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Double exchange in iron–sulfur clusters and a proposed spin-dependent transfer mechanism

J.-J. Girerd[1], V. Papaefthymiou[2], K.K. Surerus[2] and E. Münck[2]

1 - Laboratoire de Spectrochimie des Elements de Transition, Equipe de Recherche Associee au CNRS, No. 420, Universite de Paris-Sud, 91405 Orsay, France, 2 - Gray Freshwater Biological Institute, University of Minnesota, Navarre, Minnesota 55392

Abstract - Mössbauer studies of the electron transport protein ferredoxin II have revealed that the reduced Fe_3S_4 cluster contains one localized Fe^{3+} site and one delocalized Fe^{2+}-Fe^{3+} pair. Analysis of the spin coupling of this mixed-valence system has shown that the coupling is dominated by double exchange. We have recently proposed a spin Hamiltonian that takes Heisenberg-Dirac-van Vleck exchange as well as double exchange into account. This spin Hamiltonian can be constructed from an effective Hamiltonian derived from perturbation theory. In applying this approach to mixed-valence systems with three paramagnetic centers we have obtained a term which to our knowledge has not been considered in the literature. The mechanism, which we propose to call exchange-transfer, yields for a spin-only d^1-d^1-d^2 system the expression $\Sigma_{a,b,c}\, C_{acb} t_{ab}(1 - 4s_b \cdot s_c)$ where t_{ab} is an operator that transfers the excess electron located on the d^2-site b to site a; s_b and s_c are spin operators of the excess electron and the electron on site c, respectively. $C_{acb} = -\beta_{ac}\beta_{cb}/(8K)$ is a coupling constant containing the product of the transfer integrals connecting the sites a and c and the sites b and c and K is the intra-atomic exchange integral. The mechanism achieves transfer of the excess electron from b to a by a "detour" through an excited state on site c.

INTRODUCTION

For the past few years we have studied a variety of iron-sulfur proteins with Mössbauer spectroscopy. These proteins contain clusters with Fe_2S_2, Fe_3S_4 or Fe_4S_4 core stoichiometries. Most of the clusters participate in one-electron redox reactions and therefore can exist in various mixed-valence states. In this article we wish to focus on the magnetic properties of these clusters. In particular, we wish to discuss that aspect of the cluster magnetism which, in the mixed-valence state, is linked to the delocalization of valence electrons.

Mössbauer spectroscopy is particularly well suited to study iron-sulfur clusters because the technique provides a wealth of information from which details about the electronic structure of the core can be deduced. Mössbauer studies, carried out in many laboratories, have shown that some iron-sulfur clusters contain iron sites to which a distinct valence can be assigned. Thus, the iron sites can have spectroscopic properties which remind us of typical Fe^{3+} or Fe^{2+} sites. Such sites are always observed in clusters with Fe_2S_2 cores. Fe_4S_4 cubanes, on the other hand, exhibit strong valence delocalization as witnessed by the observations that the parameters for the quadrupole splitting, ΔE_Q, and isomer shift, δ, are roughly the average of those observed for monomeric Fe^{3+} and Fe^{2+} sites.

The magnetic properties of iron-sulfur clusters are dominated by strong exchange interactions which couple the spins of the individual iron sites to a resultant system spin S. Not surprisingly, the magnetic properties are intimately linked to the extent of electron delocalization. Thus, the coupling of the Fe^{3+} site (S_1 = 5/2) and the Fe^{2+} site (S_2 = 2) of reduced Fe_2S_2 clusters is described well by the Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian $H = JS_1 \cdot S_2$, as testified by the successful model put forward by Gibson and coworkers (ref. 1-4). Until recently, the magnetic couplings of the delocalized Fe_4S_4 clusters were not understood. The experimental data which provided the decisive clues for understanding the mechanism of the delocalized clusters came from Mössbauer studies (ref. 5) of reduced Fe_3S_4 clusters. These studies showed (ref. 5) that the spin Hamiltonian needs to be augmented by a term describing the contribution of delocalized electrons. This mechanism, called double exchange (ref. 6,7) or resonance interaction (ref. 8) is quite different from the familiar mechanism described by $H = JS_1 \cdot S_2$.

In this article we very briefly discuss the experimental data which showed that the double exchange mechanism needs to be incorporated into the Hamiltonian. This will be followed by a brief discussion of the spin Hamiltonian which we have introduced recently (ref. 5,9) with essentially intuitive arguments. For a detailed discussion of this point the reader is referred to the article by Münck et al. (ref. 9). Quite recently, we have been concerned with the derivation of the spin Hamiltonian from fundamental theory. In the course of these studies we discovered that the spin Hamiltonian description of mixed-valence clusters containing more than two sites with unpaired electrons requires the inclusion of yet another mechanism. To our knowledge this mechanism, which we propose to call exchange-transfer, has not been described in the literature. Much of the new work described below was carried out just a few weeks before this article was submitted for this conference. Thus, this article should be viewed as a progress report.

EXPERIMENTAL EVIDENCE FOR DOUBLE EXCHANGE IN Fe_3S_4 CLUSTERS

Ferredoxin II (Fd II) isolated from *Desulfovibrio gigas* is a small electron-transport protein which contains an Fe_3S_4 cluster. As shown in Fig. 1 this cluster can be depicted to have a cubane Fe_4S_4 core from which one iron atom has been removed. Indeed, by incubating the protein in the presence of Fe^{2+}, the cubane Fe_4S_4 cluster is formed readily (ref. 10). Moreover, by incubating with excess Zn^{2+}, Cd^{2+}, Ga^{3+} or Co^{2+} interesting hybrid clusters of the MFe_3S_4 type can be formed (ref. 9,11,12). The cluster of Fd II has two stable oxidation states. In the oxidized state the cluster has a system spin S = 1/2 which results from antiferromagnetic coupling of three high-spin ferric ions ($S_1 = S_2 = S_3$ = 5/2). The magnetic properties of this state have been analyzed with a Heisenberg Hamiltonian (ref. 13).

