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Quantitative Interpretation of the Goodenough−Kanamori Rules: A Critical Analysis

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Expressions in the early literature for kinetic exchange in magnetically coupled systems are critically analyzed by second-order perturbation theory and substituted by corrected versions. The widely held belief that kinetic exchange is always antiferromagnetic is found to be incorrect. Ferromagnetic kinetic exchange terms are found to be more important than hitherto assumed. The quantity I/U, where I stands for intraatomic exchange interactions and U is the energy difference between the ground electron configuration and a charge-transfer configuration, plays a crucial role in the competition between ferromagnetic and antiferromagnetic contributions. I/U readily exceeds the value $^1/_5$ considered as an upper limit by Anderson. I is found to be proportional to the number of unpaired electrons on a given magnetic center.

1. Introduction

With the recent developments in the area of molecular magnetism[1,2] there has been a revival of some old concepts, which were developed thirty to forty years ago to rationalize the properties of insulating magnetic materials. The principal aim of these modern lines of research is the design and construction of molecule-based ferromagnets. These might offer some advantages over classical magnetic materials by their chemical nature. A molecular material is easier to modify and manipulate, building blocks can be combined in many different ways, and they can be incorporated into existing architectures. It is conceivable that the magnetic properties could thus be combined with optical, mechanical, and electrical properties, hence creating combinations which cannot be achieved with the classical magnets.

The old rules and concepts of exchange interactions play an important part in this research, in particular the competition between ferromagnetic and antiferromagnetic contributions to the net exchange. The most widely used effective Hamiltonian to account for the interactions between nearest-neighbor magnetic moments is the so-called Heisenberg−Dirac−van Vleck (HDvV) operator[3]

$$\hat{H}_{\mathrm{HDvV}} = J\hat{\mathbf{S}}_{\mathrm{A}}\cdot\hat{\mathbf{S}}_{\mathrm{B}} \qquad (1)$$

which often appears in the form $-J\hat{\mathbf{S}}_{\mathrm{A}}\cdot\hat{\mathbf{S}}_{\mathrm{B}}$ or $-2J\hat{\mathbf{S}}_{\mathrm{A}}\cdot\hat{\mathbf{S}}_{\mathrm{B}}$. In our formulation eq 1, ferro- and antiferromagnetic situations are represented by negative and positive J values, respectively. This operator has been extremely successful not only in the field of magnetically ordered materials[4,5] but also in the areas of low-dimensional magnetic materials[6] and clusters of magnetic ions.[7]

Two distinct contributions to J were recognized in the early days: (i) kinetic exchange, originating in a one-electron-transfer process, and (ii) potential exchange due to true two-center two-electron exchange interactions. The latter contribution is always ferromagnetic. It was recognized that in insulating transition metal ion systems kinetic exchange usually dominates.[8] Numerous theoretical models with widely varying degrees of sophistication were then proposed to calculate the kinetic exchange contributions.[8−12] In general it can be said that the most sophisticated *ab initio* calculations have only recently yielded reliable results.[13,14] One of the earliest theoretical approaches was a valence bond approach in which the mixing of an electron-transfer configuration into the ground-state configuration was the key element.[8] Experimental studies, in an interplay with theoretical considerations, led to the formulation of the so-called Goodenough−Kanamori rules, a set of semiempirical rules which proved to be highly successful in rationalizing magnetic properties in a great variety of compounds on a qualitative level.[5,8,15−19] By consideration of the symmetry and the electron occupancy of the interacting orbitals on neighboring magnetic centers the sign and relative magnitude of the resulting kinetic exchange can be predicted.

The most important contribution originates when an electron in a half-filled orbital a_i on center A interacts with an electron in a half-filled orbital b_j on center B. According to ref 20 this contribution is given by

$$\frac{2}{n_{\mathrm{A}}n_{\mathrm{B}}}\frac{h_{ij}^{2}}{U} \qquad (2)$$

where n_{A} and n_{B} are the numbers of unpaired electrons on

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(1) Ferlay, S.; Mallah, T.; Ouahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701.

(2) Mallah, T.; Thiébaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554.

(3) Van Vleck, J. H. *Phys. Rev.* **1934**, *45*, 405.

(4) Van Vleck, J. H. *J. Chem. Phys.* **1941**, *9*, 85.

(5) Anderson, P. W. *Phys. Rev.* **1950**, *79*, 350.

(6) de Jongh, L. J.; Miedema, A. R. *Experiments on Simple Magnetic Model Systems*; Taylor and Francis Monographs on Physics; Taylor and Francis: London; 1974.

(7) Bleaney, B.; Bowers, K. D. *Proc. R. Soc.* **1952**, *A 214*, 451.

(8) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.

(9) Glerup, J. *Acta Chem. Scand.* **1972**, *26*, 3775.

(10) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(11) Girerd, J. J.; Journaux, Y.; Kahn, O. *Chem. Phys. Lett.* **1981**, *82*, 534.

(12) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand.* **1983**, *A37*, 161.

(13) Fink, K.; Fink, R.; Staemmler, V. *Inorg. Chem.* **1994**, *33*, 6219.

(14) Wang. C.; Fink, K.; Staemmler, V. *Chem. Phys.* **1995**, *192*, 25.

(15) Goodenough, J. B. *Phys. Rev.* **1955**, *79*, 564.

(16) Goodenough, J. B. *J. Phys. Chem. Solids* **1958**, *6*, 287.

(17) Kanamori, J. *J. Phys. Chem. Solids* **1959**, *10*, 87.

(18) Wollan, E. O.; Child, H. R.; Koehler, W. C.; Wilkinson, M. K. *Phys. Rev.* **1958**, *112*, 1132.

(19) Anderson, P. W. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1963; Vol. 1, Chapter 2.

(20) Goodenough, J. B. *Magnetism and the Chemical Bond*; Interscience: New York, 1963.

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centers A and B, respectively. h_{ij} is a so-called transfer integral defined by

$$h_{ij} = \langle a_i|\hat{h}|b_j\rangle \tag{3}$$

where $\hat{h}$ is the appropriate one-electron interaction Hamiltonian. The quantity U in eq 2 is the U defined in the Hubbard model.[21] It corresponds to the energy difference between the ground electron configuration and the electron-transfer configuration where one electron has been removed from the one center and restored on the other. The term in eq 2 is always antiferromagnetic.

For the situation of a half-filled orbital on A interacting with an empty orbital on B the contribution to J according to ref 20 is given by

$$-\frac{2}{n_A n_B}\frac{h_{ij}^{2}}{U}\frac{I}{U} \tag{4}$$

The quantity I takes account of the intraatomic exchange interactions within the charge-transfer electron configuration.

For the interaction of a half-filled orbital on A with a full orbital on B the contribution according to ref 20 is also given by

$$-\frac{2}{n_A n_B}\frac{h_{ij}^{2}}{U}\frac{I}{U} \tag{5}$$

Both contributions 4 and 5 are ferromagnetic. They are smaller than the antiferromagnetic contribution 2 by the factor I/U.

The last possible type of interaction is that between an empty orbital and a full orbital. Its contribution to J has been reported as ferromagnetic,[19] but no algebraic expression is available.

Expressions 2−5 represent a quantitative formulation of the Goodenough−Kanamori rules. An analysis of these expressions has led to the surprising conclusion that they cannot all be correct. One of the aims of the present paper, therefore, is the presentation of this analysis and the correction of the formulas. The missing formulas for the interaction of a filled with an empty orbital will be supplemented.

