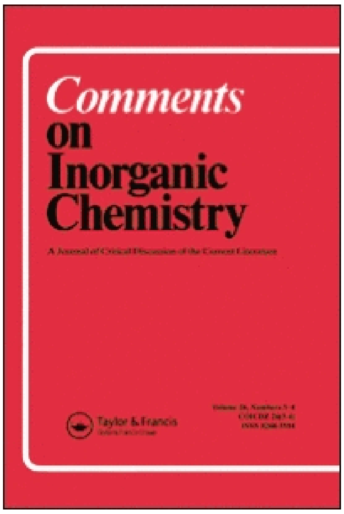

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When Must Double Exchange Be Used?

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When Must Double Exchange Be Used?

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Recently it has been suggested that thermal electronic properties of magnetic mixed valence systems have to be studied by using an effective Hamiltonian different from the Heisenberg one, so successful for localized electron systems. The object of this paper is to specify conditions of validity of both Hamiltonians. In the first part, the theory of electron exchange in systems with electrons localized by electron–electron repulsion is quickly reviewed. The second part summarizes the results demonstrated for mixed valence systems of class III: for these systems, $H_{\text{eff}} = H_e + H_t + H_{et}$, where H_t is the transfer Hamiltonian, H_e is the exchange (Heisenberg) one and H_{et} is what we call the exchange-transfer one. In the last part we explain that as vibrations can relocalize the moving electrons (class II mixed valence systems), H_{eff} can take again the form of the Heisenberg one at the minima of the potential surfaces but with a vibronic ferromagnetic contribution to the exchange parameter. At the saddle points, $H_{\text{eff}} = H_e + H_t$. This last observation allows us to rationalize the values of the activation energy for thermal electron transfer in these systems.

Key Words: *mixed valence systems, Heisenberg Hamiltonian, electron exchange, electron transfer, vibronic coupling*

Recently "double exchange" has been proposed to play a role in the electronic properties of some polynuclear complexes such as

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iron–sulfur clusters$^{1-7}$ and a Fe(II)Fe(III) tris-μ-hydroxo complex^{8,9} with a strongly stabilized $S = 9/2$ ground state. Here we would like to summarize differences between double exchange and electron exchange theories and explore when the double exchange concept has to be used and when it is not adequate.

The paper contains three "movements." In the first movement we summarize the theory of electron exchange, stressing that it is pertinent to systems in which electrons are localized by electron–electron repulsion. In the second movement, we explain that for delocalized systems a different theory has to be used. In the third movement, we show that localization by vibrations can lead back to electron exchange.

FIRST MOVEMENT: ELECTRON EXCHANGE

One Magnetic Orbital Per Site

The archetype of an electron exchange system is a Cu(II)Cu(II) dinuclear complex. In the states of lower energy, the electron distribution of such a complex corresponds faithfully to this oxidation state assignment. Focusing on the magnetic orbitals of this Cu(II)Cu(II) pair, we can give the following simple picture of its electron distribution:

Each magnetic orbital (which can be denoted by *a* and *b*) is populated by one single electron. This is so because the electron distribution corresponding to Cu(III)Cu(I) gives states of high energy. Such a state can be depicted by

and the origin of its high energy lies mainly in the repulsion of the two electrons when they are on the same site. Electrons repel each other and stay separate on different sites. This repulsion has been proposed by Mott, Hubbard[10] and Anderson[11] to be very important in determining the electronic properties of such systems. It is denoted by U_0.

The states of lower energy correspond to different mutual orientations of the spins; the different possible situations are represented in this simple model by two-electron wave functions $|ab\rangle$, $|a\bar{b}\rangle$, $|\bar{a}b\rangle$, $|\bar{a}\bar{b}\rangle$, which give rise to a spin singlet and a spin triplet state, the energy spectrum of which can be obtained through the use of the Heisenberg effective Hamiltonian:

$$H_{\mathrm{eff}} = -J_0 S_A \cdot S_B. \tag{1}$$

It is well understood[11] that $J_0 = -4\beta^2/U_0 + 2j$. β is the simple Hückel resonance integral and reflects the delocalization energy from one site to the neighbouring one. j is the exchange integral between orbitals a and b; it is positive and leads to ferromagnetic coupling if it dominates the first term.

