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Interplay of Electron Exchange and Electron Transfer in Metal Polynuclear Complexes in Proteins or Chemical Models

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I. Introduction

Many proteins contain active sites made of several metal ions linked together by chemical groups (carboxylic acid, imidazole) attached to the protein backbone; very often, small anions (O^{2-} , S^{2-}) bridge those metal ions (Figure 1). Nature has selected such elaborated *polynuclear sites* to accomplish redox chemistry, oxygen fixation, and chemical transformation of substrate or to act as electron carriers (Table I), although some of those reactions are achieved by proteins with use of only one metal ion.³ In the following text, we focus on proteins with more than one metal ion and their chemical models. A recent volume has been dedicated to this subject.⁴

The high variety of biological metal polynuclear complexes can be organized by considering the number of metal ions implied (Table I). Examples of *dinuclear sites* are found in the following proteins: Methemerythrin⁵ contains two Fe(III) ions bridged by one oxo and two carboxylato groups forming the core $[Fe_2O-(RCO_2)_2]^{2+}$ (Figure 1a), where RCO_2 stands for a carboxylate group from the protein; oxidized two-iron

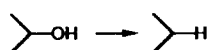
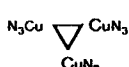


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TABLE I. Examples of Polynuclear Sites of Metalloproteins (Oxidation States of the Metal Ions and Basic Magnetic Properties Indicated)

protein	function	site	struct work (ref)	oxidn state	electron spin coupling properties (J^b , cm ⁻¹)	ref	intracluster electron transfer properties ^c	ref
Dinuclear Sites								
two-iron ferredoxin hemerythrin	electron carrier	Fe ₂ S ₂	6 ^a	2 Fe(III) Fe(III)Fe(II)	-366 -166	85 75	loc (Möss, 230 K)	76
	O ₂ fixation	Fe ₂ O(RCO ₂) ₂	5 ^a	2 Fe(III) Fe(III)Fe(II)	-268 -40	86 88	loc (NMR, 300 K) loc (Möss, 200 K)	88 89
				2 Fe(II)	-76 < J < -24 -30	87 88		
methane monooxygenase	CH ₄ + O ₂ + NADH + H ⁺ → CH ₃ OH + NAD ⁺ + H ₂ O	close to hemerythrin	90 ^d	2 Fe(III)	J small, J < 0	48		
				Fe(III)Fe(II) 2 Fe(II)	J small, J < 0	48 48		
ribonucleotide reductase		close to hemerythrin	92 ^d	2 Fe(III)	-216	91		
purple acid phosphatase hemocyanin	unknown	close to hemerythrin		2 Fe(II) 2 Fe(III) 2 Fe(II)	< -80 -20	101 93, 94		
	O ₂ fixation	N ₃ Cu---CuN ₃	7 ^a	2 Cu(II) Cu(II)Cu(I) 2 Cu(I)	J << 0 $S = 1/2$ dia			102
catalase	H ₂ O ₂ → H ₂ O + 1/2 O ₂	close to hemerythrin with Fe replaced by Mn	9 ^a	2 Mn(III)				
				Mn(III)Mn(IV) Cu(II)Zn(II)				103
superoxide dismutase cytochrome c oxidase	2O ₂ ⁻ → O ₂ + O ₂ ²⁻ O ₂ + 4e ⁻ + 4H ⁺ → 2H ₂ O	heme-Cu	113	Fe(III)Cu(II)	$S = 2$	114		
Trinuclear Sites								
ascorbate oxidase	O ₂ + 4e ⁻ + 4H ⁺ → 2H ₂ O	N ₃ Cu 	96 ^a	3 Cu(II)	$S = 1/2 +$ ($S_{ab} = 0$)	104		
Fd II from <i>D. gigas</i>	electron carrier	Fe ₃ S ₄	13 ^a	3 Fe(III) 2 Fe(III)-1 Fe(II)	< -200 -40 -40	97 105 97	one pair deloc, one Fe(III) loc	32
Fd I from <i>A. vinelandii</i>	electron carrier	Fe ₃ S ₄	98 ^a			76		
Tetranuclear Sites								
HiPIP _{ox}	electron carrier	Fe ₄ S ₄	99 ^a	3 Fe(III)-1 Fe(II)	$S = 1/2, -200$ -100	106 107	Fe atoms are identical by pair	83
HiPIP _{red}	electron carrier	Fe ₄ S ₄	100 ^a	2 Fe(III)-2 Fe(II)	$S = 0, -400$	106	deloc	76
4 Fe Fd red	electron carrier	Fe ₄ S ₄		1 Fe(III)-3 Fe(II)	$S = 1/2$	108	Fe atoms are identical by pair	108, 76
Fe protein of nitrogenase from <i>A. vinelandii</i>	electron carrier	Fe ₄ S ₄		1 Fe(III)-3 Fe(II)	$S = 3/2$	109	deloc	109, 76
Mn site of OEC	2H ₂ O → O ₂ + 4e ⁻ + 4H ⁺	Mn ₄	115, ^d 116 ^d		$S = 1/2$ or $3/2$ in step S_2	117, 118		

	Higher Nuclearity Fe(III) + 2 Fe(III)-2 Fe(II)	110 ^a	111
sulfite reductase	heme + Fe ₄ S ₄	S = 5/2 native	S = 1/2 complexed by SO ₃ ²⁻
FeMo cofactor of nitrogenase from <i>A. vinelandii</i>	Fe ₅₋₇ MoS ₆₋₉	18, ^d 112	
ferritin	Fe ₄₅₀₀	21	

^a Such a reference stands for a X-ray diffraction structural work. ^b $H = -JS_1 \cdot S_2$. When ambiguity is possible, the spin value of ground state is given. ^c loc = localized; deloc = delocalized. ^d EXAFS work. Some proteins of this table can have another metallic site than the one quoted here.

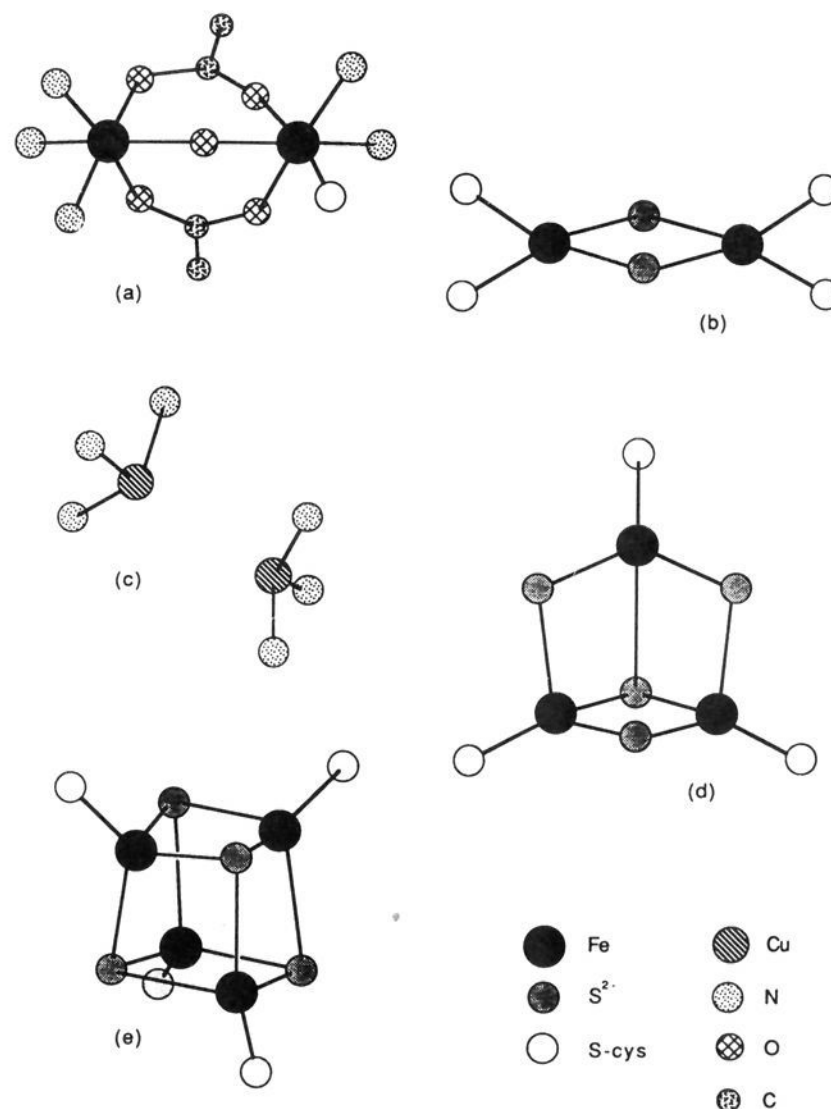


Figure 1. Structures of polynuclear active sites of metalloproteins: (a) methemerythrin; (b) two-iron ferredoxin; (c) deoxyhemocyanin; (d) three-iron site in oxidized Fd II; (e) four-iron iron-sulfur cubes.

ferredoxin⁶ has two Fe(III) ions bridged by two S²⁻ anions ([Fe₂S₂]²⁺) (Figure 1b); and hemocyanin⁷ holds two Cu(I) ions close together apparently unbridged (Figure 1c). Recently, a catalase⁸⁻¹² has been identified, the active site of which is thought to be similar to the hemerythrin one but with Fe(III) replaced by Mn(III) ([Mn₂O(RCO₂)₂]²⁺). *Trinuclear sites* are found, for instance, in three iron-sulfur proteins: Oxidized ferredoxin II (Fd II)¹³ has three Fe(III) ions bridged by four S²⁻ anions ([Fe₃S₄]⁺) (Figure 1d). The same type of site is known for inactive aconitase.¹⁴ Among *tetranuclear sites*, the most famous are the four iron-sulfur clusters² (Figure 1e): In reduced four-iron ferredoxins, the cluster is in the 3 Fe(II)-1 Fe(III) state. In oxidized four-iron ferredoxins or reduced HiPIP (high-potential iron protein), the cluster is in the 2 Fe(II)-2 Fe(III) state, and in oxidized HiPIP, it is in the 3 Fe(III)-1 Fe(II) state. Another very important four-metal atom complex is the four-manganese center that, in plants, achieves the catalysis of water oxidation to dioxygen.¹⁵⁻¹⁷ More complicated systems are found in nitrogenase,^{18,19} sulfite reductase,²⁰ and ferritin.²¹ Chemists have prepared models of those active sites:²² The [Fe₂S₂]²⁺ unit has been synthesized²² as have been [Fe₂O(RCO₂)₂]²⁺ and [Mn₂O(RCO₂)₂]²⁺.^{1,10-12} [Fe₄S₄]ⁿ⁺ clusters have been prepared ($n = 1$ and 2 ;² $n = 3$ ^{23,24}), and a [Mn₄O₃Cl]⁶⁺ cluster has been isolated.²⁵

This review deals with the electronic properties of those biological metallic sites and/or their models. We hope to show that besides the biochemical significance, these studies are of interest for physics: Such systems

are wonderful opportunities to study experimentally and theoretically fundamental electronic processes in metal polynuclear complexes such as *electron exchange* and *electron transfer*.

We will show how experimentalists and theoreticians studying iron-sulfur clusters were forced to go beyond the usual exchange scheme and to revive double-exchange concept and to precisely establish the relation between electron exchange and intracuster electron transfer.

II. Organization of the Review

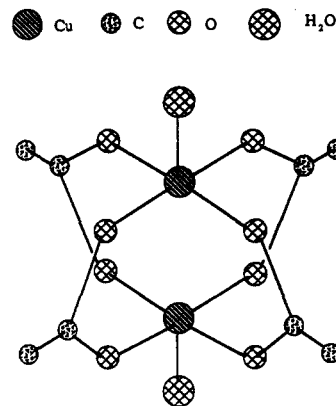
The first step in studying electronic properties of metal polynuclear complexes is to assign oxidation state to metal ions. This will govern many of their properties: The five unpaired electrons of Fe(III) ion will have most often their spins parallel to give the high-spin state $S = 5/2$ just as an Fe(II) ion (d^6) will be $S = 2$, a Mn(IV) ion (d^3) $S = 3/2$, a Mn(III) ion (d^4) $S = 2$, and a Cu(II) ion (d^9) $S = 1/2$.

Such metal ions gathered in a cluster can present *electron-exchange* phenomenon that gives to the cluster magnetic properties drastically different from those of the individual ions. Such considerations are of paramount importance to understand the EPR spectra of those sites (natural or synthetic) as well as the magnetization, NMR, and Mössbauer studies.⁴ In short, when a pair of metal ions is considered, two possibilities are encountered: The ion spins "prefer" (energetically) to be either parallel or antiparallel. A typical system is the $[\text{Fe}_2\text{O}(\text{RCO}_2)_2]^{2+}$ core of methemerythrin where both Fe(III) ions have their $S = 5/2$ spins preferentially antiparallel. We will discuss this phenomenon in more detail.

