ruled out. Superexchange calculations have varied in complexity from the "four-electron model",<sup>11,12</sup> through mixed MO and valence-bond treatments such as one by Harcourt and Martin<sup>13</sup> (10 orbitals and 18 electrons), to an extended Hückel calculation by Bersuker and Titova<sup>14</sup> involving 44 orbitals, 18 electrons, and 10 atoms. An explicit calculation with the four-electron model<sup>8</sup> shows that the singlet-triplet splitting simply depends on too many integrals for one to deduce a functional form for  $J_0^{\text{Ex}}$  by direct inspection. The situation is different, however, with respect to studies of direct atom-atom exchange. The number of centers and electrons is greatly reduced, and the number of orbitals is at one's disposal. Moreover, although the interaction between unpaired electrons on different atoms is "direct" exchange, the fundamental mechanisms of the interaction remain the same.<sup>15</sup> The prototype problems, here, are the long-range interaction between two ground state hydrogen atoms, and the alkali-alkali interactions. The first such

calculation was that of Siguiar<sup>6</sup> who first derived, in 1927, all of the integrals giving the singlet and triplet energies of the valence-bond problem for  $\text{H}_2$ . The value of  $J_0 = (E_{\text{triplet}} - E_{\text{singlet}})$  calculated in this way is correct for the smaller values of  $R$ , but crosses over at large values giving the wrong sign of  $J_0$  (ferromagnetic). The correct asymptotic form for the long-range coupling in this case was derived by Herring and Flicker<sup>17</sup> who obtained an explicit formula of the form  $J_0 = AR^{5/2} \exp(-2R/a_0)$ , where  $a_0$  is the Bohr radius. This form for the exchange interaction satisfies a theorem proved by Herring which states that the long-range exchange interaction between any pair of identical atoms or molecules (without orbital degeneracy) must almost certainly be antiferromagnetic.<sup>18</sup> A general form for the exchange interaction between open-shell atoms has been proposed by Mason and Monchick,<sup>19</sup> which is

$$J_0^{\text{Ex}}(R) = P(R) \exp(-aR) \quad (7)$$

where  $P(R)$  is a polynomial in  $R$ . A slight variant of this analytical form (in which the argument of the exponential is  $-aR + b/R$ ) has been found necessary by Knox and Rudge<sup>20</sup> for fitting singlet-triplet splittings for alkali-alkali and alkali-hydride interactions.

Let us next compare the value of the *experimental* exponential coefficient " $\epsilon$ ", given in eq 3, with similar values obtained in other studies. A comparison with other experimental superexchange studies in solids (see Table I) shows only that  $\epsilon$  appears to decrease with increasing values of  $R^0$ , the value of  $R$  about which the experimental measurements were made for a complex in the solid state. The results of Knox and Rudge (*calculated* from the analytic wave functions of Clementi) are interesting for comparison, since they give values of the exponential coefficient  $\epsilon$  vs. increasing atomic number. Their results, for the sequence  $\text{H}_2$ ,  $\text{Li}_2$ ,  $\text{Na}_2$ ,  $\text{K}_2$ ,  $\text{Rb}_2$ , and  $\text{Cs}_2$  are  $\epsilon = 2.0, 1.24, 1.16, 1.12, 1.09, \text{ and } 1.05 \text{ au}^{-1}$ . These results, for the case of the  $\text{Li}_2$  molecule, have recently been independently confirmed by Uang and Stwalley.<sup>21</sup> These authors have fitted the singlet and triplet energies for  $\text{Li}_2$  vs.  $R$  to Konowalow's (MCSCF) potential functions,<sup>22</sup> and a piecewise tensioned spline in order to get a smooth fit over a large distance. When their long-range numerical singlet-triplet splittings are fitted to the function used by Knox and Rudge (by using  $b/R = 0$ ), one finds  $\epsilon = 1.21 \text{ au}^{-1}$ , which compares favorably to the ab-initio result, quoted above for  $\text{Li}_2$ .

The value for  $\epsilon$  found from the limit curve for superexchange is, for comparison,  $\epsilon = 1.80 \text{ Å}^{-1}$  or  $0.952 \text{ au}^{-1}$ . The similarity of this experimental value to the theoretical results of  $\epsilon$  in the alkali-alkali sequence (particularly for large effective principal quantum numbers) is encouraging, and indicates that the slope of the limit curve in Figure 1 may well be determined by the same type of processes as govern the limiting value of  $\epsilon$  in the alkali-alkali sequence.

It is also informative to compare the general form for  $J_0^{\text{Ex}}(R)$  found from the studies of diatomic molecules with the results of theoretical studies of superexchange in semiconductors. One may regard the semiconducting state as one type of limit for superexchange, resulting from allowing the orbitals transferring the spin-polarization to change from localized to completely delocalized into a band. Theoretical expressions for  $J_0^{\text{Ex}}$  in semiconducting compounds have been derived by Nakayama<sup>1</sup> and by Geertsma et al.<sup>23</sup> Both find that asymptotic, long-range forms for superexchange are of the same form as eq 7, with  $P(R)$  simply being proportional to either  $R^{-1}$  or  $R^{-2}$ , depending on the "mechanism" (i.e., order of perturbation

theory) considered (in addition to these forms, there is also the possibility of a sinusoidal dependence of  $J_0^{\text{Ex}}$  on  $R$  in semiconductors, like the RKKY mechanism in metals<sup>24,25</sup>).