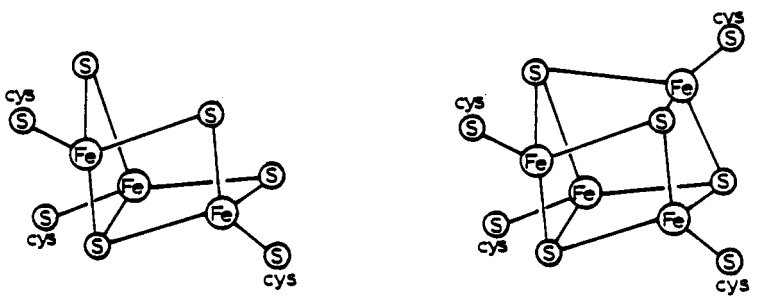


Fig. 1. Structures of Fe_3S_4 and Fe_4S_4 clusters. Earlier crystallographic studies of the 3-Fe cluster of an *Azotobacter vinelandii* ferredoxin, which indicated a planar Fe_3S_3 structure, were in error. Recent studies (ref. 14,15) show that Fe_3S_4 clusters have a core structure similar to that depicted here; currently the crystallographic resolution is not high enough to determine details of the structure. The core shown here was obtained by taking the structure of an Fe_4S_4 cubane (ref. 16) and removing one iron.

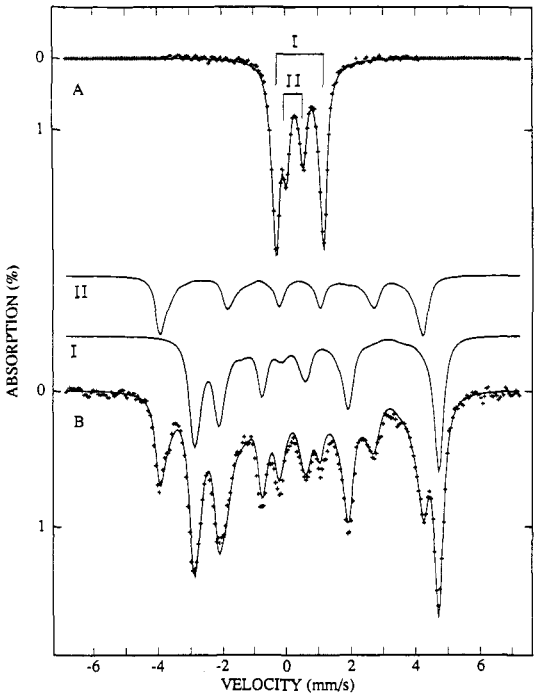


Fig. 2. Mössbauer spectra of the reduced Fe_3S_4 cluster (S=2) of Fd II recorded at 4.2 K in zero field (A) and at 1.3 K in parallel applied field of 1.0 T (B). The solid lines in (B) are theoretical curves for the delocalized pair (I) and the Fe^{3+} site (II). The sum is drawn through the data. Parameters, fitting procedures and additional spectra are given in ref. 5.

Upon one-electron reduction of the cluster, a state with system spin S = 2 is observed (ref. 17,18). The zero field Mössbauer spectrum of Fig. 2A shows two quadrupole doublets with intensity ratio 2:1. Doublet II has ΔE_Q = 0.52 mm/s and δ = 0.32 mm/s; these parameters are typical for Fe^{3+} sites in a tetrahedral environment of thiolate ligands. The two remaining irons are not distinguishable by Mössbauer spectroscopy. The values of ΔE_Q = 1.47 mm/s and δ = 0.46 mm/s are just the average of typical Fe^{3+} and Fe^{2+} sites in FeS_4 monomers. Thus, both iron sites are at the $Fe^{2.5+}$ level which suggests that the electron, which the cluster has acquired upon reduction, is shared equally between the two irons of doublet I. These two sites thus form a delocalized pair.

The spectrum shown in Fig. 2B was recorded at 1.3 K in an applied field of 1.0 T. The solid lines show a fit to a spin Hamiltonian which includes zero field splitting parameters, electronic and nuclear Zeeman terms as well as magnetic and electric hyperfine interactions; for details see ref. 5. For the present topic, two results of the analysis are of particular interest. First, the two irons of site I are still indistinguishable even within the excellent resolution of the spectra. Thus, the data can be analyzed as a superpositon of two spectra with 2:1 intensity ratio. Second, the data show clearly that the magnetic hyperfine coupling tensor of the Fe^{3+} site has positive components. This information implies (ref. 19) that the local spin S_3 = 5/2 is coupled antiparallel to the system spin S = 2. By analyzing the hyperfine interactions with a vector coupling model Münck and Kent (ref. 19) have shown that the spin of the delocalized dimer is S_{12} = 9/2; this result was confirmed by a more refined analysis (see below). Formally, S_{12} = 9/2 can result from ferromagnetic coupling between a ferric (S_1 = 5/2) and a ferrous ion (S_2 = 2). However, since both irons are equivalent, it would not be clear at all which iron would have S_1 = 5/2 and which iron would have S_2 = 2. Further, parallel spin alignment in conjunction with valence delocalization suggested that these phenomena are linked. Anderson and Hasegawa (ref. 7) have shown in 1955 that a delocalized electron provides a coupling mechanism (called double exchange) which causes ferromagnetic alignment of the spins.

A SPIN HAMILTONIAN WITH DOUBLE EXCHANGE

The basic idea of double exchange or resonance splitting can be illustrated by means of Fig. 3. Consider two metals A and B with two orbitals a_1, a_2 and b_1, b_2. Let us assume that we have three electrons which we allocate to a_1, b_1 and a_2. In Fig. 3 (left) we have indicated the configuration which gives rise to a quartet state with S = 3/2 and M_S = +3/2. We will call the electron in a_2 the "extra" electron. Since this electron is on A we designate this quartet state as $|A\rangle = |a_1 b_1 a_2\rangle$. Alternatively, if the extra electron were on B we would obtain another quartet, $|B\rangle = |a_1 b_1 b_2\rangle$. The Hamiltonian of the system is

$$H = h(1) + h(2) + h(3) + g_{12} + g_{13} + g_{23} \tag{1}$$

where h(i) is the one-particle Hamiltonian containing the kinetic energy of electron i and the potential energy of i due to the nuclei A and B; g_{ij} describes the repulsion between the electrons. The states $|A\rangle$ and $|B\rangle$ are not eigenstates of H. By choosing $|A\rangle$ and $|B\rangle$ as basis states we obtain a 2x2 matrix which contains off-diagonal elements,