There is a more important point, however. On the basis of the fact that contributions 4 and 5 are smaller than contribution 2 by the factor I/U and assuming that I/U will not exceed a value of $^1/_5$, Anderson concluded that kinetic exchange is always antiferromagnetic, *i.e.*, contribution 2 is dominating. This conclusion has not been seriously questioned until very recently,[22] and it has been become a paradigm among magnetochemists. When ferromagnetic interactions were found in magnetic clusters, they were usually ascribed to potential exchange.[23,24] The orthogonality principle was invoked, implying that strong ferromagnetic interactions can only occur when the magnetic orbitals are mutually orthogonal.[24] In the concept of spin-polarization, which is used to account for ferromagnetic interactions in both organic and inorganic systems, the two-electron exchange operator plays an important part.[25,26] This is not the subject of the present paper; we are dealing with kinetic exchange only, *i.e.*, a pure one-electron interaction.

We will show that kinetic exchange can lead to ferromagnetic interactions. The quantity I/U in eqs 4 and 5 will be examined in detail. We will show that, depending on the electron configuration, it can attain values up to $^1/_2$. As a result the ferromagnetic contributions 4 and 5 become competitive with the antiferromagnetic contribution 2. In addition, we have recently shown[22] and will briefly summarize here that for some specific situations we can have ferromagnetic interactions of the order of magnitude, but reversed sign, of eq 2!

2. Theory

We consider in the following a dimer AB built up of the two monomeric constituents A and B. In our analysis of the exchange interactions we will use the Hamiltonian

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_{AB} \tag{6}$$

where

$$\hat{H}_A = \hat{T}_A + \hat{V}_A + \sum_{i<j}\frac{1}{r_{ij}} \tag{7}$$

and a similar term can be written for $\hat{H}_B$. In eq 7 $\hat{T}_A$ is the kinetic energy operator for all electrons on A, and $\hat{V}_A$ is the one-electron potential energy operator. The third term is the interelectronic repulsion operator for the electrons centered on A.

$\hat{H}_{AB}$ is composed of the following two terms:

$$\hat{H}_{AB} = \hat{V}_{AB} + \sum_i\sum_j\frac{1}{r_{ij}} \tag{8}$$

$\hat{V}_{AB}$ is a collection of all the one-electron terms which must be added to the Hamiltonian as a result of bringing A and B together. Similarly, the second term of eq 8 represents all the additional electron−electron repulsion terms which are not included in $\hat{H}_A + \hat{H}_B$. Throughout this paper we neglect spin−orbit coupling effects, *i.e.*, all spin quantum numbers which will be used later on are good quantum numbers.

Let us now specify the characteristics of our AB dimer more precisely. A and B have the electron configurations $(a)^{N_A}$ and $(b)^{N_B}$, respectively. a and b symbolize a collection of nondegenerate orbitals centered on A and B, respectively. The orbitals a and b together form an orthonormal set. These orbitals are not pure metal orbitals, but they contain contributions from terminal as well as bridging ligands also. N_A and N_B represent the total number of electrons on A and B, respectively. The number of unpaired electrons on A and B are designated n_A and n_B, respectively. The effect of $\hat{H}_A$ and $\hat{H}_B$ (eq 7) can be summarized as follows. The degeneracy of the single-ion terms arising from the $(a)^{N_A}$ electron configuration is partially lifted by $\hat{H}_A$. These are the normal splittings seen in, for instance, a Tanabe−Sugano diagram. Similarly for center B.

Our main interest is in the lowest energy single-ion term arising from the $(a)^{N_A}$ electron configuration. It is characterized as $S_A\Gamma_A$, where $S_A = n_A/2$ is the spin quantum number and Γ_A is the relevant orbital representation. A similar designation is made for center B. We are interested in the energy differences between the possible dimer functions $S\Gamma M\gamma$ obtained from the direct product of single-ion ground terms

$$|GR, S\Gamma M\gamma\rangle = ((a)^{N_A}S_A\Gamma_A) \otimes ((b)^{N_B}S_B\Gamma_B),$$
$$S = S_A + S_B, ..., |S_A - S_B| \tag{9}$$

All the functions of eq 9 are degenerate in the absence of the interaction $\hat{H}_{AB}$ (8). The second term of eq 8, *i.e.*, the two-

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(21) Hubbard, J. *Proc. R. Soc. A 276*, 238.
(22) Weihe, H.; Güdel, H. U. *Chem. Phys. Lett.* **1996**, *261*, 123.
(23) Daudey, J. P.; de Loth, P.; Malrieu, J. P. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series; Reidel: Dordrecht, 1985.
(24) de Loth, P.; Karafiloglou, P.; Daudey, J. P.; Kahn, O. *J. Am. Chem. Soc.* **1988**, *110*, 5676.
(25) McConnel, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.
(26) Tchougreff, A. L. *J. Chem. Phys.* **1992**, *96*, 6026.

electron operator, always lowers the energies of the highest dimer spin multiplets relative to the energies of the lowest spin multiplets. The term potential exchange was used for this interaction.[8] Even though this operator acts diagonally on the manifold of terms of eq 9, its effect is small, since two-center two-electron exchange integrals are small. Values of ≈ 1 cm^{-1}, 1 cm^{-1}, 10 cm^{-1}, and 5 cm^{-1} have been estimated for the dinuclear complexes $Cu_2(CH_3CO_2)_4\cdot 2H_2O$, $[L_5CrOCrL_5]$, $L_4Ni(\mu\text{-}O)_2NiL_4$, and $Ti_2Cl_9^{3-}$, respectively.[13,14,27,28] These complexes represent a good variety of bridging geometries and intermetallic distances, and we can safely conclude that ferromagnetic J values of the order of a few hundred wavenumbers cannot be due to potential exchange. In the present paper we are interested in large effects, and potential exchange will be neglected. Of course this is no longer justified when dealing with exchange splittings of only a few wavenumbers.

We are left with the effect of the one-electron operator $\hat{V}_{AB}$, the kinetic exchange in Andersons terms.[8] We use second-order perturbation theory with $\hat{V}_{AB}$ as a perturbation operator to calculate the energies of the ground-state dimer functions, eq 9. Functions arising from the charge-transfer (CT) electron configuration $(a)^{N'_A}(b)^{N'_B}$, with $N'_A = N_A \pm 1$ and $N'_B = N_B \mp 1$, can interact with the functions arising from the $(a)^{N_A}(b)^{N_B}$ ground electron configuration under the action of $\hat{V}_{AB}$. This CT electron configuration is obtained by removing an electron from an orbital a_i on A and restoring it on B in orbital b_j. In analogy with eq 9 we write the similar expression for the CT dimer functions $|CT,S'\Gamma'M'\gamma'\rangle$ as follows:

$$|CT,S'\Gamma'M'\gamma'\rangle = ((a)^{N_A-1}S'_A\Gamma'_A) \otimes ((b)^{N_B+1}S'_B\Gamma'_B)$$

$$S' = S'_A + S'_B, ..., |S'_A - S'_B| \qquad (10)$$

The key matrix element in the perturbation treatment thus becomes

$$\langle GR,S\Gamma M\gamma|\hat{V}_{AB}|CT,S'\Gamma'M'\gamma'\rangle \equiv C(S;S'_A,S'_B)h_{ij} \qquad (11)$$

where h_{ij} is the transfer integral, eq 3,[20] and $C(S;S'_A,S'_B)$ is, as indicated, a spin dependent factor. We note in passing that the two-electron operator eq 8 also has matrix elements between the functions $|GR,S\Gamma,M,\gamma\rangle$ and $|CT,S',\Gamma',M',\gamma'\rangle$. Like most authors we neglect this contribution in the following. This is again justified as long as we are dealing with large effects, *i.e.*, energy splittings of a few hundred wavenumbers. We also note that, although ligand orbitals do not explicitly occur in our formalism, they are involved through their admixture with the metal orbitals. Physically our formal metal-to-metal electron transfer process can thus acquire considerable ligand-to-metal or metal-to-ligand charge-transfer character.