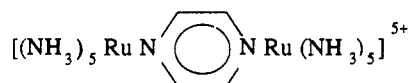
In some cases, intracuster *electron transfer* can occur from one metal ion to a close neighbor, leading to characteristic properties. This electron transfer can be induced by electromagnetic radiation, which will lead to optical properties, or by thermal energy. An Fe(II)Fe(III) cluster in a chemically symmetric environment will not exhibit thermal electron transfer to lead to Fe(IV)Fe(II) because such a process would need a very high excitation energy; a rough estimate of this energy can be obtained from the case of two isolated Fe(II) ions as the difference in ionization potentials: $\Delta E = 57.1 - 30.64 = 26.46$ eV. Even if, in a cluster, this excitation energy is much reduced due, in particular, to a change in electrostatic repulsion between metallic ions in the Fe(III)Fe(III) state and in the Fe(II)Fe(IV) state, this excitation energy will remain large. On the other hand, an Fe(II)Fe(III) cluster (such systems are said to be *mixed valent*) is a very good candidate for internal electron transfer since, for a chemically symmetric environment, the transformation Fe(II)Fe(III) \rightarrow Fe(II-I)Fe(II) costs no energy. We will study intracuster electron transfer and see the role of vibrations of the atoms surrounding the metal ions.

These phenomena have been studied in solid-state physics²⁶ and solid-state chemistry.²⁷

Molecular inorganic chemists have been able to prepare metal polynuclear complexes, which have allowed detailed measurements and a theoretical understanding of electron exchange²⁸ or internal electron transfer²⁹ separately. The archetype of molecules synthesized to investigate electron exchange is a Cu(II)Cu(II) dinuclear unit as in copper acetate³⁰



and for internal electron transfer it is a Ru(II)Ru(III) one of the type synthesized by Taube and co-workers.³¹



Those Cu(II)Cu(II) units did not exhibit internal electron transfer toward Cu(I)Cu(III) (too high excitation energy), and the Ru(II)Ru(III) systems did not present electron-exchange properties since Ru(II) (d^6) is low spin ($S = 0$).

Iron-sulfur biological clusters and their models were the first clusters² on which it was possible to study simultaneously electron exchange and internal electron transfer and their interplay as they imply high-spin Fe(II) and Fe(III) ions. Since then, many other polynuclear complexes of biological relevance have been discovered (Table I) that present similar behavior.

Recently we studied the $[\text{Fe}_3\text{S}_4]^0$ cluster in Fd II^{32,33} and demonstrated that indeed, in iron-sulfur clusters, both phenomena determine the spectroscopic properties. In this paper we explicitly state the relation between electron exchange and internal electron transfer.

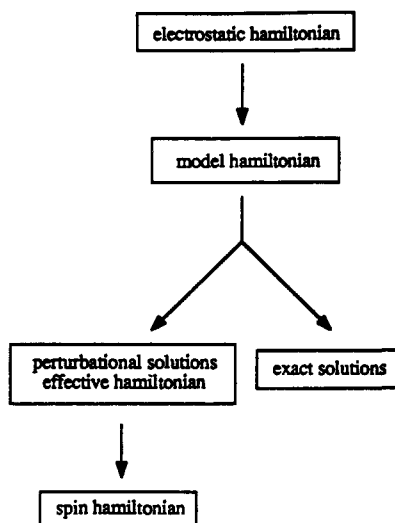
It is perhaps useful at this point to explain our strategy in calculations. It is well-known that electron exchange is a pure electrostatic phenomenon.¹²⁹ The same holds for electron transfer: Electron delocalizes from center A to center B because it is attracted by the nuclei of center B. So, in order to analyze those phenomena, the starting point is the electrostatic *real Hamiltonian* including electron kinetic energy, electron attraction by nuclei, and electron-electron repulsion. Manipulation of the electrostatic real Hamiltonian implies heavy calculations. As we are looking for a phenomenological theory, it is legitimate to simplify such an Hamiltonian, keeping only leading interactions (or thought to be such...). This simplified Hamiltonian is called a *model Hamiltonian*. In what follows, we use one of the most famous electrostatic model Hamiltonians, the Hubbard-Anderson one.^{38,39} Chemists are familiar with the Hückel model Hamiltonian in which only orbital energies α_i and Coulomb interactions β_{ij} between orbitals are retained. A Hückel Hamiltonian implemented with a simple modelization of electron-electron repulsion defines the Hubbard-Anderson Hamiltonian; in the latter, electron-electron repulsion is taken into account only when two electrons are on the same center (it is called U_0). We denote model Hamiltonians by H_M .

The experimentalist specialized in properties of the ground state or of the lowest excited states does not need a full solution of the model Hamiltonian. Here arises the use of perturbation theory. For the situations

encountered in this review, the model Hamiltonian can be written as $H_M = H_0 + V$, where H_0 is the one formed of the monocentric terms only (α_i, U_0) and V is the part related to the electronic interactions between centers (β_{ij}). V is considered as a perturbation since we are studying weak interactions.

Physically, interesting situations occur only when the ground state E_0 of H_0 is degenerate. Then, V lifts this degeneracy, and the energetic gaps so induced are the physical observables. Second-order perturbation theory on a degenerate level has been formalized in degenerate perturbation theory.⁴¹ This allows one to build an *effective Hamiltonian* H_{eff} , which acts only in E_0 and reproduces the splitting due to V .

A next simplifying step is to take into account the correspondence between the functions of E_0 (which are antisymmetrized functions of spin and space coordinates) and spin-only functions. Ultimately, we build a *spin Hamiltonian* equivalent to H_{eff} ; it acts on spin functions only and is denoted H_S . Such a spin Hamiltonian is the most interesting one for experimentalists since it allows us to interpret and parametrize data. We just defined a work program that can be illustrated in the following way:



This program, when achieved, leads to theoretical interpretations for the values observed for the spin Hamiltonian parameters.¹³⁰ It has been successfully followed for the exchange phenomenon, but it has to be explored again for new situations that are beyond the reach of exchange spin Hamiltonian.

III. Electron Exchange

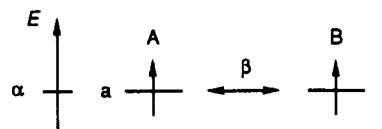
Let us consider in more detail the example of methemerythrin. The active site contains the $[\text{Fe}_2\text{O}(\text{RCO}_2)_2]^{2+}$ core in which the two iron ions are in the 3+ oxidation state and have spin $S = 5/2$. When a dinuclear core is formed, the spin of the Fe_A ion, S_A , interacts with S_B , the spin of the Fe_B ion. In general, this interaction can be represented by the *spin Hamiltonian* (Heisenberg or exchange Hamiltonian)

$$H_S = -JS_A \cdot S_B \quad (1)$$

where J is an interaction energy. J can be found by temperature-dependent magnetic susceptibility measurements, NMR, and EPR studies.^{4,28} Some values for biological systems are given in Table I. The resolution of Heisenberg Hamiltonian for dinuclear and trinuclear clusters has been reviewed.³⁴

As said before, it is well-known that this interaction does not originate from spin-spin interaction: It can be written like that, but its origin is purely electrostatic as can be seen by looking at the demonstration of the Heisenberg spin Hamiltonian. Let us see how the program delineated before to go from the electrostatic model Hamiltonian to the exchange spin Hamiltonian has been achieved^{42,43} and how a relation between J and the orbital interaction quantities has been obtained. We follow the main lines of the Leuenberger and Güdel demonstration.⁴³ Studying such a calculation also prepares us to build a different spin Hamiltonian adapted to new systems.

Let us consider for simplicity the Cu(II)Cu(II) case. Each Cu(II) is d^9 and so has a single unpaired electron. Let us call "a (b)" the orbital containing this unpaired electron on Cu_A (Cu_B). This orbital has mainly d character but is delocalized toward the ligands. We suppose that those two orbitals are the only ones playing a role in the phenomenon. This will be true if the orbitals of the bridging ligands are low enough in energy versus the d orbitals. Our assumption can break down if this is no longer true.³⁵ So we arrive at the following extremely simplified model:



The orbitals a and b overlap. For a qualitative discussion one can do as in the Hückel theory of molecular orbitals: Although the overlap is recognized as physically important, it is neglected in the calculation for the sake of simplicity since it has only quantitative effects. Despite this mathematical atrocity, Hückel theory has given much insight in chemistry. A seemingly more rigorous alternative is to orthogonalize the wave functions,³⁶ but then the quantities are no longer localized and chemical understanding is lost. Nevertheless, our approximation has to be kept in mind.

Electrons will circulate from one center to the other. The quantities ruling those displacements will be the energy of the orbitals a and b (α) and the interaction energy between those two orbitals (β) (Hückel integral). We need another important quantity, which is the cost in energy to put two electrons in orbital a or in orbital b , noted U_0 . Due to this effect, electrons will avoid double occupation of the orbitals. The Hamiltonian of our simplified system (model Hamiltonian, H_M) is thus³⁷

$$H_M = \alpha(n_a + n_b) + \beta \sum_{\sigma} (c_{a\sigma}^+ c_{b\sigma} + c_{b\sigma}^+ c_{a\sigma}) + U_0(n_{a\alpha} n_{a\beta} + n_{b\alpha} n_{b\beta}) \quad (2)$$

where $c_{k\sigma}^+$ is the creation operator associated with the spin orbital $k\sigma$ and $c_{k\sigma}$, $n_{k\sigma}$, and n_k are the annihilation operator, the spin orbital occupation operator, and the orbital occupation operator, respectively (see the Appendix). This model Hamiltonian has been introduced in solid-state physics and is called the Hubbard-Anderson³⁸⁻⁴⁰ model Hamiltonian.

This Hamiltonian can be separated in two parts $H = H_0 + V$ with

$$H_0 = \alpha(n_a + n_b) + U_0(n_{a\alpha} n_{a\beta} + n_{b\alpha} n_{b\beta}) \quad (3)$$

$$V = \beta \sum_{\sigma} (c_{a\sigma}^+ c_{b\sigma} + c_{b\sigma}^+ c_{a\sigma}) \quad (4)$$

H_0 involves only local terms, and V contains interaction terms. If the interaction between centers is weak,

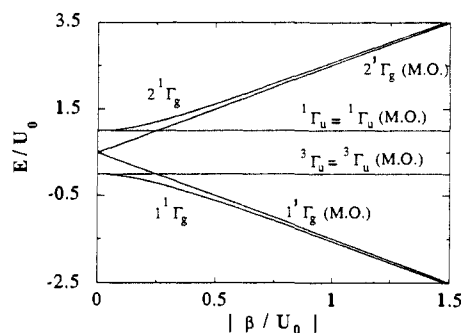


Figure 2. Energy levels for a two-electron, two-center, one-orbital per site problem in units of U_0 as a function of $|\beta/U_0|$ with exact solutions of Hamiltonian 2 and solutions in the molecular orbital model. The MO solution for the ground state is the asymptote of the exact solution. Notice that energy 2α was subtracted.

then V can be treated as a perturbation on the solutions of H_0 .

For this Cu(II)Cu(II) problem we have two eigenvalues at zero order that define two eigenspaces: the subspace \mathbf{E}_0 of energy $E_0^0 = 2\alpha$ (degeneracy 4: $|\alpha\alpha\beta\beta\rangle$, $|\alpha\beta\beta\alpha\rangle$, $|\alpha\alpha\beta\alpha\rangle$, $|\alpha\beta\beta\beta\rangle$) corresponds to Cu(II)Cu(II) states with the electrons staying on different Cu(II) ions. The subspace \mathbf{E}_1 of energy $E_1^0 = 2\alpha + U_0$ (degeneracy 2: $|\alpha\alpha\alpha\beta\rangle$, $|\beta\alpha\beta\beta\rangle$) corresponds to Cu(III)Cu(I) excited states where the two electrons are on the same copper ion.

Second-order degenerate perturbation theory⁴¹ allows one to build an effective Hamiltonian

$$H_{\text{eff}} = P_0 V P_0 + P_0 \left(\sum_i \frac{V P_i V}{E_0^0 - E_i^0} \right) P_0 \quad (5)$$

that acts in subspace \mathbf{E}_0 and gives solutions to the total problem accurate through second order. P_i is the projection operator in subspace \mathbf{E}_i .

One can check that $P_0 V P_0 = 0$: From a Cu(II)Cu(II) configuration, the effect of V is to give a Cu(III)Cu(I) configuration orthogonal to the starting one. Calculation gives

$$H_{\text{eff}} = -\frac{2\beta^2}{U_0} P_0 (n_{b\alpha} n_{a\beta} + n_{b\beta} n_{a\alpha} + c_{b\alpha}^+ c_{a\alpha} c_{a\beta}^+ c_{b\beta} + c_{b\beta}^+ c_{a\beta} c_{a\alpha}^+ c_{b\alpha}) P_0 \quad (6)$$

H_{eff} splits \mathbf{E}_0 into two subspaces, one singly degenerated with $E = 2\alpha - 4\beta^2/U_0$ (the singlet state) and the other triply degenerated with $E = 2\alpha$ (the triplet space).