$$\begin{array}{c|cc} & |A\rangle & |B\rangle \\ \hline |A\rangle & \varepsilon_A(3/2) & \beta_2 \\ |B\rangle & \beta_2 & \varepsilon_B(3/2) \end{array} \tag{2}$$

where $\langle A|H|A\rangle = \varepsilon_A(3/2)$ and $\langle B|H|B\rangle = \varepsilon_B(3/2)$, and where $\beta_2 = \langle a_2(1)|h(1)|b_2(1)\rangle$ is a one-electron transfer or hopping integral (we have neglected contributions from the g_{ij} to the transfer term and we have also assumed that the elements $\langle a_1|h|b_2\rangle = \langle a_2|h|b_1\rangle = 0$). Two limiting cases are of interest. For $\varepsilon_B - \varepsilon_A \gg |\beta_2|$ the lowest quartet state is $|A\rangle$, and the electron is thus localized on A. (ε_A and ε_B may differ because of site inequivalencies due to ligand field or vibronic (ref. 20) effects). For $\varepsilon_A = \varepsilon_B$, on the other hand, the two quartet states mix to form the two delocalized states

$$\phi_{1,2} = 1/\sqrt{2}(|A\rangle \pm |B\rangle)$$

at energies $E_{1,2} = \varepsilon_A(3/2) \pm \beta_2$. Since β_2 mixes the two configurations, it describes the tendency of the system to delocalize. The transfer process is caused by electrostatic interactions, and thus the extra electron does not change its spin upon hopping between A and B. According to Hund's first rule the interaction of the delocalized electron with the electrons in a_1 and b_1 favors the triplet state, and delocalization leads therefore to a parallel alignment of the spins in a_1 and b_1. More generally, the mobile electron mediates ferromagnetic coupling between the core spins S_0 of site A and B. If we would have considered the doublet states, the off-diagonal element in Eq (2) would have been $\beta_2/2$ (β_2 does not mix configurations with different S).

Anderson and Hasegawa (ref. 7) have shown that the off-diagonal term in Eq (2) can be written as $\beta(S + 1/2)/(2S_0 + 1)$. This yields for $\varepsilon_A(S) = \varepsilon_B(S)$ a resonance splitting of $\pm\beta(S + 1/2)/(2S_0 + 1)$. This dependence on (S + 1/2) rather than S(S + 1) as in the usual HDvV mechanism is the distinctive feature of double exchange.

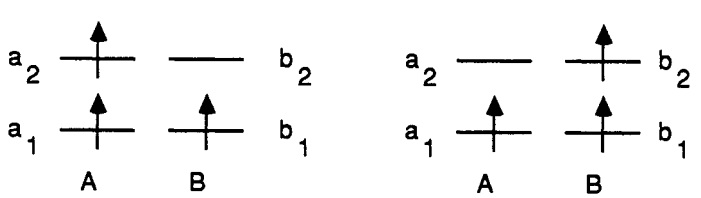


Fig. 3. The two quartet configurations resulting from placing the extra electron on A (left) and B (right).

Using ideas of Anderson and Hasegawa and of Noodleman and Baerends (ref. 8) and suggestions of Borshch et al. (ref. 21) we have constructed a spin Hamiltonian which takes into account HDvV exchange as well as double exchange (ref. 5). In ref. 9 we have outlined in some detail the rational for the construction of this Hamiltonian. The major new feature is an operator $\mathbf{T}_{AB}$ that produces the desired $\beta(S + 1/2)/(2S_0 + 1)$ off-diagonal elements in Eq (2). For a mixed-valence AB dimer the spin Hamiltonian takes the form (ref. 5,9)

$$H = [{}^{A}J_{AB}{}^{A}S_A \cdot {}^{A}S_B + E_A]\mathbf{O}_A + [{}^{B}J_{AB}{}^{B}S_A \cdot {}^{B}S_B + E_B]\mathbf{O}_B + B\mathbf{T}_{AB} \tag{3}$$

Here E_A and E_B are the energies of the dimer when the excess electron is on A and B, respectively; S_A and S_B are the spins of site A and B. We have added a superscript because the numerical values of S_A and S_B depend on the location of the extra electron. Thus, for an Fe^{2+}-Fe^{3+} mixed-valence dimer we have ${}^{A}S_A = 2$ and ${}^{A}S_B = 5/2$ when the extra electron is on A, and ${}^{B}S_A = 5/2$ and ${}^{B}S_B = 2$ when the electron is on B. The operators $\mathbf{O}_A$ and $\mathbf{O}_B$ are occupation operators which have the effect $\mathbf{O}_A|A\rangle = |A\rangle$, $\mathbf{O}_A|B\rangle = 0$, $\mathbf{O}_B|B\rangle = |B\rangle$ and $\mathbf{O}_B|A\rangle = 0$. A definition of these operators in the language of second quantization is given below.

The term $B\mathbf{T}_{AB}$ is constructed to produce the desired Anderson-Hasegawa off-diagonal elements. $\mathbf{T}_{AB}$ is a transfer operator that converts $|A\rangle$ into $|B\rangle$ (or $|B\rangle$ into $|A\rangle$) and "looks up" the dimer spin S_{AB} to produce the $(S_{AB} + 1/2)$ factor. The $(2S_0 + 1)$ factor has been absorbed into B. Thus

$$\mathbf{T}_{AB}|A\rangle = \mathbf{T}_{AB}|{}^{A}S_A{}^{A}S_B;\ S_{AB}\rangle = (S_{AB} + 1/2)|{}^{B}S_A{}^{B}S_B;\ S_{AB}\rangle = (S_{AB} + 1/2)|B\rangle \tag{4}$$

Because the transfer term does not mix states with different dimer spin, we have ${}^{A}S_{AB} = {}^{B}S_{AB} = S_{AB}$. In ref. 9 we have discussed the extension of the spin Hamiltonian to more complicated systems, as well as its application for limiting cases.