In refs 9 and 22 matrix elements of the type in eq 11 were obtained for a specific electron configuration. Here we are interested in a general expression, and for this we make use of Wigner−Racah algebra as discussed in ref 29. This is developed in the Appendix, and we obtain the following simple expression:

$$C(S;S'_A,S'_B) = \sqrt{N_A(N_B+1)}\sqrt{2S_A+1}\sqrt{2S'_B+1} \times \begin{Bmatrix} S_A & S_B & S \\ S'_B & S'_A & {}^1/_2 \end{Bmatrix} f_A f_B \qquad (12)$$

The curly bracket is a 6*j* -symbol. Closed expressions for the relevant 6*j* -symbols and for the two fractional parentage coefficients f_A and f_B are given below. We distinguish four cases depending on the occupancy of the relevant interacting orbitals a_i and b_j prior to the electron transfer from A to B:

1. a_i is half-filled and b_j is half-filled ($[{}^1/_2]_A \rightarrow [{}^1/_2]_B$)
2. a_i is half-filled and b_j is empty ($[{}^1/_2]_A \rightarrow [0]_B$)
3. a_i is full and b_j is half-filled ($[1]_A \rightarrow [{}^1/_2]_B$)
4. a_i is full and b_j is empty ($[1]_A \rightarrow [0]_B$)

From this we see that the possible values of S'_A and S'_B are $S'_A = S_A \pm {}^1/_2$ and $S'_B = S_B \pm {}^1/_2$, respectively. The only four 6*j* -symbols which need to be evaluated are thus[30]

$$\begin{Bmatrix} S_A & S_B & S \\ S_B - {}^1/_2 & S_A - {}^1/_2 & {}^1/_2 \end{Bmatrix} = \left[\frac{-S(S+1) + \Sigma(\Sigma+1)}{2S_A(2S_A+1)2S_B(2S_B+1)}\right]^{1/2} \qquad (13)$$

$$\begin{Bmatrix} S_A & S_B & S \\ S_B + {}^1/_2 & S_A - {}^1/_2 & {}^1/_2 \end{Bmatrix} = \left[\frac{S(S+1) - \Delta(\Delta-1)}{2S_A(2S_A+1)(2S_B+1)(2S_B+2)}\right]^{1/2} \qquad (14)$$

$$\begin{Bmatrix} S_A & S_B & S \\ S_B - {}^1/_2 & S_A + {}^1/_2 & {}^1/_2 \end{Bmatrix} = \left[\frac{S(S+1) - \Delta(\Delta+1)}{(2S_A+1)(2S_A+2)2S_B(2S_B+1)}\right]^{1/2} \qquad (15)$$

$$\begin{Bmatrix} S_A & S_B & S \\ S_B + {}^1/_2 & S_A + {}^1/_2 & {}^1/_2 \end{Bmatrix} = \left[\frac{-S(S+1) + (\Sigma+1)(\Sigma+2)}{(2S_A+1)(2S_A+2)(2S_B+1)(2S_B+2)}\right]^{1/2} \qquad (16)$$

In eqs 13−16 we defined $\Delta = S_A - S_B$ and $\Sigma = S_A + S_B$.

In the Appendix (see eqs A.6−A.8) we derive the following expressions for the factors f_A and f_B. When we add an electron into an empty orbital on B, S'_B can take the values $S_B \pm {}^1/_2$. In both cases f_B takes the value

$$f_B = \sqrt{\frac{1}{N_B+1}} \qquad (17)$$

When the electron is added into an orbital on *B* which is already occupied by one electron, we need only to consider $S'_B = S_B - {}^1/_2$. f_B then takes the value

$$f_B = \sqrt{\frac{n_B+1}{n_B(N_B+1)}} \qquad (18)$$

When we take an electron from a half-filled orbital on A, f_A takes the value

$$f_A = \sqrt{\frac{1}{N_A}} \qquad (19)$$

And, finally, when the electron is removed from a filled orbital

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(27) Hansen, Å. E.; Ballhausen, C. J. *Trans. Faraday Soc.* **1965**, *61*, 631.
(28) Ceulemans, A.; Heylen, G. A.; Chibotaru, L. F.; Maes, T. L.; Pierloot, K.; Ribbing, C.; Vanquickenborne, L. C. *Inorg. Chim. Acta* **1996**, *251*, 15.
(29) Damhus, T. *Mol. Phys.* **1983**, *50*, 497.
(30) Rotenberg, M.; Bivins, R.; Metropolis, N.; Wooten, J. K., Jr. In *The 3-j and 6-j Symbols*; MIT Press: Cambridge, 1959. (Equations 2.13−2.16.

on A, we must consider two cases:

$$f_A = \sqrt{\frac{n_A + 2}{(n_A + 1)N_A}} \tag{20}$$

for $S'_A = S_A + {}^1/_2$, and

$$f_A = \sqrt{\frac{n_A}{(n_A + 1)N_A}} \tag{21}$$

for $S'_A = S_A - {}^1/_2$.

The relevant *C*-factors of eq 11, for each type of electron transfer will now be derived separately.

2.1. $[^1/_2]_A \rightarrow [^1/_2]_B$. This type of electron transfer naturally leads to a CT configuration with $S'_A = S_A - {}^1/_2$ and $S'_B = S_B - {}^1/_2$. Using eqs 12, 13, 18, and 19 we obtain

$$C(S;S'_A,S'_B) = \left[\frac{-S(S+1) + \Sigma(\Sigma+1)}{n_A n_B}\right]^{1/2} \tag{22}$$

2.2. $[^1/_2]_A \rightarrow [0]_B$. This electron transfer leads to $S'_A = S_A - {}^1/_2$, $S'_B = S_B \pm {}^1/_2$, and we get

$$C(S;S'_A,S_B{+}^1/_2) = \left[\frac{S(S+1) - \Delta(\Delta-1)}{n_A(n_B+1)}\right]^{1/2} \tag{23}$$

$$C(S;S'_A,S_B{-}^1/_2) = \left[\frac{-S(S+1) + \Sigma(\Sigma+1)}{n_A(n_B+1)}\right]^{1/2} \tag{24}$$

2.3. $[1]_A \rightarrow [^1/_2]_B$. This electron transfer leads to $S'_A = S_A \pm {}^1/_2$ and $S'_B = S_B - {}^1/_2$, and we get

$$C(S;S_A{+}^1/_2,S'_B) = \left[\frac{S(S+1) - \Delta(\Delta+1)}{(n_A+1)n_B}\right]^{1/2} \tag{25}$$

$$C(S;S_A{-}^1/_2,S'_B) = \left[\frac{-S(S+1) + \Sigma(\Sigma+1)}{(n_A+1)n_B}\right]^{1/2} \tag{26}$$