If one notes that $s_a^z s_b^z = 1/4(n_{a\alpha} - n_{a\beta})(n_{b\alpha} - n_{b\beta})$ and that in subspace \mathbf{E}_0 , $n_{a\alpha} + n_{a\beta} = 1$ and $n_{b\alpha} + n_{b\beta} = 1$, we have

$$n_{a\alpha} n_{b\beta} + n_{a\beta} n_{b\alpha} = 1/2 - 2s_a^z \cdot s_b^z \quad (7)$$

Taking into account that $c_{a\alpha}^+ c_{a\beta} = s_a^+$, one finally gets

$$H_{\text{eff}} = P_0 \left(-\frac{4\beta^2}{U_0} \right) \left(\frac{1}{4} - s_a \cdot s_b \right) P_0 \quad (8)$$

If one considers the isomorphism between subspace \mathbf{E}_0 and a space built on the spin wave functions $|\alpha\alpha\rangle$, $|\beta\beta\rangle$, $|\alpha\beta\rangle$, and $|\beta\alpha\rangle$ (where the individual spins are written in the order $|m_A m_B\rangle$), an operator equivalent to (6) is $H_S = -(4\beta^2/U_0)(1/4 - s_a \cdot s_b)$, which is equivalent to eq 1 with $J = -4\beta^2/U_0$.

If we take into account ferromagnetic coupling,^{37,44} one gets

$$J = -\frac{4\beta^2}{U_0} + 2j \quad (9)$$

which allows one to understand experimental J values qualitatively or semiquantitatively; j is the exchange integral between orbitals a and b . In particular, Hay et al.⁴⁵ have given examples of correlation of the J value with the quantity β in a series of similar compounds of different geometry. This model works because U_0 and j are less sensitive to structural variations than β . Kahn et al.⁴⁶ have also expressed J as a function of β without neglecting overlap and have explored factors favoring ferromagnetism.

As far as antiferromagnetic coupling is concerned, the larger the overlap is, the larger the quantity β will be and the stronger the coupling will be.

Perhaps this treatment will be obscure for colleagues used to analyzing the electronic properties of polynuclear complexes or clusters in terms of molecular orbital theory. MO theory is in fact contained in the Hubbard-Anderson model. When one solves Hamiltonian 2 as did Falicov and Harris,¹¹⁹ four states are found with the following energies:

$$E(2^1\Gamma_g) = 2\alpha + 1/2 U_0 + 1/2 (U_0^2 + 16\beta^2)^{1/2}$$

$$E(3^1\Gamma_u) = 2\alpha$$

$$E(1^1\Gamma_u) = 2\alpha + U_0$$

$$E(1^1\Gamma_g) = 2\alpha + 1/2 U_0 - 1/2 (U_0^2 + 16\beta^2)^{1/2}$$

These energies are represented in Figure 2 (energy 2α has been subtracted).

In the same figure are reported the energies calculated by MO theory with the following MO's: $\phi_+ = (a + b)/\sqrt{2}$ and $\phi_- = (a - b)/\sqrt{2}$. Those energies are

$$E(2^1\Gamma_g(\text{MO})) = 2\alpha + 1/2 U_0 - 2\beta$$

$$E(3^1\Gamma_u(\text{MO})) = 2\alpha$$

$$E(1^1\Gamma_u(\text{MO})) = 2\alpha + U_0$$

$$E(1^1\Gamma_g(\text{MO})) = 2\alpha + 1/2 U_0 + 2\beta$$

We assume that β is negative. Notice that the solutions are symmetric in β .

In the limit $|\beta/U_0| \gg 1$, one can see on Figure 2 the equivalence of the MO theory and the exact treatment of the Hubbard-Anderson Hamiltonian.

For transition-metal ions of the first line in low oxidation states or of the second or third line and when those metal ions are very close to each other, $|\beta/U_0| \gg 1$ is expected to be valid. For such cases, U_0 is small (diffuseness of the orbitals) and β is large. This limit corresponds to a metal-metal bond situation.

On the other hand, one can remark from Figure 2 that MO theory fails in the limit $|\beta/U_0| \ll 1$. The gap between the $1^1\Gamma_g(\text{MO})$ and the $3^1\Gamma_u$ states is large, in contradiction with the vanishing gap expected from the exact calculation and experimentally observed. This limit corresponds to electron-exchange phenomenon.

For polynuclear complexes dealt with in this review, $|\beta/U_0| \ll 1$ is assumed to be true since they implied first-line transition-metal ions in high oxidation states with weak metal-metal interactions. We tried to follow the recommendation of Cotton and Wilkinson¹²⁰ by

keeping the name "cluster" for systems exhibiting metal-metal bonds ($|\beta/U_0| \gg 1$) and "polynuclear complexes" for systems with metal ions in weak interaction ($|\beta/U_0| \ll 1$). The continuity between those two limits is apparent in Figure 2.

As can be seen from Table I, the most well-known bridged structures used in Nature, i.e., the $[\text{Fe}_2\text{S}_2]^{2+}$ and $[\text{Fe}_2\text{O}(\text{RCO}_2)_2]^{2+}$ cores, are very strongly antiferromagnetically coupled. The existence of a relation between this strong coupling and the biochemical function of the site is an open question. It has been suggested that this coupling could be related to redox behavior, but more data are needed to check this hypothesis.⁴⁷

The fact that ribonucleotide reductases exist in Fe and Mn forms and that the corresponding exchange energies are very different^{1,10-12} casts some doubt on such a relation; perhaps those structures are strongly coupled just as a consequence of using small bridging groups as O^{2-} and S^{2-} that are easily available in Nature and give short metal-bridge bonds and strong orbital overlaps. So, in general (the weakly coupled Mn(II)-I-O-Mn(III) bent unit seems an exception¹⁰⁻¹²), they lead to strong antiferromagnetic coupling.

Recently methane monooxygenase,⁴⁸ a dinuclear Fe(III)Fe(III) protein, has been shown to be much less strongly coupled than hemerythrin. This seems to be related to a hydroxo bridge in place of an oxo bridge.

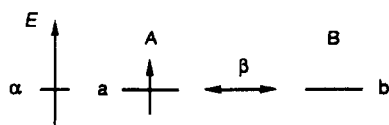
Even if no biochemical role could be assigned to electron exchange, this phenomenon is essential to understand the spectroscopic properties of polynuclear natural active sites as we said before. For instance, the EPR studies of the oxygen-evolving center imply considerations of electron exchange between four manganese ions and are still a matter of intense debate.¹⁵

Another example has been given by the study of aconitase. An inactive form has an $[\text{Fe}_3\text{S}_4]^+$ site consisting of three Fe(III) in a triangular topology giving a ground state $S = 1/2$, and at high pH a linear $[\text{Fe}_3\text{S}_4]^+$ unit has been identified with a ground state¹⁴ $S = 5/2$. Those properties can be fully understood in terms of exchange spin Hamiltonian.⁴⁹

IV. Mixed-Valence Complexes and Internal Electron Transfer

This subject has also been studied in great detail.²⁹ Among the most famous artificial compounds of this class is the Creutz and Taube complex (see above), the study of which has been invaluable in finding the laws of intramolecular electron transfer.³¹ Recently, a Cu(II)Cu(I) state of hemocyanin has been studied in detail.⁵⁰

The properties of such complexes can be understood through the study of the preceding two-site problem with one orbital per site but with only one electron or hole (for the three-electron case):



In the metal cluster, the energy of the orbital on center i will depend on the position of the ligands around metal ion i and this position of ligands will differ whether the orbital is occupied or not by the electron (a high oxidation state will mean a short metal-ligand bond). We have to take into account these phenomena.

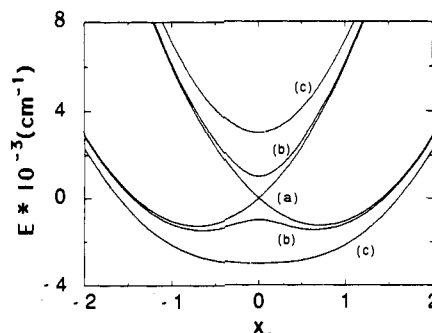


Figure 3. Potential energy curves (cm^{-1}) as a function of the antisymmetric reduced normal coordinate x_- for a two-site, one-electron problem. The vibronic coupling parameter $\lambda^2/k = 5000 \text{ cm}^{-1}$. Key: (a) orbital interaction $\beta = 0$; (b) $\beta = 1000 \text{ cm}^{-1}$; (c) $\beta = 5000 \text{ cm}^{-1}$.

A possible model Hamiltonian is then

$$H_0 = \alpha(n_a + n_b) + U_0(n_{a\alpha}n_{a\beta} + n_{b\alpha}n_{b\beta}) + \lambda(q_A n_a + q_B n_b) + \frac{p_A^2}{2m} + \frac{p_B^2}{2m} + \frac{1}{2}kq_A^2 + \frac{1}{2}kq_B^2 \quad (10)$$

where the dynamics of the coordination spheres around A and B is introduced. The normal mode of vibration q_A (q_B) corresponds to the pulsation of the coordination sphere, k is the force constant, m is the associated mass, and p_A (p_B) is the nucleus impulsion. λ is the vibronic constant that expresses the fact that when site A is occupied by one electron, the equilibrium value of q_A is not the same than when it is empty.

For a one-particle problem, the U_0 term vanishes. The solutions of H_0 are

$$E_0 = \alpha + \frac{p_+^2 + p_-^2}{2m} + \frac{k(q_+^2 + q_-^2)}{2} + \frac{\lambda(q_+ \pm q_-)}{\sqrt{2}} \quad (11)$$

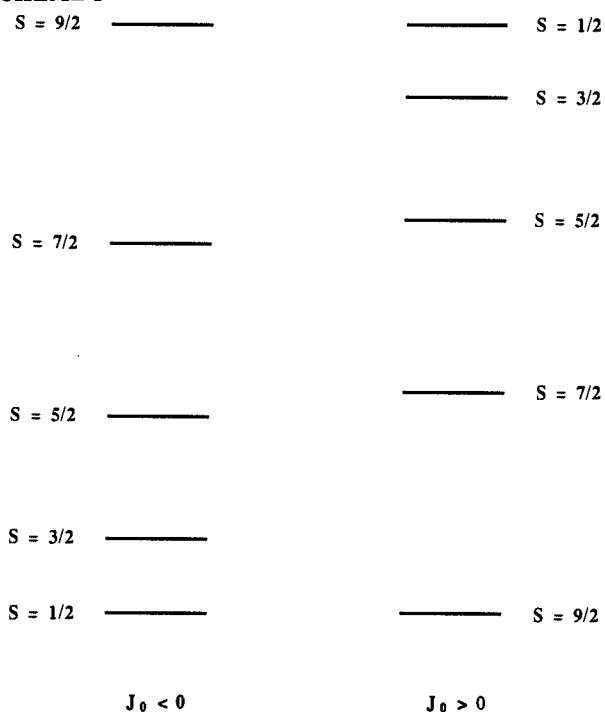
with $q_+ = (q_A + q_B)/\sqrt{2}$ and $q_- = (q_A - q_B)/\sqrt{2}$. One sees that, for this problem, the q_+ and q_- coordinates play different roles. The q_+ coordinate plays just an additive role, in contrast to the q_- coordinate. We focus on the role of q_- . The quantity $\frac{1}{2}kq_-^2 \pm (\lambda/\sqrt{2})q_-$ (which represents the potential energy associated to this coordinate) is represented in function of the adimensional coordinate $x_- = q_-/(\lambda/k)$ in Figure 3a. The stable system has a dissymmetric structure with the Cu(II) coordination sphere more compact than the Cu(I) one (x_- is not zero at the energy minimum).

How those curves will be modified by taking into account the interaction β is well-known.⁵² The energy is obtained by diagonalization of a 2×2 matrix, and the dependence on x_- of the energy is

$$E_{\pm} = \frac{\lambda^2 x_-^2}{2k} \pm \left(\frac{\lambda^4 x_-^2}{2k^2} + \beta^2 \right)^{1/2} \quad (12)$$

This treatment parallels that given in refs 51-53. When $|\beta| < \lambda^2/2k$, the lowest eigenvalue exhibits two minima corresponding to situations where the Cu(I) has a wider coordination sphere than the Cu(II). This condition defines class II mixed-valence systems.⁵⁴ When one solves the vibronic problem,⁵¹⁻⁵³ levels are found inside the wells: When temperature rises, the system can start to delocalize. We will not go into the detailed quantum treatment of vibrations in those systems (see for instance ref 52). By optical absorption, the system can go from the ground state to the excited

SCHEME I



state. This will be a vertical transition due to Franck-Condon principle. The energy of this transition will be

$$E_{op} = \frac{\lambda^2}{k} \quad (13)$$

Its intensity will be zero for $\beta = 0$ and will increase with β^2 as shown by the value of the transition moment calculated as the vertical transition from one minimum of E_- to the E_+ curve

$$M^2 = \frac{R^2\beta^2}{(\lambda^2/k)^2} \quad (14)$$

where R is the distance between the two metallic centers in angstroms. M^2 can be determined⁵⁵ experimentally through intensity measurements since $M^2 = 4.2 \times 10^{-4} \epsilon_{\max} \Delta_{1/2} / E_{op}$, where ϵ_{\max} stands for the maximum value of the extinction coefficient ($M^{-1} \text{ cm}^{-1}$) and $\Delta_{1/2}$ is the half-height width (cm^{-1}) (E_{op} is also in cm^{-1}).