Let us now return to reduced Fd II. The experimental data show the presence of one delocalized pair A-B. This suggests a model with $B_{AB} = B$ and $B_{AC} = B_{BC} = 0$. We have further assumed that all coupling constants J are the same; this condition can be relaxed somewhat without effecting the results for the ground state in an essential way. With these assumptions, the spin Hamiltonian can be written as (using $E_A = E_B = E_C$)

$$\begin{aligned} H = {} & J[{}^{A}S_A \cdot {}^{A}S_B + ({}^{A}S_A + {}^{A}S_B)S_C]\mathbf{O}_A + \\ & J[{}^{B}S_A \cdot {}^{B}S_B + ({}^{B}S_A + {}^{B}S_B)S_C]\mathbf{O}_B + B\mathbf{T}_{AB} \end{aligned} \tag{5}$$

The excess electron is never on site C; hence ${}^{A}S_C = {}^{B}S_C = S_C$. The terms in bracket are diagonal in the basis $|({}^{A}S_A{}^{A}S_B)\ S_{AB}, S_C;\ S\rangle = |S_{AB};\ S\rangle^{A}$, $|({}^{B}S_A{}^{B}S_B)\ S_{AB}, S_C;\ S\rangle = |S_{AB};\ S\rangle^{B}$. The transfer term mixes only states with the same S and the same S_{AB}, and the eigenvalues of (ref. 5) are simply

$$E = J/2\ S(S + 1)\ \pm\ B(S_{AB} + 1/2) \tag{6}$$

with eigenvectors

$$|S_{AB};\ S\rangle_{\pm} = (|S_{AB};\ S\rangle^{A} \pm |S_{AB};\ S\rangle^{B})/\sqrt{2} \tag{7}$$

In Fig. 4 we have plotted the energies of the lowest levels vs. B/J. It can be seen that the system state with $S = 2$ and $S_{AB} = 9/2$ becomes the ground state for $B/J > 2$. This is just the desired state. We have also computed the magnetic hyperfine interactions for sites I and II (for details see ref. 5). The theoretical values, together with the experimental data, are listed in Table 1. Given the simplicity of our assumptions the agreement between theory and experiment is excellent; both the signs and the magnitudes are accounted for. Note that the coefficients of the electronic ground state $|S_{AB};\ S\rangle_{-}$ do not depend on B/J, i.e. the magnetic hyperfine parameters are independent of B/J. Thus, except for $B/J > 2$ the exchange and double exchange parameters are undetermined. Recent susceptibility studies by Day and coworkers

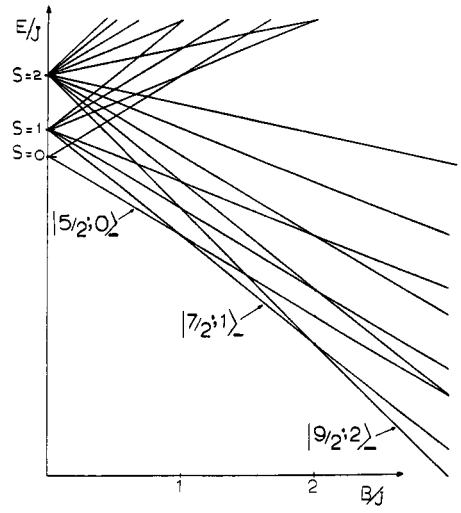


Fig. 4. Correlation diagram for reduced Fd II plotted for antiferromagnetic (J>0) HDvV exchange. The excess electron was allowed to delocalize between sites A and B.

TABLE 1. Magnetic hyperfine parameters of reduced Ferredoxin II (ref. 5)

Site	A_x(MHz)	A_y(MHz)	A_z(MHz)	A_{av}(MHz)	A_{theory}(MHz)
I	-20.5	-20.5	-16.4	-19.1	$A_A = A_B = -19.2$
II	+13.7	+15.8	+17.3	+15.6	$A_C = +16.7$

(ref. 18) show that no excited state configuration with $S \neq 2$ is populated at temperatures up to 200K.

To date no experimental B-values have been reported for any clusters. However, Noodleman and Baerends (ref. 8) and Sontum, Noodleman, and Case (ref. 22) have provided theoretical estimates for B and J. These workers have developed an elegant method (ref. 22,23) for estimating B and J from a broken symmetry analysis of Xα-calculations. In this method values for J are obtained by comparing the energies of a broken symmetry calculation with those obtained from a spin Hamiltonian. The value for B is obtained from the energy separation of symmetric and antisymmetric states such as those of Eq (7). In this way Sontum, Noodleman and Case (ref. 22) have obtained $J = 297\ cm^{-1}$ and $B = -406\ cm^{-1}$ for a reduced Fe_3S_4 cluster. Thus, the B-term appears to have a sizable magnitude.

Our Mössbauer study has revealed that reduced Fd II has a low-lying state which seems to be totally delocalized. S. A. Borshch has informed us (ref. 24) that this can be understood with a model that takes HDvV exchange, double exchange and vibronic interactions into account. However, we have noticed (ref. 25) that suitable delocalized states can also be produced by allowing in Eq (5) J-values such that $J(Fe^{3+}\text{-}Fe^{3+}) \approx 2J(Fe^{3+}\text{-}Fe^{2+})$.

Finally, the description of the magnetic properties of Fe_4S_4 clusters requires the inclusion of double exchange (ref. 9). Noodleman (ref. 26) has recently published a model for $[Fe_4S_4]^{3+}$ cores that includes both Heisenberg and double exchange; this model successfully describes the salient features of the experimental data.

THE EFFECTIVE HAMILTONIAN

In order to develop a more fundamental understanding of the spin Hamiltonian of Eq (3) we have investigated the problem by developing an effective Hamiltonian H_{eff} which can be put into equivalence with a suitable spin Hamiltonian. This spin Hamiltonian will contain the standard Heisenberg-Dirac-van Vleck (HDvV) term and the double exchange term. In addition, we have found that the spin Hamiltonian will have to be augmented by yet another term when mixed-valence clusters containing more than two metals with unpaired electrons are considered. Stevens (ref. 27) has eloquently described the benefits of using a second quantization description for the task at hand; in the following we will use this method. For a derivation of the HDvV Hamiltonian with second quantization methods we refer the reader to a paper by Leuenberger and Güdel (ref. 28).