2.4. $[1]_A \rightarrow [0]_B$. This last case is slightly more complicated and leads to four different sets of matrix elements, since $S'_A = S_A \pm {}^1/_2$ and $S'_B = S_B \pm {}^1/_2$. We get

$$C(S;S_A{-}^1/_2,S_B{-}^1/_2) = \left[\frac{-S(S+1) + \Sigma(\Sigma+1)}{(n_A+1)(n_B+1)}\right]^{1/2} \tag{27}$$

$$C(S;S_A{+}^1/_2,S_B{-}^1/_2) = \left[\frac{S(S+1) - \Delta(\Delta+1)}{(n_A+1)(n_B+1)}\right]^{1/2} \tag{28}$$

$$C(S;S_A{-}^1/_2,S_B{+}^1/_2) = \left[\frac{S(S+1) - \Delta(\Delta-1)}{(n_A+1)(n_B+1)}\right]^{1/2} \tag{29}$$

$$C(S;S_A{+}^1/_2,S_B{+}^1/_2) = \left[\frac{-S(S+1) + (\Sigma+1)(\Sigma+2)}{(n_A+1)(n_B+1)}\right]^{1/2} \tag{30}$$

3. *J* Values

The *C*-factors obtained in section 2 will now be used to compute the energies of the $S\Gamma$-terms of eq 9 under the $\hat{V}_{AB}$ perturbation. This will here be done to second order. The procedure is as follows: we compute the second-order corrections to the energies and equate these with the eigenvalues of the HDvV spin Hamiltonian eq 1. The second-order corrections $E_2(S\Gamma)$ to the energies of the $S\Gamma$ terms are

$$E_2(S\Gamma) = \frac{-[C(S;S'_A,S'_B)]^2 {h_{ij}}^2}{E_0(S'\Gamma') - E_0(S\Gamma)} \tag{31}$$

$E_0(S\Gamma)$ and $E_0(S'\Gamma')$ are zeroth order energies of the GR and CT functions, respectively. The correction $E_2(S\Gamma)$ leads to an *S* dependent lowering of the dimer ground-state levels. The *S* dependency of the 6*j* symbols eqs 13−16 directly leads to a Landé type energy splitting. The eigenvalues of eq 1 also correspond to a spin dependent Landé energy pattern, and equating the corresponding terms we get

$$E_2(S\Gamma) = \frac{J}{2}S(S+1) + \text{constant} \tag{32}$$

where the constant can be neglected in our discussion of energy splittings. Eqs 31 and 32 will now be used to derive expressions for *J* in terms of the model parameters n_A, n_B, h_{ij}, and $U = E_0(S'\Gamma') - E_0(S\Gamma)$. As in section 2, the contributions to *J* from each type of interaction will be presented separately.

3.1. $[^1/_2]_A \rightarrow [^1/_2]_B$. In the absence of the interaction $\hat{H}_{AB}$ the $|S'_A,S'_B,S\rangle$ CT functions are all degenerate at an energy U' above the $|S_A,S_B;S\rangle$ GR functions, which are also degenerate. Using eqs 22 and 31 we get

$$J([^1/_2]_A{\rightarrow}[^1/_2]_B) = \frac{2}{n_A n_B}\frac{{h_{ij}}^2}{U'} \tag{33}$$

For this type of interaction the opposite electron transfer is always possible, and we get

$$J([^1/_2]_A{\leftarrow}[^1/_2]_B) = \frac{2}{n_A n_B}\frac{{h_{ij}}^2}{U''} \tag{34}$$

For a homonuclear homovalent dimer, *i.e.*, A = B, and A and B in identical environments we naturally have $U' = U'' \equiv U$, and the total contribution to the *J* value is thus antiferromagnetic and given by

$$J([^1/_2]_A{\leftrightarrow}[^1/_2]_B) = \frac{4}{n_A n_B}\frac{{h_{ij}}^2}{U} \tag{35}$$

3.2. $[^1/_2]_A \rightarrow [0]_B$. Because of the possibilities $S'_B = S_B \pm {}^1/_2$ this type of interaction has two contributions to the *J* value, one ferromagnetic and one antiferromagnetic. In the absence of the interaction the CT functions with $(S'_A, S'_B) = (S_A - {}^1/_2, S_B + {}^1/_2)$ are all degenerate at an energy U' above the GR functions. Similarily, the the CT functions with $(S'_A, S'_B) = (S_A - {}^1/_2, S_B - {}^1/_2)$ are degenerate at an energy U'' above the GR functions. Combining eqs 23 and 31 we get

$$J([^1/_2]_A{\rightarrow}[0]_B,S'_B{=}S_B{+}^1/_2) = -\frac{2}{n_A(n_B+1)}\frac{{h_{ij}}^2}{U'} \tag{36}$$

Similarly, by combining eqs 24 and 31, we find

$$J([^1/_2]_A{\rightarrow}[0]_B,S'_B{=}S_B{-}^1/_2) = \frac{2}{n_A(n_B+1)}\frac{{h_{ij}}^2}{U''} \tag{37}$$

The competition between eqs 36 and 37 is governed by the energy ordering of the ($S_B + {}^1/_2$) and ($S_B - {}^1/_2$) terms arising from the $(b)^{N_B+1}$ electron configuration. Due to Hund's rule, $U' < U''$, and we define

$$U'' - U' \equiv \mathcal{I}_{n_B+1} \tag{38}$$

In eq 38 $\mathcal{I}_{n_B+1}$ is the so-called intraatomic exchange integral,[20] which is discussed more thoroughly in section 4.2. Since the magnitude of $\mathcal{I}$ is roughly a linear function of the number of unpaired electrons of the actual configuration, we indicate this dependence with the subscript $n_B + 1$, see also section 4.2. By combining eqs 36, 37, and 38, and assuming that the CT energies U' and U'' are much larger than $\mathcal{I}_{n_B+1}$, we get the following total ferromagnetic contribution to the J value:

$$J([{}^1/_2]{\rightarrow}[0]_B) = -\frac{2}{n_A(n_B+1)}\frac{h_{ij}^{\;2}}{U}\frac{\mathcal{I}_{n_B+1}}{U} \tag{39}$$

where we have set $U' \approx U'' = U$.

3.3. $[1]_A \rightarrow [{}^1/_2]_B$. This case can be treated as discussed in section 3.2, and we find a resulting ferromagnetic contribution to the J value:

$$J([1]_A{\rightarrow}[{}^1/_2]_B) = -\frac{2}{(n_A+1)n_B}\frac{h_{ij}^{\;2}}{U}\frac{\mathcal{I}_{n_A+1}}{U} \tag{40}$$