These results, those for diatomic molecules, and our conclusions on the nature of the superexchange limit function lead us to propose that long-range superexchange in any molecule of great complexity may be represented by the function

$$J_0^{\text{Ex}}(R) = AR^\beta \exp(-\epsilon R) \quad (8)$$

where other geometrical variables are considered as being held fixed. This function satisfies Herring's theorem for superexchange (in the sense that an antiferromagnetic interaction at relatively small values of  $R$  is still antiferromagnetic at large  $R$ ), and indicates that the parameter  $\beta$  may be interesting to study since it appears to have negative values when d-d superexchange occurs via orbitals delocalized into a valence band. It may be seen from eq 8 that the relative sign of  $\beta$  can be deduced from an accurate plot of  $\ln(J_0^{\text{Ex}})$  vs.  $R$ . If  $\beta > 0$ , the curve is slightly concave downward; if  $\beta < 0$ , the resulting curve is then concave upward by an even smaller degree. Thus, negative values of  $\beta$  are relatively difficult to determine. Experimental data of sufficient accuracy for this purpose (i.e., of determining  $\beta$ ) may be obtained by EPR measurements of exchange splittings vs. pressure, as has been demonstrated by Kozuhar and Tsintsadze,<sup>26</sup> in a study of the exchange interactions between three different types of  $\text{Ni}^{2+}\dots\text{Ni}^{2+}$  ion pairs in  $\text{Ni}_x\text{Zn}_{1-x}\text{SiF}_6\cdot 6\text{H}_2\text{O}$ .

The second point for discussion is: How shall we interpret values of  $(J_0^{\text{Ex}}, R)$  which lie far to the right of the limit curve of Figures 1 and 2? These points could represent examples of superexchange of longer range than previously known, or they could simply be in error. We have found two exchange coupled systems which must be one or the other of these types. The first case is the magnetic exchange coupling and structural data of Felthouse and Hendrickson<sup>27</sup> on two benzidine bridged complexes of Cu(II). The intramolecular Cu-Cu distances are 12.2 to 12.3 Å, with corresponding exchange coupling coefficients (measured in two different complexes) of about 6.6–7.4  $\text{cm}^{-1}$ . The point (7.0, 12.2) in Figure 1 (point 34) lies far to the right of the antiferromagnetic limit curve. The closest Cu-Cu intermolecular distance, however, is reported to be 7.5 Å. Using this value of  $R$  we obtained another data point (7.0, 7.5) which now lies well within the dotted limit curve of Figure 1. The statistical evidence in this case favors an intermolecular exchange path of 7.5 Å rather than an intramolecular exchange path of 12.2 Å (Felthouse et al. have defended the intramolecular distance of 12.2 Å with CNDO calculations which primarily identify the symmetry nature of MO's with energies near to the half-filled 3d orbitals. Their analysis of the crystal structure also shows that no nitrate or other counterions could be positively identified as propagators for an intermolecular superexchange, although a double hydrogen-bonded pathway could be identified). An independent and reliable determination of the path of the superexchange is clearly needed in this case.

The other system in which an unusually long-range superexchange interaction has been reported is in the semiconducting chalcogenide spinel  $\text{Fe}_{0.5}\text{Cu}_{0.5}\text{Rh}_2\text{S}_4$ .<sup>28</sup> The low-temperature ( $T < T_{\text{Neel}} = 140$  K) spin arrangement in this compound has been determined to be antiferromagnetic, with the high-spin  $\text{Fe}^{3+}$  ions carrying the spin magnetic moments. The exchange interactions giving rise to the observed antiparallel arrangements of the  $\text{Fe}^{3+}$  ions (which occupy a face-centered cubic lattice) have been identified by neutron diffraction as being "ordering of the

second kind", so that the next-nearest neighbors at 9.85 Å dominate the exchange interaction via the pathway<sup>23</sup> Fe-S-Rh-S-Rh-S-Fe, rather than the nearest-neighbor interactions at 6.96 Å. Since the Neel temperature is relatively large, the 9.85-Å superexchange must also be relatively large. Using the range of  $\theta/T_N$  values given by Anderson<sup>29</sup> along with the effective field theory expression for the Curie temperature  $\theta$ , one arrives at a fairly large estimate for  $J_0^{\text{Ex}} \sim 5\text{--}16 \text{ cm}^{-1}$ . This does not account for the nearest-neighbor contribution to the spin ordering, which must be of the same type, so we are only certain that  $J_0^{\text{Ex}} \leq 5\text{--}16 \text{ cm}^{-1}$  for the 9.85-Å distance. Due to this large uncertainty in  $J_0^{\text{Ex}}$ , we have not included this point in Figure 1. This is the only system which appears to deviate from the limit curve of Figure 1, and the superexchange enhancement (which the probable position of this point in Figure 1 indicates) may be due to interaction with extended semiconducting band states. This may not be accidental, since Torrance et al.<sup>30</sup> have shown that the presence of conduction electrons donated by La in the semiconductor SmS enhances the exchange coupling between neighboring  $\text{La}^{3+}$  ions.