The Hamiltonian of a dimer can be written as

$$H = \Sigma_{i,k} \langle i|h|k\rangle\, c^{+}_{i}c_{k} + \Sigma_{i,k,l,m} \langle i,k|g|m,l\rangle\, a^{+}_{i}a^{+}_{k}a_{l}a_{m} \tag{8}$$

where i,k,l,m designate orthonormal one-electron functions. c^{+}_{i} and c_{k} are creation and annihilation operators, and $\langle i|h|k\rangle = \langle \Psi_i(1)|h(1)|\Psi_k(1)\rangle$ and $\langle ik|g|ml\rangle = \langle \Psi_i(1)\Psi_k(2)|g(1,2)|\Psi_m(1)\Psi_l(2)\rangle$ are the matrix elements of one- and two-electron operators, respectively.

In the following we label each orbital by three indices (mkσ); m designates the site, k the orbital on the site m, and σ refers to the spin of the electron which occupies (m,k). $n_{mk\sigma} = c^{+}_{mk\sigma}c_{mk\sigma}$ is the occupation operator for the spin-orbital (mkσ). It will be useful to split the matrix elements into single-ion terms and interaction terms. Then the one-electron part can be written as

$$\Sigma_{m,k,\sigma}\, \alpha_k n_{mk\sigma} + \Sigma_{m\neq m',k,\sigma}\, \beta_{mm',k}\, c^{+}_{mk\sigma}c_{m'k\sigma}$$

with $\alpha_k = \langle mk\sigma|h|mk\sigma\rangle$ and the transfer integral is $\beta_{mm',k} = \langle mk\sigma|g|m'k\sigma\rangle$. In the preceding expression we have neglected elements such as $\langle mk\sigma|h|m'k'\sigma\rangle$. We will split the two-electron matrix elements into intra-ionic repulsion (U) and intra-ionic exchange (K) terms, neglecting inter-ionic two-electron interactions. Retention of the exchange term $K = \langle mk\sigma,mk'\sigma'|g|mk'\sigma,mk\sigma'\rangle$ allows us to take Hund's first rule into account when we couple the electron spins locally to a site spin. Collecting all the terms, and after some rearrangements, we obtain

$$\begin{aligned} H = {} & \Sigma_{mk}\, \alpha_k n_{mk} + 1/(2U)\, \{\Sigma_{m,k\neq k'}\, n_{mk}n_{mk'} + \Sigma_{mk\sigma}\, n_{mk\sigma}n_{mk-\sigma}\} \\ & - 1/(2K)\, \{\Sigma_{m,k\neq k',\sigma}\, (n_{mk\sigma}n_{mk'\sigma} + c^{+}_{mk\sigma}c_{mk-\sigma}c^{+}_{mk'-\sigma}c_{mk'\sigma})\} \\ & + \Sigma_{m\neq m',k,\sigma}\, \beta_{mm',k}\, c^{+}_{mk\sigma}c_{m'k\sigma} \end{aligned} \tag{9}$$

For polymetallic complexes which lack strong metal-metal bonds the interaction between the centers, i.e. the last term in Eq (9), can be treated as a perturbation. Thus we write $H = H_0 + V$ with

$$V = \Sigma_{m\neq m',k,\sigma}\, \beta_{mm',k}\, c^{+}_{mk\sigma}c_{m'k\sigma}. \tag{10}$$

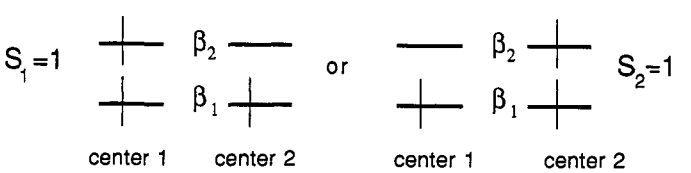
By dividing the eigenstates of H_0 into a ground manifold $|0\rangle$, energy E_0, projector $P_0 = \Sigma\, |0\rangle\langle 0|$, and excited state manifolds $|e\rangle$, $P_e = \Sigma\, |e\rangle\langle e|$, we can construct an effective Hamiltonian (ref. 27,29)

$$H_{eff} = P_0VP_0 - P_0\{\Sigma_e VP_eV/(E^0_e - E^0_0)\}P_0 \tag{11}$$

H_{eff} will contain products of creation and annihilation operators. These can be replaced by spin operators and thus a spin Hamiltonian can be constructed.

Two centers: exchange and double exchange

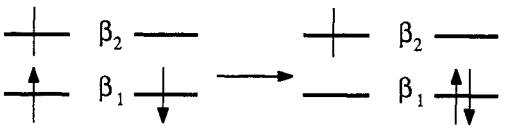
We consider a mixed-valence system with three electrons consisting of two centers 1 and 2, each center having two orbitals at energy α_1 and α_2. We assume that $\Delta = \alpha_2 - \alpha_1 \ll K,U$. Taking Hund's first rule into account the ground configurations will be of the type,



By forming a local triplet either on center 1 or on center 2 we can construct two quartets and two doublets which belong to the ground manifold $\mathcal{E}_0$, with energy $E^0_0 = 2\alpha_1 + \alpha_2 + U - K$. The perturbation contains terms with $\beta_{mm',1} = \beta_1$ and $\beta_{mm',2} = \beta_2$.

The term involving β_2 has two effects. By starting with a local triplet on center 1 the β_2-term can move the excess electron to center 2. With a triplet on center 2, the new configuration belongs to the ground manifold and β_2 contributes in first order; this gives rise to the double exchange term. Alternatively, we can form a singlet on center 2, giving an excited configuration at energy 2K above the ground manifold. In this case β_2 contributes in second order and one obtains the HDvV exchange term.