3.4. $[1]_A \rightarrow [0]_B$. This type of interaction has four contributions to the J value, since there are four different sets of terms from the CT configuration which have matrix elements to the ground state, see eqs 27–30. In the absence of the interaction the CT functions with $(S'_A, S'_B) = (S_A + {}^1/_2, S_B + {}^1/_2)$ are all degenerate at energy U', the functions with $(S'_A, S'_B) = (S_A - {}^1/_2, S_B + {}^1/_2)$ are degenerate at energy U'', the functions with $(S'_A, S'_B) = (S_A + {}^1/_2, S_B - {}^1/_2)$ are degenerate at energy U''', and the functions with $(S'_A, S'_B) = (S_A - {}^1/_2, S_B - {}^1/_2)$ are degenerate at energy U''''. Using eqs 27–30 and 31 we obtain two antiferromagnetic and the two ferromagnetic contributions as follows:

$$J([1]_A{\rightarrow}[0]_B, S'_A{=}S_A{-}{}^1/_2, S'_B{=}S_B{-}{}^1/_2) = \frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^{\;2}}{U''''} \tag{41}$$

$$J([1]_A{\rightarrow}[0]_B, S'_A{=}S_A{+}{}^1/_2, S'_B{=}S_B{-}{}^1/_2) = -\frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^{\;2}}{U'''} \tag{42}$$

$$J([1]_A{\rightarrow}[0]_B, S'_A{=}S_A{-}{}^1/_2, S'_B{=}S_B{+}{}^1/_2) = -\frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^{\;2}}{U''} \tag{43}$$

$$J([1]_A{\rightarrow}[0]_B, S'_A{=}S_A{+}{}^1/_2, S'_B{=}S_B{+}{}^1/_2) = \frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^{\;2}}{U'} \tag{44}$$

With the same arguments as outlined in section 3.2 we have $U' < (U'', U''') < U''''$. This means that the weakest and the strongest interactions are both antiferromagnetic, while the two intermediate ones are both ferromagnetic. We define

$$U' = U' \tag{45}$$

$$U'' = U' + \mathcal{I}_{n_A+1} \tag{46}$$

$$U''' = U' + \mathcal{I}_{n_B+1} \tag{47}$$

$$U'''' = U' + \mathcal{I}_{n_A+1} + \mathcal{I}_{n_B+1} \tag{48}$$

With the assumption that all the $\mathcal{I}$ values are much smaller than the U values and setting $U' \approx U'' \approx U''' \approx U'''' = U$, the total contribution to the J value then becomes:

$$J([1]_A{\rightarrow}[0]_B) = \frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^{\;2}}{U}\frac{(\mathcal{I}_{n_A+1} - \mathcal{I}_{n_B+1})}{U} \tag{49}$$

The sign of this contribution to the J value is determined by the difference of the two intraatomic exchange integrals $\mathcal{I}_{n_A+1}$ and $\mathcal{I}_{n_B+1}$.

4. Discussion

Since there is quite an elaborate formalism involved in obtaining the perturbation matrix elements (11) via the *C*-factors of section 2 eqs 22–30, we have made an independent check of these formulas. This was done by first generating explicit expressions for the relevant functions of eqs 9 and 10, and then evaluating eq 11. The same results were obtained in every case, and we are thus confident that the formulas for the matrix elements are correct. However, the second-order treatments in section 3 were all based on the assumptions that $U \gg |h_{ij}|$ and $U \gg \mathcal{I}_n$. We will therefore in the following two sections discuss the quantities U, h_{ij}, and $\mathcal{I}_n$ and examine the validity of these assumptions.

4.1. The Quantities U and h_{ij}. All the contributions to the total J value contain the ratio h_{ij}^2/U. A brief review-like note on the two parameters h_{ij} and U is therefore in order.

The charge-transfer energy U is a critical parameter of the model. It is formally defined as a difference between one-center and two-center repulsion integrals,[21] and it corresponds to the energy difference between the ground electron configuration and a CT configuration.

For an estimate of U values we can start by using ionization potentials of the free ions.[8] For trivalent and divalent homonuclear dimeric complexes of the first-row transition metal ions we would thus expect an energy range of 16–24 and 14–18 *eV*, respectively.[8,31] In a complex or crystal these values can be significantly reduced,[8] and we assume a typical energy range for U between 5 and 10 *eV* (40000–80000 cm^{-1}). Roughly the same numbers are valid for heteronuclear dimeric complexes in which the monomeric constituents are in the same oxidation state.[31]

We note in passing that a rather different situation arises in mixed-valence complexes, when the two metals A and B in the dimer have different oxidation states. For simplicity we consider here only dimers in which the valencies are localized. To such a dimer we must associate two different U values, one which is associated with an electron transfer from A to B, $U_{A\rightarrow B}$, and one which is associated with the opposite transfer $U_{A\leftarrow B}$. By using the ionization potential arguments we find that $U_{A\rightarrow B} \gg$

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[31] *Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988–1989 (table with ionization potentials).

[32] Kahn, O. *Struct. Bonding* **1987**, *68*, 89. Kahn refers to many relevant papers concerning magnetic properties of heterodinuclear heterovalent transition metal dimers.

$U_{A\leftarrow B}$, if the oxidation state of A is higher than that of B. For such dimers $U_{A\leftarrow B}$ will usually be small and can even be negative.[31] Small U values below 20000 cm^{-1} have also been reported for Mo, W, Tc, and Re dimers with direct strong metal−metal bonds.[33] However, mixed-valence systems and complexes with strong metal−metal bonds are not the subject of this paper, and we will use the above mentioned energy range of 40000−80000 cm^{-1} as a reasonable estimate of U values.

Molecular orbital techniques[10,19] can be used for an estimate of the order of magnitude of the transfer integrals h_{ij}. The quantity h_{ij} can be correlated with the energy difference between the symmetric and the antisymmetric linear combinations of the atomic orbitals a_i and b_j. Typical $|h_{ij}|$ values obtained by extended Hückel and angular overlap approximations on a variety of dinuclear 3d complexes are in the range 0−6000 cm^{-1}.[9,10,34] Our approximation $|h_{ij}| \ll U$ is thus valid. In addition, both quantities h_{ij} and U are transferable from one dimer to another as long as the main structural features are conserved (see section 4.4). Hence, the effective parameter h_{ij}^2/U can be considered as transferable between structurally similar dimers (see section 4.4).

4.2. The Quantity $\mathcal{I}$. The so-called intraatomic exchange integral[20] $\mathcal{I}$ appears in the formalism of section 3 when we add an electron into an empty orbital on B or/and when we remove an electron from a full orbital on A. We will in the following investigate the effect and meaning of the single-ion property $\mathcal{I}$ for the first case. The second case is equivalent.

We start on center B with a configuration $(b)^{N_B,n_B}$, corresponding to a total of N_B electrons, n_B of which are unpaired. The lowest energy term from this electron configuration is $S_B\Gamma_B$. This is the ground term of B with $S_B = n_B/2$. Adding an electron into an empty orbital on B leads to the electron configuration $(b)^{N_B+1,n_B+1}$. We are interested in those two terms from this new configuration which arise from the spin- and space-coupling of $S_B\Gamma_B$ and the extra electron. We designate them by $S'_B\Gamma'_B$ and $S''_B\Gamma''_B$, where $S'_B = S_B + {}^1/_2$ and $S''_B = S_B - {}^1/_2$. $\mathcal{I}$ is their first-order energy difference:

$$\mathcal{I} = \left\langle S''_B\Gamma''_B \middle| \sum_{i<j}\frac{1}{r_{ij}} \middle| S''_B\Gamma''_B \right\rangle - \left\langle S'_B\Gamma'_B \middle| \sum_{i<j}\frac{1}{r_{ij}} \middle| S'_B\Gamma'_B \right\rangle \tag{50}$$