The thermal electron transfer will have as activation energy

$$E_{\theta} = \frac{\lambda^2}{4k} + \frac{\beta^2}{\lambda^2/k} - |\beta| \quad (15)$$

The last quantity of interest easily calculated in this model is the delocalization coefficient defined as τ in

$$|-\rangle = \tau|a\rangle + (1 - \tau^2)^{1/2}|b\rangle \quad (16)$$

for one of the minima ($x_- > 0$) of curve E_- . This coefficient is such that

$$\tau^2 = \frac{\beta^2}{(\lambda^2/k)^2} \left[\frac{1}{2} + \left(\frac{1}{4} - \frac{\beta^2}{(\lambda^2/k)^2} \right)^{1/2} \right]^{-1} \quad (17)$$

When $\beta^2/(\lambda^2/k)^2 \ll 1$, these formulas reduce to Hush ones.⁵⁵

When $|\beta| \geq \lambda^2/2k$, the lowest curve has only one minimum in $x_- = 0$, which means that the lowest energy for the system corresponds to a symmetrical dimer with two $\text{Cu}(1.5+)$. In this case ($|\beta| \geq \lambda^2/2k$), the wave

functions become $|-\rangle = [a] - [b]/\sqrt{2}$ and $|+\rangle = [a] + [b]/\sqrt{2}$. With $|\beta| = \lambda^2/2k$, one obtains from formula 13 $E_{op} = 2|\beta|$ and from formula 14 $M^2 = R^2/4$. These formulas remain valid whenever $|\beta|$ is greater than $\lambda^2/2k$. The formula for the transition moment seems to overestimate this quantity.

Ironically, the Creutz and Taube complex, $\text{Ru(II)-pyz-Ru(III)}$, on which this theory was generally applied has been shown recently to differ substantially from this picture.^{56,57} With such an extended bridge, a third orbital (localized on the pyrazine ligand) has to be taken into account. Nevertheless, with monoatomic bridging ligands like oxo or sulfido groups, validity of the preceding theory can be expected.

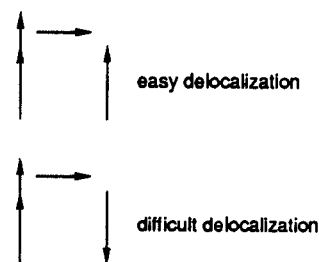
V. Internal Electron Transfer and Electron Exchange

A. Dinuclear Sites

As we saw above, Fe(II)Fe(III) mixed-valence systems exhibit both electron exchange and electron transfer.

Intuitively we understand that if the valences are frozen, an Fe(II)Fe(III) system has to be described by a Heisenberg Hamiltonian with $S_{\text{Fe(II)}} = 2$ and $S_{\text{Fe(III)}} = 5/2$. This will give states from $S = 1/2$ to $S = 9/2$ (Scheme I).

If we take symmetrical molecules, there are indeed as many chances to find the Fe(II) ion on the left as on the right end of the molecule. So it means that we have a double-spin ladder with each spin state (S) occurring twice. Now, due to the orbital interaction between A and B, this degeneracy will be lifted. Anderson⁵⁸ has proposed that this splitting will go as $2|B|(S + 1/2)$ where $|B|$ is an interaction energy. The system gains more delocalization energy when the two spins are parallel than when they are antiparallel. This idea was put forward first by Zener⁵⁹ who called this spin-dependent electron transfer "double exchange".



Reference 58 did not explicitly include the existence of electron exchange between the centers, which is not realistic. De Gennes studied this complication for extended systems.⁶⁰ The superposition of electron exchange and double exchange was also studied in ref 61.

Those ideas have been revived almost simultaneously in chemistry in refs 62-66.

To calculate those effects, we proposed³² a new spin Hamiltonian

$$H_S = BT_{AB} - J_0(S_A \cdot S_B O_A + S_A \cdot S_B O_B) \quad (18)$$

with

$$T_{AB}|S_A, S_B, S\rangle^A = (S + 1/2)|S_A, S_B, S\rangle^B \quad (19)$$

$$T_{AB}|S_A, S_B, S\rangle^B = (S + 1/2)|S_A, S_B, S\rangle^A$$

Hamiltonian 18 acts in a basis the dimension of which is twice the dimension of the electron-exchange problem

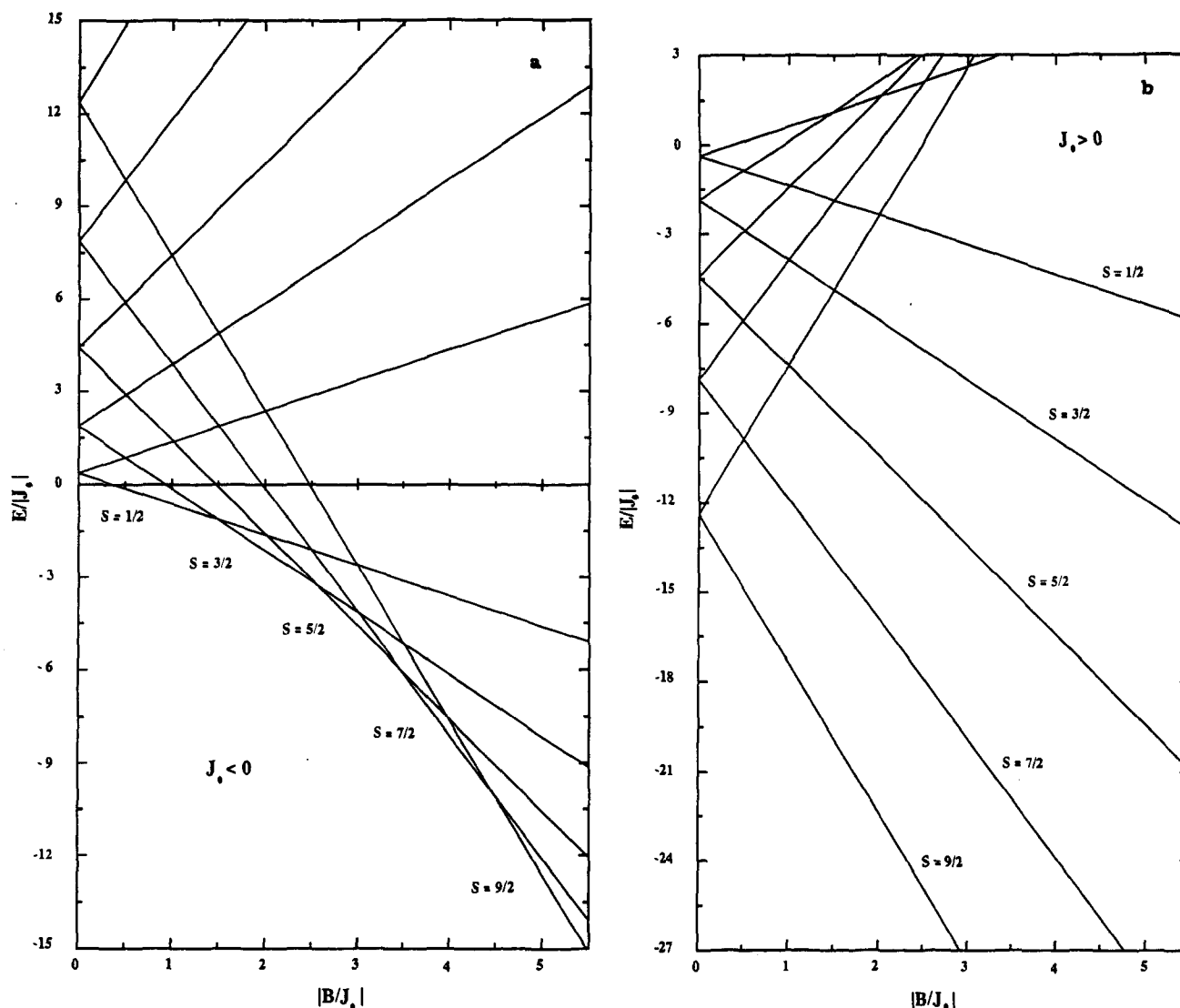


Figure 4. Eigenvalues of the exchange-double exchange spin Hamiltonian in units of $|J_0|$ as a function of $|B/J_0|$ for a $(6/2; 2)$ dinuclear unit with valences delocalized: (a) $J_0 < 0$; (b) $J_0 > 0$.

without electron transfer: One possible basis is made of spin-coupled functions $|S_A, S_B, S\rangle^A$ and $|S_A, S_B, S\rangle^B$, where A and B refer to the position of the extra particle. By particle, we mean electron for d^n-d^{n+1} systems with $n + 1 \leq 5$ and hole for $n + 1 \geq 6$. For an Fe(II) Fe(III) system, when the extra hole is on A, $S_A = 5/2$ and $S_B = 2$ and when it is on B, $S_B = 5/2$ and $S_A = 2$. O_A is such that $O_A|S_A, S_B, S\rangle^A = |S_A, S_B, S\rangle^A$ and $O_A|S_A, S_B, S\rangle^B = 0$. The same holds for O_B . One can see that (18) includes a transfer term and electron-exchange terms. This Hamiltonian could be called the "exchange-double exchange spin Hamiltonian".

The eigenvalues of (18) are

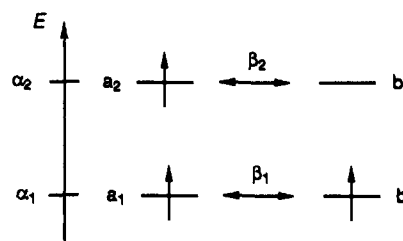
$$E_{\pm}(S) = -1/2 J_0 S(S + 1) \pm B(S + 1/2) \quad (20)$$

The energies (in units of $|J_0|$) of those levels for an Fe(II)Fe(III) complex are given in Figure 4a as a function of the ratio $|B/J_0|$ in the case $J_0 < 0$. For $B = 0$, the levels obey the Heisenberg Hamiltonian; for $|B/J_0| \neq 0$, the Heisenberg Hamiltonian is no longer followed. If $|B/J_0| < 1.5$, the ground state has $S = 1/2$. For $|B/J_0| > 4.5$, the ground state has $S = 9/2$. A competition between antiferromagnetic coupling and double exchange exists: For small values of $|B/J_0|$, the anti-

ferromagnetic coupling dominates and the energy of delocalization is $2|B|$. For large values of $|B/J_0|$, electron transfer is the leading term and the system will have its spins parallel. The energy of delocalization is $10|B|$. One can already guess the easier valence trapping in the $S = 1/2$ state than in the $S = 9/2$ one (see later text).

In Figure 4b, we have given the diagram for $J_0 > 0$. In this case, for any value of the ratio $|B/J_0|$ the ground state has a spin equal to $9/2$: Spin coupling and electron transfer are no longer antagonistic.

Recently⁶⁷ we published a formal demonstration of (18) following the program above. Let us consider a two-site, two-orbitals per site (a_1, a_2, b_1, b_2), three-electron problem:



We will use Hamiltonian 21.