A configuration at energy K can be obtained through the β_1-term, as shown in the diagram



Note that in a mixed-valence system the excited configurations are at much lower energy (K) than in monovalent systems (U). With

$$V_k = \beta_k \Sigma_{m\neq m',\sigma}\, c^+_{mk\sigma} c_{m'k\sigma}$$

the effective Hamiltonian will be

$$H_{\text{eff}} = P_0 V_2 P_0 - P_0\{V_1 P_1 V_1/K + V_2 P_2 V_2/(2K)\}P_0 \tag{12}$$

We consider the second order terms first. Using the projector

$$P_2 = \Sigma_{m\neq m',\sigma}\, n_{m1\sigma}(n_{m'1\alpha}n_{m'2\beta} + n_{m'1\beta}n_{m'2\alpha} - c^+_{m'1\beta}c_{m'1\alpha}c^+_{m'2\alpha}c_{m'2\beta}$$
$$- c^+_{m'1\alpha}c_{m'1\beta}c^+_{m'2\beta}c_{m'2\alpha})/2$$

we find after some calculation

$$V_2P_2V_2 = \beta_2^2\, \Sigma_{m\neq m',\sigma}\, (1/2)n_{m1\sigma}(n_{m2\beta}n_{m'1\alpha} + n_{m2\alpha}n_{m'1\beta}$$
$$- c^+_{m2\alpha}c_{m2\beta}c^+_{m'1\beta}c_{m'1\alpha} - c^+_{m'1\alpha}c_{m'1\beta}c^+_{m2\beta}c_{m2\alpha})$$

Since

$$\begin{aligned} c^+_{m2\beta}c_{m2\alpha} &= s^-_{m2} \\ c^+_{m2\alpha}c_{m2\beta} &= s^+_{m2} \\ n_{m2\alpha}n_{m'1\beta} + n_{m2\beta}n_{m'1\alpha} &= (1/2) - 2s^z_{m2}s^z_{m'1} \end{aligned} \tag{13}$$

for singly occupied orbitals (see ref. 29), we obtain

$$V_2P_2V_2 = \beta_2^2\, \Sigma_{m\neq m'}(1/2)\{(1/2) - 2s_{m2}\cdot s_{m'1}\}\ \mathbf{n}_{m2} \tag{14}$$

where we have used the relation $n_{m1\alpha} + n_{m1\beta} = 1$. (The state (m,1) is singly occupied.)

A similar treatment yields

$$V_1P_1V_1 = \beta_1^2\, \Sigma_{m\neq m'}\{(1/2) - 2s_{m1}\cdot s_{m'1}\}\ \mathbf{n}_{m2} \tag{15}$$

In Eqs (14) and (15) we have retained the occupation operators $\mathbf{n}_{m2} = \mathbf{n}_{m2\alpha} + \mathbf{n}_{m2\beta}$; they remind us that orbital 2 on center m is occupied when we evaluate the expressions in the curly brackets. We can combine Eqs (14) and (15) after one further modification is made. This modification involves the use of the Wigner-Eckart

theorem to replace s_{m2} by the ionic spin S_m; since $S_m = 1$ we pick up the equivalence factor 1/2. The operator $s_{m'1}$ is replaced by 1/2 $S_{m'}$ when the excess electron is on m' or by $S_{m'}$ with $S_{m'} = 1/2$ when the excess electron is on m. With these modifications, and dropping spin-independent terms, we have arrived at the Heisenberg part of the spin Hamiltonian

$$H_s = J\{S_1 \cdot S_2 O_1 + S_1 \cdot S_2 O_2\} \tag{16}$$

with $J = \beta_2^2/(4K) + \beta_1^2/K$. The operators $O_m = n_{m2}$ keep track of the extra electron and thus control the values of S_1 and S_2. In our computations of Fe_3S_4 and Fe_4S_4 systems we found it useful to add the subscript of the occupation operator as a superscript to the spin operators, as indicated in Eq (3).

The first order term in Eq (12) yields the double exchange term. Since $P_0V_2P_0$ acts within the ground manifold for which we desire a spin Hamiltonian we can identify this term with the transfer term in Eq (3). Thus we equate

$$\{\Sigma_\sigma c^+_{1,2\sigma} c_{2,2\sigma} + \Sigma_\sigma c^+_{2,2\sigma} c_{1,2\sigma}\} \quad \text{with } t_{12},$$

where t_{12} is a transfer operator. In our example, orbital 2 contains at most one electron. Thus, t_{12} can be understood as an operator that transfers either a spin-up or a spin-down electron from center 2 to center 1 or from center 1 to center 2. If the matrix elements of $\beta_2 t_{12}$ are evaluated within the correct spin representation, the resultant matrix will be identical to that obtained when V_2 is evaluated within the ground manifold. For the coupled representation $|(S_1^0 s_1)\, S_1{=}S_1^0{+}s_1,\, S_2^0; S\rangle$, $|S_1^0, (S_2^0 s_2)\, S_2{=}S_2^0{+}s_2;\, S\rangle$ the action of t_{12} can be written as

$$t_{12}|(S_1^0 s_1)\, S_1,\, S_2^0;\, S\rangle = (S+1/2)/(2S_0+1)\, |S_1^0, (S_2^0 s_2)\, S_2;\, S\rangle \tag{17}$$

In our example $S_1^0 = S_2^0 = S_0 = 1/2$ are the "core" spins on each ion; the indices of s_1 and s_2 indicate whether the excess electron is located at site 1 or 2. The immediate effect of t_{12} on the ket $|(S_1^0 s_1)\, S_2,\, S_2^0;\, S\rangle$ is to change s_1 to s_2 but leaving s_2 coupled to S_1^0. The Racah coefficient $(S+1/2)/(2S_0+1)$ occurs when we work in a coupling scheme for which the intermediate spin is $S_2 = S_2^0 + s_2$ and $S_2 = S_2^0 + 1/2$. In our previous work (ref. 5,9) we have absorbed $(2S_0 + 1)$ in the coupling constant, and we have not assumed a direction of transfer in the arrangement of indices. Thus in Eq (3) we have implied that

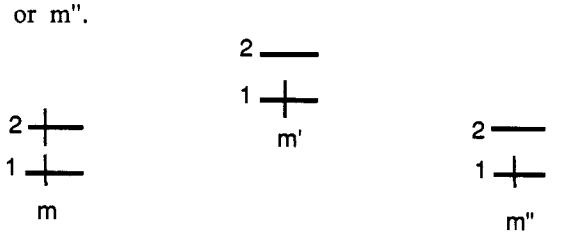
$$T_{12} = (2S_0 + 1)\, P_0\, t_{12}\, P_0 \quad \text{and} \quad B = \beta_2/(2S_0 + 1) \tag{18}$$

With this we obtain for the spin Hamiltonian of the dimer

$$H_s = J\{S_1 \cdot S_2\, O_1 + S_1 \cdot S_2\, O_2\} + BT_{12} \tag{19}$$

Exchange-transfer

In this section we consider a mixed-valence system with three centers, each having two orbital states at energies α_1 and α_2. Among these centers we distribute four electrons. One of the ground configurations, with the excess electron localized on center m, is shown in the diagram. Again, the ground configuration has a local triplet on center m. Two other ground configurations are obtained by moving the extra electron from m to m' or m".