$\mathcal{I}$ is positive as a result of Hund's rule. $\mathcal{I}$ is in fact *not one* intraatomic exchange integral, but it can be expressed as a *weighted sum* of true exchange integrals I_{ij} of the type

$$I_{ij} = \left\langle b_i(1)b_j(2) \middle| \frac{1}{r_{12}} \middle| b_i(2)b_j(1) \right\rangle \tag{51}$$

where the indices i and j run over the half-filled orbitals. Making the approximation that all the relevant I_{ij}'s are equal, *i.e.*, $I_{ij} = I$, we find that $\mathcal{I}$ is proportional to the number of unpaired electrons of the actual electron configuration. In our specific case with $n_B + 1$ unpaired electrons we have

$$\mathcal{I}_{n_B+1} = (n_B + 1)I \tag{52}$$

or in general with n unpaired electrons

$$\mathcal{I}_n = nI \tag{53}$$

Equation 53 thus establishes the n dependence of the parameter $\mathcal{I}_n$. The assumption $I_{ij} = I$ for all i, j seems at first sight rather crude. From Griffith[35] we find for d-orbitals that the 10 possible exchange integrals all lie in the interval $C < I_{ij} < C + 4B$, with a mean value of

$$\langle I_{ij}\rangle = C + \frac{5}{2}B \tag{54}$$

B and C are the Racah interelectronic repulsion parameters. By using the experimentally verified relation[36] $4B < C < 5B$ we find that eq 53 is at most a factor of 1.5 wrong.

A very gratifying experimental verification of eq 53 is obtained by a comparison of the first spin-flip excitation energies of analogous transition metal complexes. In first order this corresponds to the energy difference between $S''_B\Gamma''_B$ and $S'_B\Gamma'_B$, *i.e.*, $\mathcal{I}_n$.

Similar octahedral complexes of the trivalent metals V^{3+} (d^2), Cu^{3+} (d^8), Cr^{3+} (d^3), and Fe^{3+} (d^5, high-spin) have their first spin-flip transitions in the energy intervals 9000−10000, 9600, 14000−15000, and 24000−25000 cm^{-1}, respectively.[36] These have the approximate ratios 2:2:3:5, exactly as predicted by eq 53. This gives $I \approx$ 4500−5000 cm^{-1}, which is also in accordance with eq 54. Typical B and C values for trivalent transition metal complexes are about 700 and 3000 cm^{-1}, respectively.[36]

Similar octahedral complexes of the divalent metals Ti^{2+} (d^2), V^{2+} (d^3), Cr^{2+} (d^4, high-spin), and Mn^{2+} (d^5, high-spin) have their first spin-flip transitions at about 7500, 11500−13000, 15000−19000, and 23000−24000 cm^{-1}, respectively.[36−38] Again, these energies correspond nicely to the ratio 2:3:4:5 expected on the basis of eq 53. We get $I \approx$ 4000−4500 cm^{-1}, again in agreement with eq 54. The repulsion parameters B and C are usually similar in magnitude for divalent and trivalent metals.[36] These two series of experimental $\mathcal{I}_n$ values nicely support the validity of eq 53.

Anderson estimated $\mathcal{I}/U$ to lie in the range ${}^1/_{10}$−${}^1/_5$,[8] and he took $\mathcal{I} \ll U$ to be a good approximation. We used this approximation in deriving eqs 39, 40, and 49. But we now see that the effective parameter I/U, but not $\mathcal{I}_n/U$, is transferable between 3d dimers. The quality of the approximation $\mathcal{I} \ll U$ clearly decreases with increasing n. For a typical value $I/U = {}^1/_{10}$ and $n = 5$, *e.g.*, high-spin Mn^{2+} or Fe^{3+}, the ratio $\mathcal{I}_n/U$ can get as large as ${}^1/_2$.

4.3. Comparison with the Goodenough−Kanamori Rules. Table 1 shows a comparison of the corresponding formulas in ref 20 and section 3 of the present paper for the four types of interactions. The formulas from ref 20 represent the quantitative part of the Goodenough−Kanamori rules.

First we note that there is no dispute about the sign, ferro- or antiferromagnetic, of the first three contributions to the total J value. For the $[{}^1/_2]_A \rightarrow [{}^1/_2]_B$ type interaction our results are identical to those in refs 8 and 20. The presence of this type of interaction in an AB system will usually lead to an antiferromagnetic overall interaction. This term is dominant because it is independent of the ratio $\mathcal{I}_n/U$, while the remaining three types of interactions all depend on it.

There are discrepancies between our results and the earlier ones for the other three types of interactions. The major one concerns the factor with the n_A and n_B dependence. For the $[{}^1/_2]_A \rightarrow [0]_B$ interaction we find a factor of $2/(n_A(n_B + 1))$ rather than the earlier reported factor $2/(n_An_B)$. For small n_B values this is a significant difference. Using the n dependence of $\mathcal{I}_n$

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(33) Hopkins, M. D.; Gray, H. B.; Miskowski, V. M. *Polyhedron* **1987**, *6*, 705.

(34) Atanasov, M.; Angelov, S. *Chem. Phys.* **1991**, *150*, 383.

(35) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, 1971. (Appendix 2, Table A26.)

(36) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Science Publishers B. V.: Amsterdam, 1984; Chapter 6.

(37) Herren, M.; Jacobsen, S. M.; Güdel, H. U. *Inorg. Chem.* **1991**, *30*, 1656.

(38) Riesen, H.; Güdel, H. U. *Inorg. Chem.* **1984**, *23*, 1881

Table 1. Comparison of Earlier Results with the Results Obtained in This Paper[a]

interaction type		earlier results	our results	$I_n = nI$
1	$[{}^1/_2]_A \rightarrow [{}^1/_2]_B$	$+\frac{2}{n_A n_B}\frac{h_{ij}^2}{U}$	$+\frac{2}{n_A n_B}\frac{h_{ij}^2}{U}$	$+\frac{2}{n_A n_B}\frac{h_{ij}^2}{U}$
2	$[{}^1/_2]_A \rightarrow [0]_B$	$-\frac{2}{n_A n_B}\frac{h_{ij}^2}{U}\frac{I}{U}$	$-\frac{2}{n_A(n_B+1)}\frac{h_{ij}^2}{U}\frac{I_{n_B+1}}{U}$	$-\frac{2}{n_A}\frac{h_{ij}^2}{U}\frac{I}{U}$
3	$[1]_A \rightarrow [{}^1/_2]_B$	$-\frac{2}{n_A n_B}\frac{h_{ij}^2}{U}\frac{I}{U}$	$-\frac{2}{(n_A+1)n_B}\frac{h_{ij}^2}{U}\frac{I_{n_A+1}}{U}$	$-\frac{2}{n_B}\frac{h_{ij}^2}{U}\frac{I}{U}$
4	$[1]_A \rightarrow [0]_B$	ferromagnetic	$\frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^2}{U}\frac{(I_{n_A+1} - I_{n_B+1})}{U}$	$\frac{2(n_A - n_B)}{(n_A+1)(n_B+1)}\frac{h_{ij}^2}{U}\frac{I}{U}$

[a] The first two columns identify the interaction type as introduced in section 2. The third column gives the contributions to the HDvV J value as reported by ref 20. The fourth and fifth columns collect our results. The fifth column was obtained with the approximation eq 53.

as found in section 4.2, eq 53, we can approximate

$$J([{}^1/_2]_A \rightarrow [0]_B) = -\frac{2}{n_A(n_B+1)}\frac{h_{ij}^2}{U}\frac{I_{n_B+1}}{U} \tag{39}$$

$$\approx -\frac{2(n_B+1)}{n_A(n_B+1)}\frac{h_{ij}^2}{U}\frac{I}{U} = -\frac{2}{n_A}\frac{h_{ij}^2}{U}\frac{I}{U} \tag{55}$$

This type of interaction is thus effectively proportional to $2/n_A$.