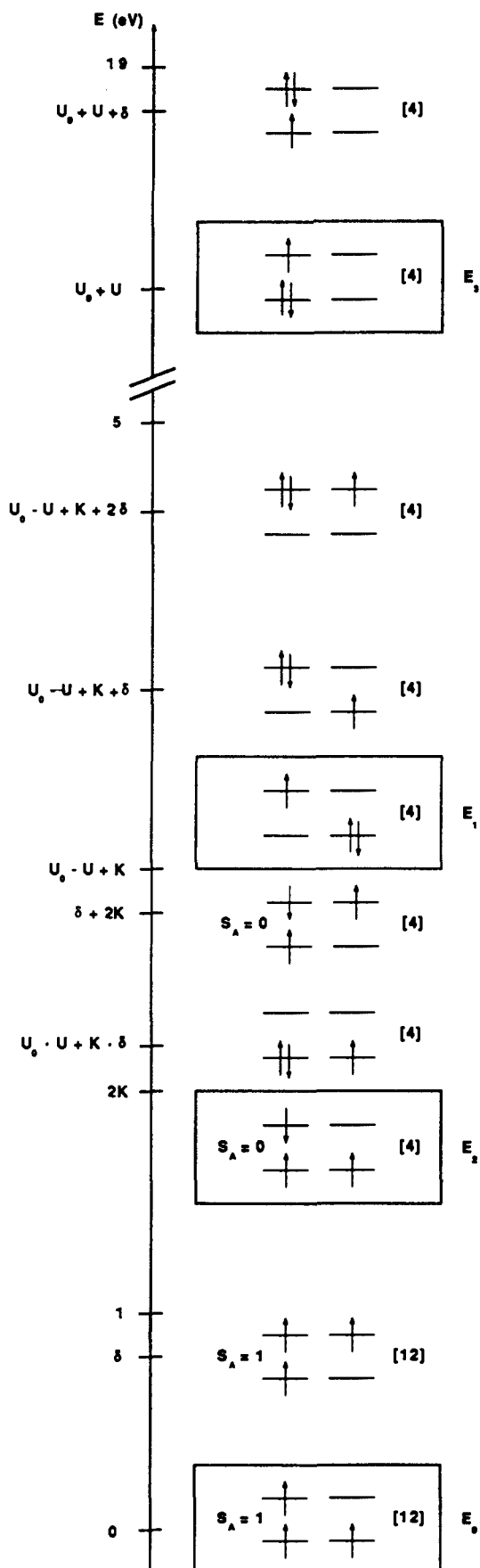


Figure 5. Eigenstates and eigenvalues of the model Hamiltonian before intercenter interaction (energy in eV): $U_0 = 10$ eV; $U = 8$ eV, $K = 1$ eV; $\delta = 0.8$ eV. To each eigenstate is associated one of the possible occupation schemes; degeneracy is indicated in brackets.

$$H_M = \sum_{k=1,2} \alpha_k (n_{a_k} + n_{b_k}) + \sum_{k=1,2} \beta_k \sum_{\sigma} (c_{a_k\sigma}^{\dagger} c_{b_k\sigma} + c_{b_k\sigma}^{\dagger} c_{a_k\sigma}) + U_0 \sum_{k=1,2} (n_{a_k\alpha} n_{a_k\beta} + n_{b_k\alpha} n_{b_k\beta}) + \frac{U}{2} \sum_{k \neq k'} (n_{a_k} n_{a_{k'}} + n_{b_k} n_{b_{k'}}) - \frac{K}{2} \sum_{k \neq k', \sigma} (n_{a_k\sigma} n_{a_{k'}\sigma} + c_{a_k\sigma}^{\dagger} c_{a_{k'}-\sigma} + c_{a_{k'}-\sigma}^{\dagger} c_{a_k\sigma} + n_{b_k\sigma} n_{b_{k'}\sigma} + c_{b_k\sigma}^{\dagger} c_{b_{k'}-\sigma} + c_{b_{k'}-\sigma}^{\dagger} c_{b_k\sigma}) \quad (21)$$

Again the terms in j (ferromagnetic interaction terms) are omitted for simplicity. U is the electron-electron repulsion between two different orbitals on the same site. K is the local exchange integral. Introduction of K is essential to get local high-spin ground states. The eigenvalues of H_0 are given in Figure 5. We will work in the ground space \mathbf{E}_0 of dimension 12, one basis of which is given in Table II. \mathbf{E}_0 is the ground state because we assume that the difference in energy between local orbitals ($\delta = \alpha_2 - \alpha_1$) is smaller than the local exchange integral K : This assumption corresponds to local high-spin state. The excitation energy of subspace \mathbf{E}_1 is $U_0 - U + K$. It contains states with two electrons in orbital a_1 (b_1) and one electron in b_2 (a_2). \mathbf{E}_0 will be connected to \mathbf{E}_1 through β_1 . States belonging to \mathbf{E}_2 are spin singlet on A (or B) with a_1 and a_2 (or b_1 and b_2) half-occupied. \mathbf{E}_0 is connected to \mathbf{E}_2 through β_2 . The \mathbf{E}_2 excitation energy is $2K$. Note that in mixed-valence systems the excited configurations perturbing the ground subspace are at a much lower energy ($2K$ or $U_0 - U + K$) than in homovalent systems (U_0). One can remark that \mathbf{E}_0 is connected through β_1 to \mathbf{E}_3 , which has an excitation energy equal to $U_0 + U$; this energy is about twice that occurring in non-mixed-valence systems. In the following calculation, we neglect the influence of \mathbf{E}_3 .

The effective Hamiltonian will be

$$H_{\text{eff}} = P_0 V P_0 - P_0 \left(\frac{V_1 P_1 V_1}{U_0 - U + K} + \frac{V_2 P_2 V_2}{2K} \right) P_0 \quad (22)$$

where $V_i = \sum_{\sigma} \beta_i (c_{a_i\sigma}^{\dagger} c_{b_i\sigma} + c_{b_i\sigma}^{\dagger} c_{a_i\sigma})$.

The first-order term is nonzero since V_2 connects functions inside \mathbf{E}_0 . We will see later that this very term will give rise to the transfer term in the spin Hamiltonian.

This first-order term can be written $\beta_2 P_0 t_{AB} P_0$ where

$$t_{AB} = \sum_{\sigma} (c_{a_2\sigma}^{\dagger} c_{b_2\sigma} + c_{b_2\sigma}^{\dagger} c_{a_2\sigma}) \quad (23)$$

Note that t_{AB} is not directional: The transfer occurs either from A to B or from B to A.

Using the same type of calculation as above, we can show that

$$P_0 V_2 P_2 V_2 P_0 = P_0 \frac{\beta_2^2}{2} \left(\frac{1}{2} - 2s_{a_2} \cdot s_{b_1} + \frac{1}{2} - 2s_{b_2} \cdot s_{a_1} \right) P_0 \quad (24)$$

$$P_0 V_1 P_1 V_1 P_0 =$$

$$P_0 \beta_1^2 \left(\left\{ \frac{1}{2} - 2s_{a_2} \cdot s_{b_1} \right\} n_{a_2} + \left\{ \frac{1}{2} - 2s_{b_1} \cdot s_{a_1} \right\} n_{b_2} \right) P_0 \quad (25)$$

Inside subspace \mathbf{E}_0 , s_{a_1} (s_{b_1}) and s_{a_2} (s_{b_1}) are coupled to give S_A (S_B) with the maximum value ($S_A = S_B = 1$) so that one has

TABLE II. Correspondence between Subspace E_0 Made of Spin Orbital Functions and Subspace E_0^S Made of Spin Functions $|S_A, m_A; S_B, m_B\rangle$ for a Two-Center, Two-Orbitals per Center, Three-Electron Problem

total moment	subspace E_0		subspace E_0^S	
	extra e^- on A	extra e^- on B	extra e^- on A	extra e^- on B
$+3/2$	$ a_1\alpha b_1\alpha a_2\alpha\rangle$	$ a_1\alpha b_1\alpha b_2\alpha\rangle$	$ 1, +1; 1/2, +1/2\rangle$	$ 1/2, +1/2; 1, +1\rangle$
$+1/2$	$ a_1\alpha b_1\beta a_2\alpha\rangle$	$ a_1\beta b_1\alpha b_2\alpha\rangle$	$ 1, +1; 1/2, -1/2\rangle$	$ 1/2, -1/2; 1, +1\rangle$
$+1/2$	$[a_1\alpha b_1\alpha a_2\beta\rangle + a_1\beta b_1\alpha a_2\alpha\rangle]/\sqrt{2}$	$[a_1\alpha b_1\alpha b_2\beta\rangle + a_1\alpha b_1\beta b_2\alpha\rangle]/\sqrt{2}$	$ 1, 0; 1/2, +1/2\rangle$	$ 1/2, +1/2; 1, 0\rangle$
$-1/2$	$ a_1\beta b_1\alpha a_2\beta\rangle$	$ a_1\alpha b_1\beta b_2\beta\rangle$	$ 1, -1; 1/2, +1/2\rangle$	$ 1/2, +1/2; 1, -1\rangle$
$-1/2$	$[a_1\alpha b_1\beta a_2\beta\rangle + a_1\beta b_1\beta a_2\alpha\rangle]/\sqrt{2}$	$[a_1\beta b_1\alpha b_2\beta\rangle + a_1\beta b_1\beta b_2\alpha\rangle]/\sqrt{2}$	$ 1, 0; 1/2, -1/2\rangle$	$ 1/2, -1/2; 1, 0\rangle$
$-3/2$	$ a_1\beta b_1\beta a_2\beta\rangle$	$ a_1\beta b_1\beta b_2\beta\rangle$	$ 1, -1; 1/2, -1/2\rangle$	$ 1/2, -1/2; 1, -1\rangle$

$$-P_0 \left\{ \frac{V_1 P_1 V_1}{U_0 - U + K} + \frac{V_2 P_2 V_2}{2K} \right\} P_0 = P_0 J_0 [1 - S_A \cdot s_{b_1} - S_B \cdot s_{a_1}] P_0 \quad (26)$$

with

$$J_0 = -\frac{\beta_2^2}{4K} - \frac{\beta_1^2}{U_0 - U + K} + 2j \quad (27)$$

Finally

$$H_{\text{eff}} = \beta_2 P_0 t_{AB} P_0 + P_0 J_0 (1 - S_A \cdot s_{b_1} - S_B \cdot s_{a_1}) P_0 \quad (28)$$

Again we can establish a correspondence between the subspace E_0 and a spin space E_0^S (Table II). An equivalent operator to the second term of eq 28 will be $-J_0(S_A \cdot S_B O_A + S_A \cdot S_B O_B)$. As for the first term of eq 28, the simplest form of the equivalent operator is found in a new basis for E_0^S : The basis of E_0^S given in Table II can be changed into the spin-adapted basis built on functions

$$|(S_A^0 s_A) S_A = S_A^0 + s_A, S_B^0, S\rangle = |S_A, S_B, S\rangle^A \quad (29)$$

and

$$|(S_A^0, (S_B^0 s_B) S_B = S_B^0 + s_B, S\rangle = |S_A, S_B, S\rangle^B \quad (30)$$

s_i refers to the spin of the traveling electron ($s_i = 1/2$) when it is on center i . S_i^0 corresponds to the core spin of center i . The core spin is defined as the highest local spin diminished of s_i ; here, $S_A^0 = S_B^0 = 1/2$. Let us introduce t_{AB}^S such as

$$t_{AB}^S |(S_A^0 s_A) S_A = S_A^0 + s_A, S_B^0, S\rangle = |(S_A^0 s_B) S_A = S_A^0 + s_B, S_B^0, S\rangle = \frac{S + 1/2}{2S^0 + 1} |(S_A^0, (S_B^0 s_B) S_B = S_B^0 + s_B, S\rangle + \frac{[(2S^0 + S + 3/2)(2S^0 + 1/2 - S)]^{1/2}}{2S^0 + 1} |(S_A^0, (S_B^0 s_B) S_B = S^0 - s_B, S\rangle \quad (31)$$

t_{AB}^S moves the electron from A to B, with the electron remaining coupled to S_A^0 . Then, we have to recouple the spin of the extra electron with S_B^0 . It is a three-spin problem that has been solved with Racah coefficients by Anderson and Hasegawa.⁵⁸

In our perturbational approach, we work in the E_0^S subspace and we have to project the preceding equation in this subspace. To do so, we introduce

$$T_{AB} = (2S^0 + 1) P_0^S t_{AB}^S P_0^S \quad (32)$$

such that

$$T_{AB} |(S_A^0 s_A) S_A = S_A^0 + s_A, S_B^0, S\rangle = (S + 1/2) |(S_A^0, (S_B^0 s_B) S_B = S_B^0 + s_B, S\rangle \quad (33)$$

P_0^S is the projector in the subspace E_0^S so that the term in $S_B = S_B^0 - s_B$ is canceled out. Finally we find (18) as equivalent operator with

$$B = \frac{\beta_2}{2S^0 + 1} \quad (34)$$

J_0 depends on β_1 and β_2 , but B depends on β_2 only. So electron-transfer intensity (B) and the one of electron exchange (J_0) are independent in such a case.

1. Effects of Asymmetry

It has to be emphasized that all the states in Figure 4a,b are fully delocalized. In actual systems, the valences may be trapped due to static differences between the two sites.

Such effects can be reproduced by introducing in (18) different E_A and E_B for the total energies of the system when the extra electron is on A or B, respectively. We have

$$H_S = BT_{AB} - J_0 \{ (S_A \cdot S_B + E_A) O_A + (S_A \cdot S_B + E_B) O_B \} \quad (35)$$

$E_A - E_B$ will be a trapping parameter, the effect of which will depend on $B(S + 1/2)/|E_A - E_B|$. It is clear that the $S = 1/2$ state will be 5 times more sensitive to trapping than the $S = 9/2$ state. This explains the localization of the strongly antiferromagnetically coupled mixed-valence dimers.

If $|E_B - E_A| \gg |B|$, we can consider BT_{AB} as a perturbation so that (we assume that $E_A < E_B$)

$$E(A) = E_A - 1/2 J_0 S(S + 1) - \frac{B^2(S + 1/2)^2}{|E_A - E_B|} \quad (36)$$

As $(S + 1/2)^2 = S^2 + S + 1/4$, we see that in this limit the double-exchange term reduces to Heisenberg coupling with

$$J_{\text{eff}} = J_0 + 2 \frac{B^2}{|E_A - E_B|} \quad (37)$$

Double exchange gives a ferromagnetic contribution to spin coupling.