As in the previous example the resulting spin Hamiltonian will contain the Heisenberg exchange terms and the double exchange terms. New terms arise when we consider the second order contribution from the β_2-term, i.e. from

$$V_2 = \Sigma_{m\neq m'\sigma}\, \beta_{mm',2}\, c^+_{m2\sigma} c_{m'2\sigma}$$

The following considerations illustrate how the new terms arise. The numerator of the second order term contains the operator sequence $P_0 V_2 P_e V_2 P_0$. Picking a specific state from the ground manifold $|0\rangle$, operation by P_0 leaves the state unaltered, $P_0|0\rangle = |0\rangle$. Lets assume that we have picked a $|0\rangle$ where the excess electron is on m, $|0\rangle_m$. The $c^+_{m''2\sigma} c_{m2\sigma}$ part of V_2 can move the electron from m to m''. If we form a local singlet on m'', the state $|e\rangle_{m''}$ belongs to an excited state manifold at energy 2K. The V_2 operator on the left has to return the system to the ground manifold. The $c^+_{m2\sigma} c_{m''2\sigma}$ part of V_2 returns the system to the original state and we obtain a term proportional to $\beta^2_{mm'',2}/(2K)$ which contributes to the familiar exchange term. However, if the sites m and m' are similar we can also return to the ground manifold by using $c^+_{m'2\sigma} c_{m''2\sigma}$. This puts the system into $|0\rangle_{m'}$ and thus we have effectively transferred an electron from m to m'. This term is proportional to $\beta_{mm'',2}\beta_{m'm'',2}/(2K)$. In the following we comment on some of the computational steps.

A suitable projector of the excited state manifold $|e\rangle$ can be written as

$$P_e = \Sigma_{m\neq m'\neq m''}\, n_{m1\sigma} n_{m'1\sigma'} (n_{m''1\alpha} n_{m''2\beta} - c^+_{m''1\beta} c_{m''1\alpha} c^+_{m''2\alpha} c_{m''2\beta} - c^+_{m''1\alpha} c_{m''1\beta} c^+_{m''2\beta} c_{m''2\alpha} + n_{m''1\beta} n_{m''2\alpha})/2 \tag{20}$$

The expression for $V_2 P_e V_2$ contains the following terms which are proportional to the products $\beta_{mm'',2}\beta_{m'm'',2}$:

$$\begin{aligned}\Sigma_{m\neq m'\neq m''}\, (\beta_{mm'',2}\beta_{m'm'',2}/2)\, (&c^+_{m'2\beta} c_{m2\beta} n_{m''1\alpha} + c^+_{m2\beta} c_{m'2\beta} n_{m''1\alpha} \\ &+ c^+_{m'2\alpha} c_{m2\alpha} n_{m''1\beta} + c^+_{m2\alpha} c_{m'2\alpha} n_{m''1\beta} - c^+_{m2\alpha} c_{m'2\beta} c^+_{m''1\beta} c_{m''1\alpha} \\ &- c^+_{m'2\alpha} c_{m2\beta} c^+_{m''1\beta} c_{m''1\alpha} - c^+_{m2\beta} c_{m'2\alpha} c^+_{m''1\alpha} c_{m''1\beta} \\ &- c^+_{m'2\beta} c_{m2\alpha} c^+_{m''1\alpha} c_{m''1\beta})\end{aligned} \tag{21}$$

In order to see the structure of the new terms we consider as an example the last term in (21). By inserting $c_{m2\beta} c^+_{m2\beta}$ after the first operator and using $c^+_{m''1\alpha} c_{m''1\beta} = s^+_{m''1}$ and $c^+_{m2\beta} c_{m2\alpha} = s^-_{m2}$ we obtain

$$- c^+_{m'2\beta} c_{m2\beta} s^-_{m2} s^+_{m''1} \tag{22}$$

The operator $c^+_{m'2\beta} c_{m2\beta}$ transfers a β-spin from m to m'. Thus the term contains a transfer operator and a product of spins.

Defining the transfer operator

$$\mathbf{t}_{mm'} = \Sigma_\sigma\, \{c^+_{m'2\sigma} c_{m2\sigma} + c^+_{m2\sigma} c_{m'2\sigma}\} \tag{23}$$

we can write the expression (22) as $- \mathbf{t}_{mm'} s^-_{m2} s^+_{m''1}$. This is possible because s^-_{m2} puts a β-spin into orbital m2 and subsequent action of $\mathbf{t}_{m'm,2\alpha}$ or $\mathbf{t}_{mm',2\sigma}$ produces zero.