An exactly analogous difference appears for the $[1]_A \rightarrow [{}^1/_2]_B$ interaction, where we find a factor of $2/((n_A + 1)n_B)$ compared to $2/(n_A n_B)$ in ref 20. And with the approximation eq 53 we get an effective $2/n_B$ dependence (see Table 1).

A discussion of the fourth type of interaction, $[1]_A \rightarrow [0]_B$, is slightly more involved. Anderson[19] listed this interaction as ferromagnetic, but without a formula for a quantitative estimate. We show that not only the magnitude but also the sign of the interaction depends on the relative magnitude of the two quantities I_{n_A+1} and I_{n_B+1}. This is due to the factor $(I_{n_A+1} - I_{n_B+1})$ of eq 49. Using again the n dependence of I_n we approximate

$$J([1]_A \rightarrow [0]_B) = \frac{2}{(n_A+1)(n_B+1)}\frac{h_{ij}^2}{U}\frac{I_{n_A+1} - I_{n_B+1}}{U} \tag{49}$$

$$\approx \frac{2(n_A - n_B)}{(n_A+1)(n_B+1)}\frac{h_{ij}^2}{U}\frac{I}{U} \tag{56}$$

Depending on the specific situation this type of interaction can thus be either ferromagnetic or antiferromagnetic, namely, ferromagnetic if $n_A < n_B$ and antiferromagnetic if $n_A > n_B$. In the case of an AB system with A and B identical we get no contribution from the $[1]_A \rightarrow [0]_B$ interaction. This conclusion is at variance with earlier discussions of this type of interaction.[19]

4.4. Comparison with Experiments and Conclusions. We have applied our model and the formulas developed in section 3 to structurally related series of exchange-coupled dimeric 3d complexes. The results are gratifying. Experimental trends, including changes from ferro- to antiferromagnetic coupling, can be quantitatively reproduced by the model. The transferability of the model parameters is thus demonstrated.[39] As an illustration we summarize the results obtained in a thorough study of trivalent 3d metal dimers with a linear M−O−M bridging geometry. A detailed account of this work is published separately.[39]

Table 2. Comparison of Experimental and Calculated J Values of Trivalent Transition Metal Dimers with a Linear Oxo Bridge[a]

$M-O-M$	J_{exp}/cm^{-1}	J_{theory}	J_{calc}/cm^{-1}
$Ti-O-Ti$	0-16	0	0
$V-O-V^{(\mathbf{a})}$	< -400	$-h'_{\xi\xi}$	-480
$Cr-O-Cr$	450-580	$\frac{8}{9}h'_{\xi\xi}$	426
$Mn(hs)-O-Mn(hs)$	240	$\frac{1}{2}h'_{\xi\xi}$	240
$Mn(ls)-O-Mn(ls)$	> 870	$2h'_{\xi\xi}$	960
$Fe(hs)-O-Fe(hs)$	180-230	$\frac{8}{25}h'_{\xi\xi} + \frac{4}{25}h'_{\theta\theta}$	210

[a] The metal ions in the dimers are six coordinate. hs and ls stand for high-spin and low-spin, respectively. The second column gives the range of experimental J values. The third column gives the theoretical expression for the J value according to eq 35. $\xi = d_{yz}$, $\theta = d_{z^2}$, and we have defined $h'_{ij} \equiv h_{ij}^2/U$. $h_{\xi\xi}$ and $h_{\theta\theta}$ are the transfer integrals between the orbitals having π and σ symmetry with respect to the M−O−M axis, respectively. The values in the last column were obtained by using the parameter values $h_{\xi\xi}^2/U = 480$ cm^{-1} and $h_{\theta\theta}^2/U = 352$ cm^{-1}, which minimize the sum of the absolute differences $|J_{exp} - J_{theory}|$. **(a)**: The linear μ-oxo−divanadium system is an orbitally degenerate system; see ref 22 for details. Proper references to the representative compounds are given in ref 39.

Table 2 contains the experimental and calculated J values. The nature of the terminal ligands is not relevant for this discussion. The expressions for J_{theory} were derived from eq 35 by assuming D_{4h} dimer symmetry and neglecting the two interactions between the orbitals having δ symmetry with respect to the M−O−M axis. We find that the magnetic properties of the dimers with $M^{3+} = Ti^{3+}$, V^{3+}, Cr^{3+}, Mn^{3+} (hs), and Mn^{3+} (ls) are essentially determined by one parameter only, namely, $h_{\xi\xi}^2/U$. The extra parameter $h_{\theta\theta}^2/U$ is needed for the high-spin Fe^{3+} dimers, since we have an interacting σ electron on each metal center. The agreement between the calculated and the experimental J values is striking. It shows that the effective parameter $h'_{\xi\xi} = h_{\xi\xi}^2/U$ is transferable from one dimer to another along this series.

The series of complexes presented in Table 2 is of particular interest because of the large range of J values it covers, from strongly ferro- to very strongly antiferromagnetic. We can thus confidently assume that the potential exchange contributions are unimportant. The strong ferromagnetic coupling in the V−O−V dimers is most significant, because it is in stark contrast to the general belief that kinetic exchange is always antiferromagnetic. One of the keys to the ferromagnetic sign of the net interaction in this case is the degeneracy of the $\xi(\equiv yz)$ and $\eta(\equiv zx)$ single-ion orbitals in the C_{4v} local symmetry at the V^{3+} site. The dimer ground state is obviously an $S = 2$ with an energy difference to the next higher states of several hundred wavenumbers. This has been elaborated and discussed more thoroughly in ref 22.

The effect of the ferromagnetic terms 39 and 40 is not visible in the series of Table 2 because of the high D_{4h} symmetry and the fact that only homonuclear dimers are included. We have investigated other series with nonlinear bridges and nonequal

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(39) Weihe, H.; Güdel, H. U. Submitted to *Inorg. Chem.*

metal ions in the dimers, and we generally find very good agreement between calculated and experimental exchange splittings.[39]

In conclusion, by a critical analysis of some old expressions in the literature on kinetic exchange we have been able to provide some corrected versions. For the interaction of a filled with an empty orbital new expressions for their contribution to the net exchange are presented. The ratio I/U is crucial for an evaluation of kinetic exchange contributions. From an analysis of the quantity I, which results from intraatomic exchange interactions, we reach the conclusion that I/U readily exceeds the range $^1/_{10}$−$^1/_5$ estimated by Anderson.[8] I is found to be roughly proportional to n, the number of unpaired electrons. In contrast to h_{ij}^2/U and I/U, I/U is not an effective parameter which is transferable within a series of complexes with the same M−O−M bridging geometry but varying isovalent transition metal ions.

The widely held belief that kinetic exchange is always antiferromagnetic is demonstrated to be incorrect. Ferromagnetic interactions due to kinetic exchange can result when the terms 39 and 40 become dominant. In addition, ferromagnetic contributions of the order of magnitude $-h_{ij}^2/U$ (see Table 2) can be observed in some specific situations.[22]

As long as we are only interested in a qualitative discussion of the sign of the exchange interaction, *i.e.*, ferromagnetic versus antiferromagnetic, there is not much difference between Goodenough's formulas and our results. But our formulas constitute a correct basis for quantitative comparisons and predictions of magnetic properties of structurally related compounds.