Hamiltonian 35 has an important consequence on hyperfine coupling.¹²⁸ Hyperfine coupling is represented by the Hamiltonian

$$H_{\text{hf}} = a_A S_A \cdot I_A + a_B S_B \cdot I_B \quad (38)$$

In general, it can be considered as a perturbation on the solutions of the exchange Hamiltonian and is equivalent to

$$H_{\text{hf}} = A_A^S S \cdot I_A + A_B^S S \cdot I_B \quad (39)$$

with

$$A_A^S = a_A \frac{S(S+1) + S_A(S_A+1) - S_B(S_B+1)}{2S(S+1)} \quad (40)$$

and

$$A_B^S = a_B \frac{S(S+1) + S_B(S_B+1) - S_A(S_A+1)}{2S(S+1)} \quad (41)$$

Now for a mixed-valence pair with delocalization the general expression of the ground state wave function will be

$$|S\rangle = c_A |S\rangle^A + c_B |S\rangle^B \quad (42)$$

c_A and c_B depend on B , E_A , E_B , and S .

It is easy to show that now

$$\begin{aligned} A_A^S &= c_A^2 A_A^S + (1 - c_A^2) B A_A^S \\ A_B^S &= c_A^2 A_B^S + (1 - c_A^2) B A_B^S \end{aligned} \quad (43)$$

where A_k^S stands for hyperfine coupling of center k when the extra electron is on center i for a pair of spin S . When the valences are trapped, we find again eq 40. When the valences are fully delocalized ($c_A^2 = 0.5$, for a symmetrical dinuclear site), we find two equivalent centers with $A_A^S = A_B^S = (A_A^S + A_B^S)/2$. Whatever the delocalization, we have the sum rule $A_A^S + A_B^S = A_A^S + A_B^S$.

Those relations allow us to understand evolution of the hyperfine interaction as a function of delocalization.

2. Vibronic Effects and Dynamic Behavior

One possible origin of asymmetry is vibronic coupling. Using

$$\begin{aligned} E_A &= \frac{1}{2} k q_A^2 + \frac{1}{2} k q_B^2 + \lambda q_A \\ E_B &= \frac{1}{2} k q_A^2 + \frac{1}{2} k q_B^2 + \lambda q_B \end{aligned} \quad (44)$$

one finds⁶³ after simple calculations

$$E_{\pm}(S) = -\frac{1}{2} J_0 S(S+1) + \frac{\lambda^2 x_{\pm}^2}{2k} \pm \left[\frac{\lambda^4 x_{\pm}^2}{2k^2} + B^2(S + \frac{1}{2})^2 \right]^{1/2} \quad (45)$$

Now instead of two curves they are as many as twice the number of spin states.

If $|B(S+0.5)| < \lambda^2/2k$, the $E_{\pm}(S)$ curve has two minima and the energy of the intervalence band is

$$E_{op}(S) = \frac{\lambda^2}{k} \quad (46)$$

This value is independent of S , but the transition moment is spin-dependent with its value given by substituting $|B|(S + 1/2)$ to β in eq 14. The activation energy is also spin-dependent

$$E_{\theta}(S) = \frac{\lambda^2}{4k} + \frac{B^2(S + 1/2)^2}{\lambda^2/k} - |B|(S + 1/2) \quad (47)$$

which corresponds to a greater difficulty to delocalize for antiferromagnetic coupling than for a ferromagnetic coupling. If $|B(S+0.5)| > \lambda^2/2k$, the $E_{\pm}(S)$ curve has its minimum at $x_{\pm} = 0$; in such a case, the energy of the intervalence band is spin-dependent and equal to

$$E_{op}(S) = 2|B|(S + 1/2) \quad (48)$$

The transition moment is equal to $R^2/4$. If the condition $|B(S+0.5)| < \lambda^2/2k$ was obeyed for all S values, we found⁶³ that the energies of the minima are such that they obey the Heisenberg Hamiltonian with a new coupling parameter

$$J_{\text{eff}} = J_0 + \frac{2B^2}{\lambda^2/k} \quad (49)$$

which can be also deduced from (37), noting that $|E_A - E_B| = \lambda^2/k$. Then, the intervalence band will be unique and its effective transition moment is obtained by the Boltzmann distribution of transition moments for each spin state

$$M^2 = \frac{R^2 B^2 \sum_S (S + 1/2)^2 (2S + 1) \exp\left[-\frac{E(S)}{kT}\right]}{(\lambda^2/k)^2 \sum_S (2S + 1) \exp\left[-\frac{E(S)}{kT}\right]} \quad (50)$$

with $E(S) = -J_{\text{eff}} S(S+1)/2$. An analogous formula had been obtained by Cox in ref 126.

One can suppose that cases could exist where the states with the highest spin value will be delocalized and the ones with the lowest spin value will be localized (see below). For those cases, eq 45 has to be used to find the energies of the states. Several intervalence bands could then be observed, with intensities reflecting transition moments and thermal populations of the spin levels.

Effects of vibrations have also been studied in refs 68 and 69.

3. Applications

In our model, the interpretation of electronic properties of magnetic mixed-valence systems needs three parameters: B , J_0 , and λ^2/k . They are related to $E_{op}(S)$, J_{eff} (if all the states are localized), M^2 , and $E_{\theta}(S)$ through the preceding equations. In the following, we will try to extract the B , J_0 , and λ^2/k values from data recently reported.

Iron-Oxo Systems. Recently Wieghardt's group⁷⁰ isolated the Fe(II)Fe(III) species $[L_2Fe_2(\mu-OH)_3](ClO_4)_2 \cdot 2MeOH \cdot 2H_2O$ (1) with $L = N, N', N''$ -trimethyl-1,4,7-triazacyclononane. The valences in this compound are delocalized. The ground state is $S = 9/2$, and a strong intervalence band is observed at 758 nm (13193 cm^{-1}) with $M^2 = 0.30 \text{ \AA}^2$ at room temperature in CH_3CN .

From $E_{op} = 10|B|$, one can find⁷¹ $|B| = 1320 \text{ cm}^{-1}$. The calculated $M^2 = R^2/4 = 1.6 \text{ \AA}^2$ is too high, but this seems to be a common feature of the formula. It is perhaps related to the fact that, due to delocalization of the electron on the bridge, the center of the electron distribution of orbital a (or b) is not exactly located on center A (or B) but displaced toward the bridging ligands, which leads to an effective R value smaller than the AB distance. If we assume that the vibronic coupling is the same as in other Fe(II)Fe(III)-oxo dinuclear species ($\lambda^2/k = 7722 \text{ cm}^{-1}$),⁷³ then the criterion for delocalization ($5|B| > (\lambda^2/2k)$) is met, which corresponds to experiment. Unhappily, no excited state has been observed, so nothing is known on J_0 except that it has to be greater than⁷¹ $-2|B|/9 = -293 \text{ cm}^{-1}$. It seems from

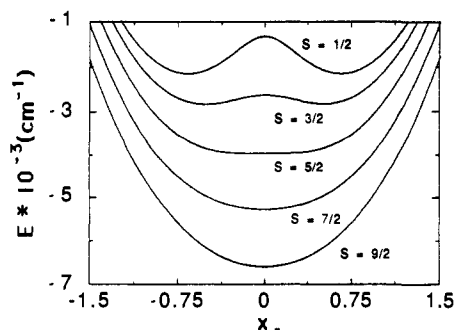


Figure 6. Proposed potential energy curves for the lowest states of $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3](\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ (1) (see text for nomenclature), an Fe(III)Fe(II) unit synthesized in ref 70. Energy (cm^{-1}) as a function of the antisymmetric reduced normal coordinate x_- with $\lambda^2/k = 7722 \text{ cm}^{-1}$; $B = 1320 \text{ cm}^{-1}$; J_0 has been arbitrarily set to zero.

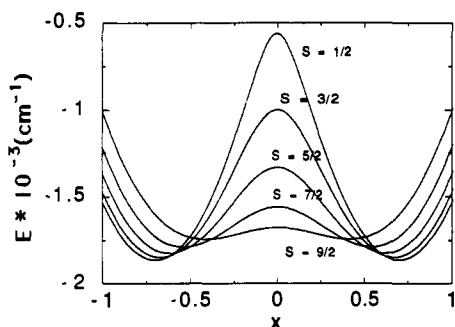


Figure 7. Proposed potential energy curves for the lowest states of $[\text{Fe}_2\text{BPMP}(\text{RCO}_2)_2]^{2+}$ (2) (see text for nomenclature), an Fe(II)Fe(III) unit synthesized in ref 72. Energy (cm^{-1}) as a function of the antisymmetric reduced normal coordinate x_- with $\lambda^2/k = 7420 \text{ cm}^{-1}$; B has been arbitrarily set to 600 cm^{-1} ; $J_0 = -107 \text{ cm}^{-1}$ such that $J_{\text{eff}} = -10 \text{ cm}^{-1}$ through eq 49.

preliminary magnetic susceptibility data,⁷⁰ which indicate at room temperature the right value for a spin $S = 9/2$ state, that J_0 is such that an important gap exists between the ground state and the first excited state.

Setting $J_0 = 0$ and using $|B| = 1320 \text{ cm}^{-1}$ and $\lambda^2/k = 7722 \text{ cm}^{-1}$, we built the theoretical curves of Figure 6. We see that, with those values of $|B|$ and λ^2/k , the $S = 9/2$ state is indeed delocalized. Delocalization in higher states diminishes with spin in such a way that $S = 1/2$ and $S = 3/2$ are predicted to be valence-trapped.

More experimental data are deeply needed to test our proposed energy scheme.

Que's group⁷² published a detailed study on another Fe(II)Fe(III)-oxo compound: $[\text{Fe}_2\text{BPMP}(\text{RCO}_2)_2]^{2+}$ (2), where BPMP stands for the anion of 2,6-bis[bis(2-pyridylmethyl)amino)methyl]-4-methylphenol. For this complex they observed an intervalence band at 7420 cm^{-1} with a transition moment equal to 0.09 \AA^2 at room temperature in CH_3CN . From NMR the spin-coupling parameter has been evaluated to $J_{\text{eff}} = -10 \text{ cm}^{-1}$. A measurement of the magnetic properties from helium temperature to room temperature would be useful to check the validity of the Heisenberg Hamiltonian in this system. At 55 K in CH_3CN solution, the system is valence-trapped in Mössbauer spectroscopy. Those experimental facts suggest that $\lambda^2/k = 7420 \text{ cm}^{-1}$. If we assume that all the spin states are represented by a two-minima curve, then we can compute from the transition moment of the intervalence band that $|B| > 171 \text{ cm}^{-1}$ and from the existence of two minima in the

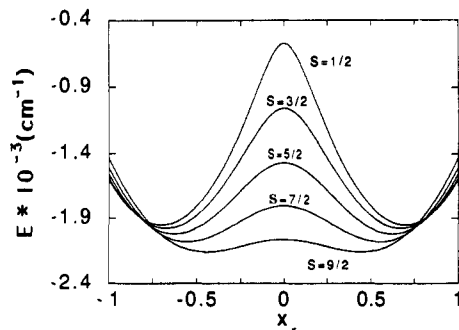


Figure 8. Proposed potential energy curves for the lowest states of $[\text{Fe}_2(\text{salmp})_2]^-$ (3) (see text for nomenclature), an Fe(II)Fe(III) unit synthesized in ref 73. Energy (cm^{-1}) as a function of the antisymmetric reduced normal coordinate x_- with $\lambda^2/k = 7722 \text{ cm}^{-1}$; B has been arbitrarily set to 600 cm^{-1} ; $J_0 = -76 \text{ cm}^{-1}$ such that $J_{\text{eff}} = +17.2 \text{ cm}^{-1}$ through eq 49.

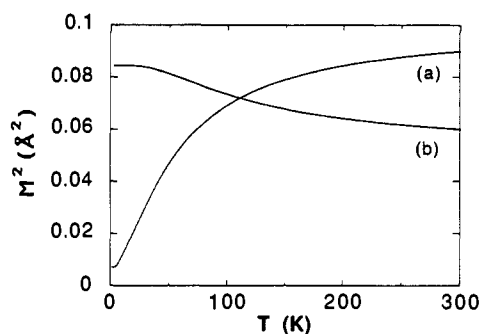


Figure 9. Proposed dependence on temperature (K) of the intensity (square of the transition moment in \AA^2) of the intervalence band: (a) for $[\text{Fe}_2(\text{salmp})_2]^-$ (3) ($J_{\text{eff}} = +17.2 \text{ cm}^{-1}$); (b) for $[\text{Fe}_2\text{BPMP}(\text{RCO}_2)_2]^{2+}$ (2) ($J_{\text{eff}} = -10 \text{ cm}^{-1}$) from eq 50.

$S = 9/2$ state that $5|B| < \lambda^2/2k$, which gives $|B| < 742 \text{ cm}^{-1}$. The $|B|$ value is thus rather uncertain but seems definitely smaller than for compound 1. Figure 7 shows the predicted energy levels under the assumption $|B| = 600 \text{ cm}^{-1}$. One can remark by looking at Figure 7 how the activation energy for thermal transfer is expected to increase with decreasing spin.