## V. Conclusions

Presently existing structural data and magnetic superexchange data indicate that there exists a limit function for long-range superexchange, which is basically exponential in character. The present empirical form of this limit function appears to apply well to both ferromagnetic and antiferromagnetic systems to insulators, but may not apply well to all superexchange interactions in semiconductors. An empirical form for the general long-range distance dependence of the isotropic superexchange coefficient is proposed which encompasses long-range superexchange behavior in cluster complexes and diatomic molecules, and some exchange phenomena in semiconductors. The coefficient " $\beta$ " in this formula should be an interesting subject for experimental investigation, because it appears to have the property of changing sign in a way characteristic of the extended nature of the states responsible for propagation of the superexchange interaction. Considerations of specific cases which lie near the edge of the apparent "range" for superexchange indicate the need for theoretical methods which can reliably identify the path of the exchange interaction and, for example, clearly give the order of strength (and sign) of the interactions between nearest-neighbors, next-nearest-neighbors, etc. Such considerations may lead to a clearer understanding of both the "mechanisms" and the wave functions which lead to the long-range superexchange effect, as well as empirical knowledge concerning the magnitude of this effect when acting over a large distance.

We wish to conclude this paper with the following comments, which largely result from a discussion with Professor K. W. H. Stevens. We view the proposed limit curve for long-range superexchange as a useful means for classification of superexchange interactions in specific systems into either ordinary (i.e., bounded by a presently known limit curve, as in Figures 1 or 2) or extraordinary cases of superexchange. Since we have, at present, no theoretical means of deciding just how long may be the range of superexchange in a given electronic system, we cannot definitely classify any particular case of unusually strong long-range superexchange (i.e., a  $(J_0^{\text{Ex}}, R_{12})$  pair) as impossible, but merely improbable when compared with the presently known data. Hence, we cannot say that a truly longer range superexchange cannot be discovered, but only that no system has yet been discovered which clearly exceeds the presently known limit function (i.e.,

proposed in this paper) by a significant amount (but see the example due to Hendrickson et al.,<sup>27</sup> which proposes just such an exception). Thus, the proposal of a limit function to long-range superexchange presents a clear challenge to experimentalists, which is to produce one or more exceptions to the limit curve we propose, and to the theorists to explain why!

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**Supplementary Material Available:** Appendix I and an additional list of references pertinent to Figures 1 and 2 (7 pages). Ordering information is available on any current masthead page.

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## General Magnetic Dipolar Interaction of Spin-Spin Coupled Molecular Dimers. Application to an EPR Spectrum of Xanthine Oxidase

R. E. Coffman\* and G. R. Buettner†

Department of Chemistry, The University of Iowa, Iowa City, Iowa 52242 (Received April 20, 1979)

An analysis is given of the general spin-spin dipolar interaction in the presence of a general bilinear superexchange interaction, and its effects on a rigid lattice EPR line shape are calculated. The general magic angle effect is considered, numerically, for specific cases of both single crystal spectra and randomly oriented microcrystallite samples. Analysis of the number of determinable spin-spin coupling coefficients suggests that a component analysis can be developed which can yield useful information about the geometrical arrangement of two interacting spin = 1/2 molecules, as well as covalency information about the interaction. This analysis is applied to a Mo(V)-iron sulfur interaction in xanthine oxidase and xanthine dehydrogenase, which has been described by Lowe and Bray. Line shape calculations show that the observed small amount of dipolar anisotropy is consistent with a separation of the Mo(V) and Fe/S groups of 14 Å or less. Considerations of the long-range nature of superexchange, from existing experimental data on superexchange, are consistent with this estimate.

### I. Introduction

Several recent EPR studies of paramagnetic metal-metal and metal-free radical interactions in metallo-enzymes and model complexes have concerned systems where the apparent distance of the dipolar and exchange interactions is decidedly long range, i.e., 8-10 Å or longer. Since exchange interactions decrease exponentially vs.  $R$  and dipolar interactions decrease as  $1/R^3$ , it is evident that dipolar anisotropy must be a prominent feature of long-range spin-spin coupling. It should therefore be possible to extract useful structural information from spin-spin interactions in EPR spectra of this type. It is also possible to obtain information about the exchange tensor, par-

ticularly the sign and magnitude of the scalar component of the exchange interaction. The vector and tensor components of the exchange interaction are frequently much smaller than the scalar component which then simplifies the form of the interaction. The dipolar "magic angle" effect may also play a prominent role in the spectrum, particularly for random orientation samples, since this effect may lead to a vanishing of the dipolar splitting at one or more "turning-points" of the spectrum. The relatively narrow EPR line widths (of solid samples) which may be expected as a result of both increased magnetic dilution and a magic-angle collapse of the dipolar splitting (and the existence of systems displaying these effects) provide a means for investigating the nature of long-range exchange interactions. For these reasons,

\*Wabash College, Crawfordsville, Ind. 47933.