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Appendix: Derivation of Eq 12

A formula to calculate the $\hat{V}_{AB}$ interaction matrix element, eq 11, is derived by Damhus.[29] We reproduce his formula in eq A.1. All the symbols have the same meaning as introduced in section 2 of this paper. In eq A.1 dim(Γ) means the dimension of the irreducible representation Γ. κ_A is an extra identification label needed if there are several terms from the $(a)^{N_A}$ configuration which transform as $S_A\Gamma_A$; and similarly with κ_B, κ'_A, κ'_B, α''_A, and α''_B. (We left these extra, often superfluous, identification labels out in the main text.) { } is a 6*j* -symbol, ( ) is a 3Γ-symbol, ⟨...|...⟩ is a coupling coefficient, and [ ] is a 9Γ-symbol. $\pi(\Gamma_A\Gamma'_A\Gamma''_A)$ is a phase factor, and $\langle ...|\hat{V}_{AB}|...\rangle$ is the one-electron parameter, *i.e.*, the transfer integral. The two quantities appearing on the last two lines of eq A.1 are fractional parentage type coefficients. The remaining symbols are defined in section 2.

$$\begin{aligned}&\langle[((a)^{N_A}\kappa_A S_A\Gamma_A)\otimes((b)^{N_B}\kappa_B S_B\Gamma_B)]S\Gamma M\gamma|\hat{V}_{AB}|\\ &\qquad[((a)^{N_A-1}\kappa'_A S'_A\Gamma'_A)\otimes((b)^{N_B+1}\kappa'_B S'_B\Gamma'_B)]S'\Gamma'M'\gamma'\rangle =\\ &\qquad\delta(S,S')\delta(M,M')(-1)^{S_A+S_B+S+N_B}\times\\ &\sqrt{N_A(N_B+1)}\sqrt{\dim(\Gamma_A)}\sqrt{\dim(\Gamma)}\sqrt{\dim(\Gamma'_B)}\sqrt{\dim(\Gamma')}\times\\ &\qquad\sqrt{(2S_A+1)}\sqrt{(2S'_B+1)}\begin{Bmatrix}S_A & S_B & S\\ S'_B & S'_A & ^1/_2\end{Bmatrix}\times\\ &\sum_{\substack{\alpha''_A\Gamma''_A\gamma''_A\\ \alpha''_B\Gamma''_B\gamma''_B\\ \Gamma''\gamma''}}\Bigg\{\pi(\Gamma_A\Gamma'_A\Gamma''_A)\sqrt{\dim(\Gamma'')}\begin{pmatrix}\bar{\Gamma} & \Gamma'' & \Gamma'\\ \gamma & \gamma'' & \gamma'\end{pmatrix}\langle\Gamma''_A\gamma''_A\,\bar{\Gamma}''_B\gamma''_B|\Gamma''\gamma''\rangle\times\\ &\qquad\langle a\alpha''_A\,\Gamma''_A\gamma''_A|\hat{V}_{AB}|b\alpha''_B\,\Gamma''_B\gamma''_B\rangle\begin{bmatrix}\Gamma_A & \Gamma & \Gamma_B\\ \Gamma''_A & \Gamma'' & \Gamma''_B\\ \Gamma'_A & \Gamma' & \Gamma'_B\end{bmatrix}\times\\ &\langle(a)^{N_A-1}(\kappa'_A S'_A\Gamma'_A)a\alpha''_A\,\Gamma''_A|\}(a)^{N_A}\kappa_A S_A\Gamma_A\rangle\times\\ &\qquad\langle(b)^{N_B}(\kappa_B S_B\Gamma_B)b\alpha''_B\,\Gamma''_B|\}(b)^{N_B+1}\kappa'_B S'_B\Gamma'_B\rangle\Bigg\}\end{aligned}\tag{A.1}$$

In order to simplify the use of formula A.1, we label all the orbitals and all the terms arising from a multielectron configuration in a point group containing one-dimensional irreducible representations only, and use the formula once for each transfer integral. This reduces the triple summation to one term with the numerical value

$$h_{ij}\,f_A\,f_B \tag{A.2}$$

where we have defined

$$\begin{aligned}h_{ij}&\equiv\langle a\alpha''_A\Gamma''_A\gamma''_A|\hat{V}_{AB}|b\alpha''_B\Gamma''_B\gamma''_B\rangle\\ f_A&\equiv\langle(a)^{N_A-1}(\kappa'_A S'_A\Gamma'_A)a\alpha''_A\Gamma''_A|\}(a)^{N_A}\kappa_A S_A\Gamma_A\rangle\\ f_B&\equiv\langle(b)^{N_B}(\kappa_B S_B\Gamma_B)b\alpha''_B\Gamma''_B|\}(b)^{N_B+1}\kappa'_B S'_B\Gamma'_B\rangle\end{aligned}\tag{A.3}$$

We see now that the right-hand side of eq A.1 equals

$$Ch_{ij} \tag{A.4}$$

where the factor C is composed of f_A, f_B, and all the non phase factors of eq A.1 in front of the triple sum (see also eq 12 in the main text).

We will now discuss the only f_A and f_B factors which are necessary for our specific purpose. f_B is related to the addition of an electron to the the $(b)^{N_B}$ configuration. In this way the term $S_B\Gamma_B$ is the parent to the possible $S'_B\Gamma'_B$ terms from $(b)^{N_B+1}$ which can be formed by this process. On the other hand, f_A is related to the addition of an electron to the $(a)^{N_A-1}$ configuration. In this case several $S'_A\Gamma'_A$ terms from $(a)^{N_A-1}$ can be parents to the desired child, namely, $S_A\Gamma_A$ from $(b)^{N_A}$. We can omit all the spatial transformation properties of the involved functions and write

$$f(N_i,n_i;S_i,S_f)\equiv\langle(x)^{(N_i,n_i)}(S_i)x|\}(x)^{(N_f,n_f)}S_f\rangle \tag{A.5}$$

In eq A.5 $(x)^{(N_i,n_i)}$ means the initial configuration with a total of N_i electrons whereof n_i of these are unpaired. $(x)^{(N_f,n_f)}$ is a similar specification of the final electron configuration. Addition of one electron increases N_i by 1, but n_f might become equal to $n_i + 1$ or $n_i - 1$, depending on whether the extra electron is added into an empty or a half-filled orbital, respectively. We naturally assume that it is possible to add the electron to $(x)^{N_i,n_i}$ without violating the Pauli principle. First, the extra electron can be added into an empty x orbital. This means that S_f can take the values $S_f = S_i + {}^1/_2$ and $S_f = S_i - {}^1/_2$. For this situation it can be shown that[29]

$$f(N_i,n_i;S_i,S_f{=}S_i{+}^1/_2) = f(N_i,n_i;S_i,S_f{=}S_i{-}^1/_2) = \sqrt{\frac{1}{N_i+1}} \tag{A.6}$$

And second, the extra electron can be added into an orbital already occupied by one electron. Similarly we find eqs A.7 and A.8:

$$f(N_i,n_i;S_i{=}S_f{+}^1/_2,S_f) = \sqrt{\frac{(n_i+1)}{n_i(N_i+1)}} \tag{A.7}$$

$$f(N_i,n_i;S_i{=}S_f{-}^1/_2,S_f) = \sqrt{\frac{n_i-1}{n_i(N_i+1)}} \tag{A.8}$$

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