By collecting all terms of expression (21), and after some manipulations we obtain for the mechanism considered

$$H_{\text{eff}} = \Sigma_{m\neq m'\neq m''}\, C_{mm''m'}\, \mathbf{t}_{mm'}\, \{(1 - 4\mathbf{s}_{m'2}\cdot\mathbf{s}_{m''1})\mathbf{O}_{m'} + (1 - 4\mathbf{s}_{m2}\cdot\mathbf{s}_{m''1})\mathbf{O}_m\} \tag{24}$$

with $C_{mm''m'} = - \beta_{mm''}\beta_{m'm''}/(8K) = C_{m'm''m}$. In Eq (24) the indices m, m' and m'' assume the triplets (1, 2, 3), (2, 3, 1) and (3, 1, 2). By allowing the indices to run through the six permutations we obtain

$$H_{\text{eff}} = \Sigma_{m\neq m'\neq m''}\, C_{mm''m'}\, \mathbf{t}_{mm'}\, (1 - 4\mathbf{s}_{m'2}\cdot\mathbf{s}_{m''1})\mathbf{O}_{m'} \tag{25}$$

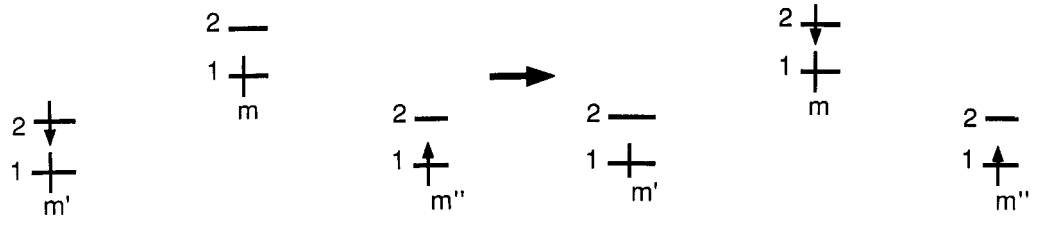
The first spin operator of the spin product belongs to the site which contains the excess electron in orbital 2. Since we have used Eq (13) the whole expression in parenthesis has to act on a basis state containing the excess electron. The occupation operator $\mathbf{O}_{m'} = \mathbf{n}_{m'2}$ ensures that the expression acts only on basis states which have the excess electron of orbital 2 on a site indicated by the index of the first spin operator.

Eq (25) describes a spin-dependent transfer process. The expression in parenthesis is zero when the spins of the mobile electron in m'2 and the electron on the intermediate site m" are parallel, i.e. the spin factor excludes the formation of a triplet state on m". In contrast to the double-exchange term, the terms of Eq (25) cannot readily be cast into a spin Hamiltonian containing the site spins $S_{m'} = s_{m'1} + s_{m'2}$. This can be seen by considering a typical matrix element which occurs for the two sites connected by $\mathbf{t}_{mm'}$,

$$<(s_{m1}s_{m2})S_m=1,\ s_{m'1};\ S_{mm'}\|\ s_{m2}\ \mathbf{t}_{mm'}\ \|(s_{m'1}s_{m'2})S_{m'}=1,\ s_{m1};\ S'_{mm'}>$$

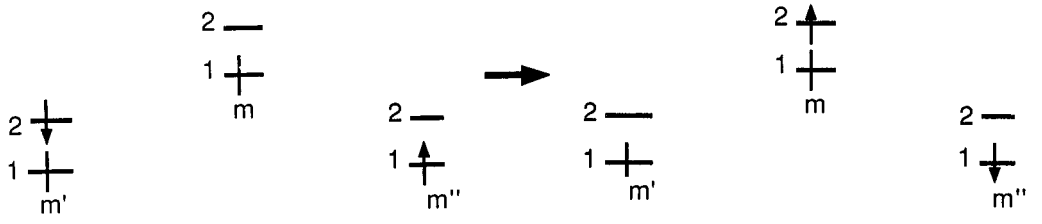
where $S_{mm'}$ or $S'_{mm'}$ is the spin of the dimer. Operation of $\mathbf{t}_{mm'}$ replaces $s_{m'2}$ by s_{m2} and produces the ket $|(s_{m'1}s_{m2})S=1,\ s_{m1};\ S'_{mm'}>$, that is a state for which the electron in m2 is still coupled to the electron in m'1. Recoupling yields the two states $|(s_{m1}s_{m2})S_m,\ s_{m'1};\ S'_{mm'}>$ with $S_m = 0$ and $S_m = 1$. Thus there are matrix elements of s_{m2} between states of different site spin S_m; this excludes the application of the replacement theorem.

The transfer by double-exchange occurs without spin-flip. Interestingly, expression (21) contains transfers with and without spin-flip. We can depict these processes in the following way.



Transfer without Spin-Flip

Starting with the excess electron on m' the operator $c^+_{m''2\beta}c_{m'2\beta}$ moves a β-spin to m" where a local singlet state is formed. Subsequently the electron is tranferred to m with $c^+_{m2\beta}c_{m''2\beta}$.



Transfer with Spin-Flip

Transfer with spin-flip can occur because the singlet state on m", $\phi = (\ |m''1\alpha>|m''2\beta> - |m''1\beta>|m''2\alpha>)/\sqrt{2}$, contains both α- and β-spins in orbitals 1 and 2. Thus $c^+_{m''2\beta}c_{m'2\beta}$ can transfer a β-spin into center m" whereas $c^+_{m2\alpha}c_{m''2\alpha}$ carries the α-spin component to m, leaving a β-spin in orbital m"1.

The new terms discussed here are analogous to those considered by Hirsch (ref. 30) in his theoretical studies of mixed-valence systems with one orbital per center. For the latter systems the new terms are proportional to β^2/U rather than β^2/K.

Double exchange is a first order process proportional to $\beta_{mm'}$. The mechanism discussed here achieves the transfer by using the "detour" through an excited state on m". Consequently, the process involves two consecutive transfer integrals $\beta_{mm''}\beta_{m'm''}$. Since the new term contains the transfer operator $t_{mm'}$ as well as features of the familiar exchange term, we may call this process exchange-transfer.

The exchange transfer process requires that two transfer integrals $\beta_{mm''}$ and $\beta_{m'm''}$ have non-zero values. This implies that the centers m and m" and the centers m' and m" are connected by a double exchange pathway. The exchange-transfer term is roughly by a factor β/K smaller than the double exchange contribution. The new term commutes with S^2 and S_z but it will mix states with different intermediate spin and it can lift degeneracies. Although expression (24) has been derived for a d^1-d^1-d^2 system, it seems that one should be able to construct a similar term, with suitable modifications, for the d^n-d^n-$d^{(n+1)}$ system. In this case, the Hund rule configuration $S = S_0 + 1/2$ and the configuration $S = S_0 - 1/2$ will take the place of the triplet and singlet states discussed here. Finally, exchange-transfer will occur in d^0-d^1-d^1 and d^9-d^9-d^{10} systems.

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