Recently Holm's group⁷³ synthesized another Fe(I-III)Fe(III) dinuclear unit: $[\text{Fe}_2(\text{salmp})_2]^-$ (3), where salmp = 2-bis(salicylideneamino)methylphenolate(3-). It was found ferromagnetic with $J_{\text{eff}} = +17.2 \text{ cm}^{-1}$ and having an intervalence band close to the value observed in the preceding compound, $E_{\text{op}} = 7722 \text{ cm}^{-1}$. From the published spectrum at room temperature in DMF, one can estimate $\epsilon_{\text{max}} = 400 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Delta_{1/2} = 2500 \text{ cm}^{-1}$, which gives $M^2 = 0.06 \text{ \AA}^2$, which is of the same order as in compound 2. The $|B|$ limits are the same as before, and the value of $|B|$ is still uncertain. Detrapping has been observed by Mössbauer spectroscopy,⁷⁴ and this occurs perhaps in the $S = 9/2$ state. In Figure 8, calculated energy levels are represented with $|B| = 600 \text{ cm}^{-1}$.

It is clear that more experimental information is needed to establish firmly our theoretical description; we expect that optical studies as a function of temperature could be very useful in that respect. For instance, with eq 50 with $J_{\text{eff}} = -10 \text{ cm}^{-1}$ for compound 2, the transition moment is expected to decrease with temperature (Figure 9a). On the other hand, taking $J_{\text{eff}} = +17.2 \text{ cm}^{-1}$ for compound 3, M^2 is predicted to increase when the temperature decreases (Figure 9b).

Iron-Sulfur Systems. $[\text{Fe}_2\text{S}_2]^+$ contains an Fe(I-III)Fe(III) pair with $J_{\text{eff}} = -166 \text{ cm}^{-1}$.⁷⁵ From Mössbauer

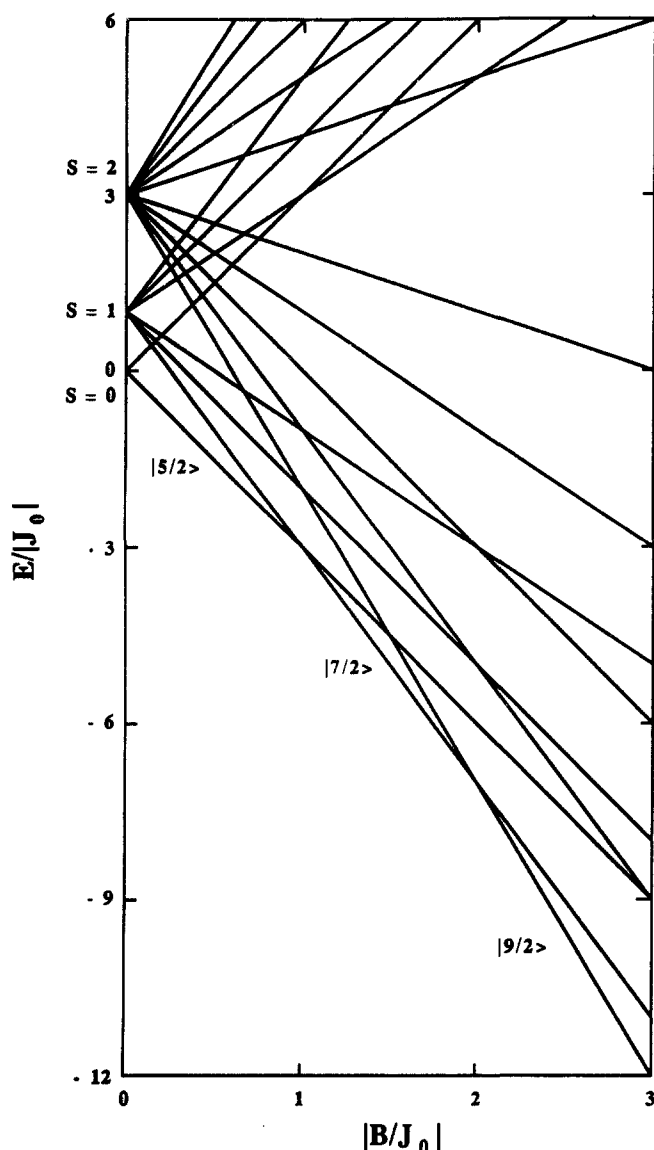


Figure 10. Energy level diagram for reduced Fe_3S_4 cluster according to eq 52 plotted for antiferromagnetic ($J_0 < 0$) Heisenberg exchange. The spin labels refer to S_{AB} . For $|B/J_0| > 2$ the system ground state has $S = 2$ and $S_{AB} = 9/2$. The extra electron was allowed to delocalize between sites A and B only.

spectroscopy⁷⁶ the valences are trapped: $\delta = 0.3$ mm/s for Fe(III) and $\delta = 0.7$ mm/s for Fe(II). The intervalence band has not yet been identified. It seems that here J_0 is quite negative and imposes spin antialignment, which then imply easy localization either by a vibronic process or by a static effect. The intrinsic localization experimentally observed¹²⁴ for this system would be, following this theory, a consequence of its strong antiferromagnetic coupling (see also ref 65).

In conclusion on Fe(II)Fe(III) systems, compound 1 from Wieghardt's group is the only one that is a good candidate to exhibit double exchange; in the others, valence trapping seems to restaure the characteristic $S(S + 1)$ dependence of the energy on the spin value.

Manganese-Oxo Systems. Known Mn(III)Mn(IV) pairs are strongly antiferromagnetic.^{77,78} The compound $[(2,2'\text{-bipy})_2\text{MnO}_2\text{Mn}(2,2'\text{-bipy})_2]^{3+}$ (4) has been studied in detail.^{78,79} The intervalence band occurs at 830 nm with $M^2 = 0.07 \text{ \AA}^2$ at room temperature in water. From EPR the valences seem localized. The spin-coupling parameter is $J_{\text{eff}} = -300 \text{ cm}^{-1}$. From the localized

character of the spin $S = 1/2$ ground state, we can deduce $|B| < \lambda^2/2k = 6000 \text{ cm}^{-1}$. It is not clear if the 830-nm band corresponds to a transition between $S = 1/2$ states only or if it includes the transition between $S = 3/2$ states. In the first case, the intervalence band must increase in intensity by cooling. In the second case, it will decrease on cooling. From a preliminary report¹²⁷ of the increase of the intervalence band intensity when temperature decreases, we can deduce that this intervalence band is due to spin $S = 1/2$ only. The $S = 3/2$ intervalence band has to be at a shorter wavelength than 830 nm; its intensity could be low due to the small population of the spin $S = 3/2$ state at room temperature.

As for other metal ions, we have already proposed a double exchange based explanation of the parallel alignment of the spins in a Ni(II)Ni(I) pair.⁶³

B. Trinuclear Sites

$[\text{Fe}_3\text{S}_4]^0$ contains two Fe(III) ions and one Fe(II) ion. Mössbauer spectroscopy³² has identified one delocalized Fe(II)Fe(III) pair and one Fe(III) ion. The spin value of the ground state has been found equal to $S = 2$, and the subspin of the mixed-valence pair has been found equal to $S_{\text{Fe(II)Fe(III)}} = 9/2$. The spin alignment observed for this Fe(II)Fe(III) pair is in strong contrast with the spin antialignment observed in $[\text{Fe}_2\text{S}_2]^+$ sites. The isomer shift of the isolated Fe(III) is $\delta = 0.32$ mm/s, and for the delocalized pair, it is $\delta = 0.46$ mm/s. We have suggested that in $[\text{Fe}_2\text{S}_2]^+$ cores the antiferromagnetic J_0 parameter imposes easy localization. Why, in a trimer that seems to be also strongly antiferromagnetically coupled, does delocalization in a pair occur? This is related to spin frustration in a triangular array of spins. In such a system it is impossible to strictly antialign the three spins: The lowest possible spin of this triad is spin $S = 0$ with subspin $S_{\text{Fe(II)Fe(III)}} = 5/2$. Then, the mixed-valence pair presents at least the delocalization energy $3|B|$, and delocalization will be already greater than for $[\text{Fe}_2\text{S}_2]^+$ ($S_{\text{Fe(II)Fe(III)}} = 1/2$) sites.

Quantitatively we have proposed to explain this situation by the Hamiltonian

$$H_S = BT_{AB} - J_0(S_A \cdot S_B + S_B \cdot S_C + S_C \cdot S_A)O_A - J_0(S_A \cdot S_B + S_B \cdot S_C + S_C \cdot S_A)O_B \quad (51)$$

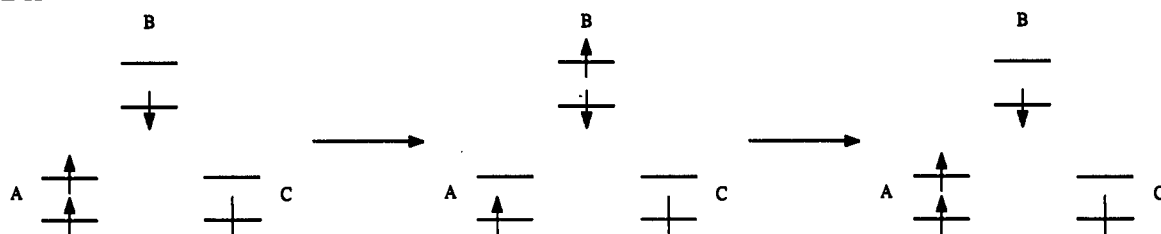
where we assume for simplicity that all the J_0 's are the same. The delocalization occurs on side AB.

The eigenvalues of eq 51 are

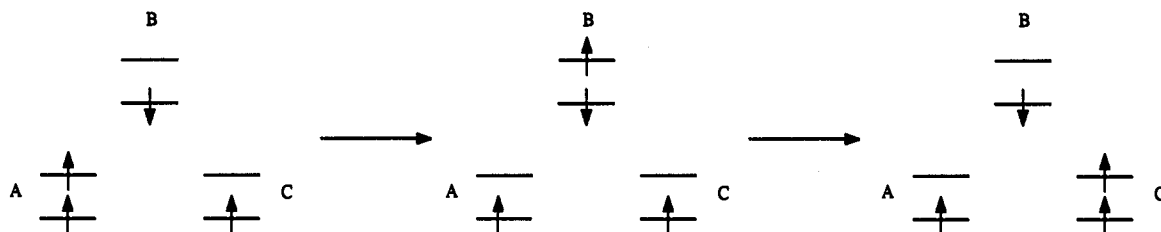
$$E = -1/2 J_0 S(S + 1) \pm B(S_{AB} + 1/2) \quad (52)$$

Those energies are represented in Figure 10. We see that the lowest state will be the $S = 2$, $S_{AB} = 9/2$ observed experimentally. We proposed that $|B|$ must be large enough versus $|J_0|$ in order to have the $S = 2$ ground state. It is worth noting that a $|B/J_0|$ value of 2.5 for instance is enough to give an $S = 2$ value for the spin of the ground state of the triad (with subspin $S_{AB} = 9/2$) but that the same value is unable to stabilize the $S_{AB} = 9/2$ in a pair. We understand why, in a triad, the mixed-valence spins can be aligned in spite of an antiferromagnetic J_0 interaction and why the mixed-valence pair becomes delocalized. Delocalization of the mixed-valence pair in triads is due to a conjunction of double exchange and spin frustration.

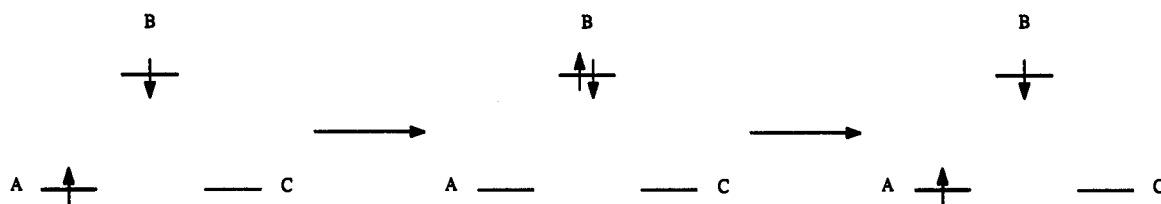
SCHEME II



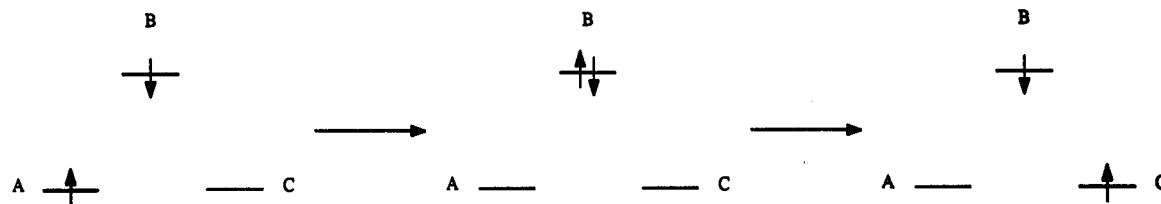
SCHEME III



SCHEME IV



SCHEME V



B and J_0 values have been calculated in ref 125 by $X\alpha$ theory.

Borshch et al.⁸⁰ have proposed that the existence of only one B could be only an appearance and that in fact this problem would be a three- B (one per side) problem. He has shown that vibronic interactions in an "equilateral" triangle can lead for some values of the parameters B , λ^2/k and J_0 to delocalization in a pair. "Equilateral" triangles have been also studied by Belinskii⁸¹ as a function of B and J_0 .

For systems of nuclearity greater than 2, we have discovered⁶⁷ an extra complication we have called exchange transfer. Detailed information can be found in ref 67. In a few words we can say the following.

We take the example of an equilateral triangle with two electrons on A and one electron on B and C each. We consider two orbitals on each center; the lowest space will be made of functions of type $|a_1\alpha b_1\sigma c_1\sigma' a_2\alpha\rangle$ where the local ground state on A (or B or C) is a spin triplet. In the framework of the preceding theory, the part of the exchange phenomenon depending on β_2 (see eq 27) corresponds to a transfer of the extra electron from A to B giving an excited local singlet on B (excitation energy $2K$), the itinerant electron moving back to A (Scheme II).

A new effect can appear since we have more than two centers: Instead of going back to A , the electron can move to C (Scheme III).

The result will be a transfer from A to C through an interaction on site B . This will give a third term in the Hamiltonian we called the exchange-transfer term. We are currently investigating the quantitative importance of this term.

It can also exist in mixed-valence systems with only one orbital per site (as soon as there are two moving electrons) like $\text{Ru(II)Ru(III)Ru(III)}$ or $\text{Cu(II)Cu(II)-Cu(III)}$ (Schemes IV and V).

The same effect has been proposed independently by Hirsch in ref 82. It has been invoked by Huang and Manousakis¹³¹ in their studies of high-temperature superconductivity.

$\text{M}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{RCO}_2)_6\text{L}_3$ systems (L = nitrogenous ligand, $M = \text{Fe}^{121}$ or Mn^{122}) have been studied and reviewed in ref 123. No double-exchange effects have been detected in those systems.

C. Tetranuclear Sites

Four iron-sulfur clusters can be studied with the exchange-double exchange spin Hamiltonian. We limit our studies to a very simple approach because we feel that a description exploring the effects of exchange transfer and vibronic interactions has not yet been given.

The less difficult problem is perhaps encountered in the $3\text{Fe(III)}-1\text{Fe(II)}$ cubes. Experimentally⁸³ those

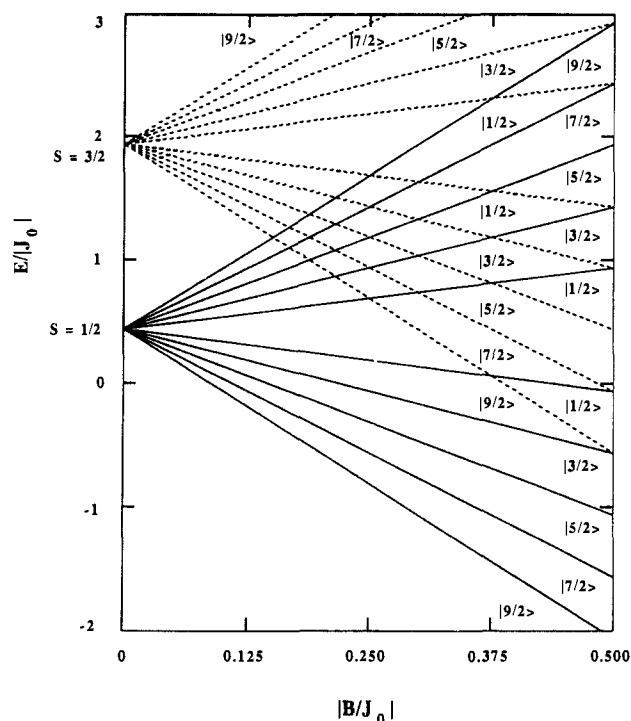


Figure 11. Energy level diagram for an Fe_4S_4 cluster (3 Fe(III)-1 Fe(II)) according to eq 54 plotted for antiferromagnetic ($J_0 < 0$) Heisenberg exchange. The spin labels refer to S_{AB} . For $S = 1/2$ one has for S_{AB}, S_{CD} the following values: $9/2, 5$ or $4; 7/2, 4$ or $3; 5/2, 3$ or $2; 3/2, 2$ or $1; 1/2, 1$ or 0 . For $S = 3/2$ one has for S_{AB}, S_{CD} the following values: $9/2, 3-5; 7/2, 2-5; 5/2, 1-4; 3/2, 0-3; 1/2, 2$ or 1 . Whatever $|B/J_0|$ is, the system ground state has $S = 1/2$ and $S_{AB} = 9/2$ with $S_{CD} = 4$ or 5 . The extra electron was allowed to delocalize between sites A and B only.

systems exhibit two pairs: one with pronounced Fe(III) character ($\delta = 0.34$ mm/s) and the other with Fe(2.5+) character ($\delta = 0.40$ mm/s). The Fe(III)Fe(II) pair has nevertheless more Fe(III) character than the delocalized pair observed in the $[\text{Fe}_3\text{S}_4]^0$ triad ($\delta = 0.46$ mm/s). This suggests that interpair delocalization occurs. The problem seems to be a more than one B problem. The ground state has $S = 1/2, S_{AB} = 9/2$, and $S_{CD} = 4$.

Nevertheless, to give a simple description, we assume that one B is greater than the others and will dominate the electronic behavior of the cluster. Then, we will use the following spin Hamiltonian, assuming again for simplicity identical exchange coupling constants

$$H_S = BT_{AB} - J_0(S_A \cdot S_B + S_A \cdot S_C + S_A \cdot S_D + S_B \cdot S_C + S_B \cdot S_D + S_C \cdot S_D)O_A - J_0(S_A \cdot S_B + S_A \cdot S_C + S_A \cdot S_D + S_B \cdot S_C + S_B \cdot S_D + S_C \cdot S_D)O_B \quad (53)$$

the solutions of which are

$$E = -1/2 J_0 S(S + 1) \pm B(S_{AB} + 1/2) \quad (54)$$

They are represented in Figure 11. We see that through the effect of double exchange the potential ground states are $S_{AB} = 9/2$ and $S_{CD} = 4$ or 5 , whatever the ratio $|B/J_0|$ is. So we find the experimental spin ordering of two ferromagnetic pairs (despite $J_0 < 0$) antiferromagnetically related to give $S = 1/2$. Noodleman⁸⁴ has refined this model by taking into account different J_0 values to achieve the $S_{CD} = 4$ ground state.

As for reduced ferredoxins, Middleton et al.¹⁰⁸ have previously proposed an $|S_{AB} = 9/2, S_{CD} = 4, S = 1/2\rangle$ ground state on experimental grounds. Those reduced cubes present the peculiarity of having different possible ground state spin values either in biological sys-

tems^{76,109,133} or in chemical models.¹³² Theoretical investigations are currently pursued on those questions.

VI. Conclusion

Using accumulated knowledge on polynuclear complexes of biological relevance, we have summarized the main features of electron exchange and intracuster electron transfer.

We have also reviewed new results obtained on metal complexes, presenting simultaneously both phenomena. These are mixed-valence systems with both metal ions magnetic such as Fe(II)Fe(III) ($S_{\text{Fe(II)}} = 2, S_{\text{Fe(III)}} = 5/2$) or Mn(III)Mn(IV) ($S_{\text{Mn(III)}} = 2, S_{\text{Mn(IV)}} = 3/2$). Fe(II)-Fe(III) systems are encountered in iron-sulfur and -oxo proteins. Manganese systems are found in the oxygen-evolving complex of plants. Artificial complexes synthesized as models of those natural sites also offer the possibility to study the interplay of electron transfer and electron exchange.

For such systems, we proposed the following spin Hamiltonian:

$$H_S = BT_{AB} - J_0\{(S_A \cdot S_B + E_A)O_A + (S_A \cdot S_B + E_B)O_B\}$$

The first term represents the electron-transfer phenomenon (energetic parameter B), and the second one refers to the electron exchange (energetic parameter J_0).

The first term gives rise to an $S + 1/2$ dependence of the energy of the spin state S , which is characteristic of what has been called by Zener and Anderson double exchange.

This Hamiltonian can be called the exchange-double exchange spin Hamiltonian.

The energies of the system when the extra electron is on A (E_A) or B (E_B) will, when different, trap this extra electron.

When J_0 is an antiferromagnetic coupling, the solutions to this spin Hamiltonian correspond to a competition between the antiferromagnetic effect (which stabilizes low-spin states) and double exchange (which stabilizes high-spin states). When J_0 dominates, the spins prefer to be antiparallel and the system becomes very sensitive to localization. The result is a low-spin-trapped mixed-valence complex. When the effect of B dominates, the spins are preferentially parallel (despite the antiferromagnetic character of J_0) and localization is not as easy for the low-spin states. $[\text{Fe}_2\text{S}_2]^+$ or $[\text{Mn}_2\text{O}_2]^{3+}$ clusters have an $S = 1/2$ ground state, and the valences are trapped. On the other hand, in $[\text{L}_2\text{Fe}_2(\mu\text{-OH})_3](\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$, the B value is high and the system is delocalized and ferromagnetic.

Higher nuclearity clusters like $[\text{Fe}_3\text{S}_4]^0$ or $[\text{Fe}_4\text{S}_4]^{n+}$ can achieve a low value for the total spin with a parallel-spin Fe(II)Fe(III) pair; the valences are then delocalized. Would the Mn_4 cluster occurring in photosynthesis present double-exchange phenomenon? The answer is not known, but the fact that double-exchange ideas have been introduced in solid-state physics for Mn(III)Mn(IV) manganite systems is puzzling in that respect.⁵⁸

The role of exchange transfer in clusters of nuclearity higher than 2 has to be explored.

We also give some theoretical indications on intervalence bands in those magnetic mixed-valence systems, and it seems that optical studies (particularly as a function of temperature) will be very important in the near future to get more detail on the physics of those polynuclear complexes.

The biological roles of these physical phenomena in metal clusters in proteins are uncertain, but they are of utmost importance in understanding the spectroscopic properties of those systems and are of interest by themselves for physical-inorganic chemistry.

Moreover, chemists can be inspired by these unusual electronic properties and imagine new synthetic systems exhibiting spin alignment due to delocalization or ones in which electron transfer would be controlled by electron exchange. In both cases, novel optical properties could also be expected.

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Appendix

Second quantization is a useful computation technique especially when a model calculation has to be done. We summarize here, very briefly, the essential results. For an extended treatment, the reader may see, for example, ref 134.

A spin orbital basis ψ_1, \dots, ψ_i is supposed to exist. An N -electron wave function will be $|\psi_{i_1}, \psi_{i_2}, \dots, \psi_{i_N}\rangle$. Those kets are antisymmetrized. Then, creation c_i^+ and annihilation c_i operators, acting on the first place of the ket, are defined by the following rules:

$$c_i^+ |\psi_1, \dots, \psi_{i-1}, \psi_{i+1}, \dots, \psi_N\rangle = |\psi_i, \psi_1, \dots, \psi_{i-1}, \psi_{i+1}, \dots, \psi_N\rangle$$

$$c_i^+ |\psi_1, \dots, \psi_i, \dots, \psi_N\rangle = 0$$

$$c_i |\psi_1, \dots, \psi_i, \dots, \psi_N\rangle = (-1)^p |\psi_1, \dots, \psi_{i-1}, \psi_{i+1}, \dots, \psi_N\rangle$$

$$c_i |\psi_1, \dots, \psi_{i-1}, \psi_{i+1}, \dots, \psi_N\rangle = 0$$

where p corresponds to the number of permutations to bring ψ_i at the first place of the ket.

With such operators, the usual electronic Hamiltonian

$$H = \sum_{i=1}^N h_i + \sum_{i < j} \frac{1}{r_{ij}}$$

where h_i is the mono-electronic Hamiltonian and the last term is the repulsion between electrons can be rewritten as

$$H = \sum_{i,k} I_i^k c_i^+ c_k + \sum_{i,k,l,m} M_{lm}^{ik} c_i^+ c_k^+ c_m c_l$$

with

$$I_i^k = \int \psi_i^* h \psi_k \, d\tau \text{ and}$$

$$M_{lm}^{ik} = \int \psi_i^*(1) \psi_k^*(2) (1/r_{12}) \psi_l(1) \psi_m(2) \, d\tau_1 \, d\tau_2$$

It allows one to retain from the start the only integrals studied in the model. The operators obey the famous anticommutation rules $c_i c_k^+ + c_k^+ c_i = \delta_{ik}$ and $c_i c_k + c_k c_i = 0$. A useful operator is the spin orbital occupation operator $n_i = c_i^+ c_i$. One can check that $n_i c_i^+ = c_i^+$ and $c_i n_i = c_i$. An orbital occupation operator $n_a = n_{\alpha a} + n_{\beta a}$ can be defined for orbital a .

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