As electrons stay on their center, the only change between wave functions is related, as pointed out above, to the values of the spin projections. So, very often, calculations are made with functions written as $|m_{S_A}, m_{S_B}\rangle$ but one has to remember that those wave functions are not pure spin functions but are indeed two electron complete wave functions with antisymmetry property in the permutation of two electrons.

Several Magnetic Orbitals Per Site

This theory can be extended to systems with more unpaired electrons per center as long as each electron stays on its center. In this case the Hamiltonian is the same as above with $S_A = n_A/2$ and $S_B = n_B/2$, n_A and n_B being the number of unpaired electrons on site A and B, respectively. The exchange energy can be decomposed into contributions J_{ij} between magnetic orbitals a_i and b_j following the relation

$$J_0 = \frac{1}{n_A n_B} \sum_{i,j} J_{ij}. \tag{2}$$

Each component J_{ij} can be written as

$$J_{ij} = -2\,\beta_{ij}^{2}\left[\frac{1}{\Delta_{i\rightarrow j}} + \frac{1}{\Delta_{i\leftarrow j}}\right] + 2j_{ij} \qquad (3)$$

where β_{ij} is the interaction between magnetic orbitals a_i and b_j, $\Delta_{i\rightarrow j}$ is the cost in energy to transfer an electron from a_i to b_j and $\Delta_{i\leftarrow j}$ the same for a transfer from b_j to a_i; j_{ij} is the exchange integral between magnetic orbitals a_i and b_j.

Additional ferromagnetic terms have been proposed[12] and have been recently used in rationalizing magnetic properties of M–O–M systems.[13]

The wave functions on which H_{eff} acts are linear combinations of functions on the form $|a_1a_2 \ldots a_{n_A}, b_1b_2 \ldots b_{n_B}\rangle$ corresponding to the highest local spin S_A and S_B. Those functions can be written $|m_{S_A}, m_{S_B}\rangle$ but again it has not to be forgotten that they are indeed complete multielectron wave functions. As H_{eff} commutes with S^2, the eigenfunctions of H_{eff} are labelled by S and are written as $|S_AS_BSM\rangle$.

This theory holds very well for single valent homopolynuclear systems like Fe(III)Fe(III) systems, for instance.[14]

Heteropolynuclear systems like Fe(III)Mn(IV) or Fe(III)Mn(III) can also be described by such a theory because the unpaired electrons in these complexes stay on their respective center.

SECOND MOVEMENT: ELECTRON DELOCALIZATION

One Magnetic Orbital Per Site

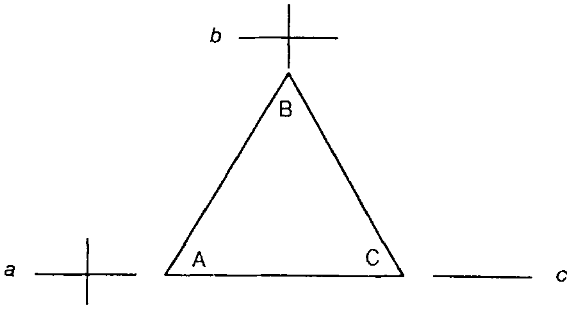
We have just seen that the Heisenberg Hamiltonian is closely related to the localization of electrons. We want now to consider what kind of effective Hamiltonian one has to use in the study of magnetic delocalized systems.

It is evident that delocalization can occur in the lowest states when an electron can occupy different sites without inducing an important change in the energy. A well known case in coordination chemistry is represented by mixed valence complexes of class III in the Robin and Day classification.[41] The simplest example is a system made of two ions of the same metal differing in one unit in oxidation state like Cu(II)Cu(III), Ru(II)Ru(III) or V(V)V(IV). A simple picture is the following:

We understand that in this case electron–electron repulsion has disappeared as a cause of localization: the electron seems free to go on any site. It is well known that in complexes this cannot be true due to coupling of the displacement of the electron with the position of the nuclei of the ligands. We will come back to this point later.

In fact the above mentioned cases are not interesting for magnetic properties since one of the two ions is diamagnetic: Ru(II), V(V) or Cu(III).

Nevertheless mixed valence systems with one orbital per center can be worth studying from a magnetic point of view if the nuclearity is higher than two as for instance an equilateral triangle with two unpaired electrons:



Electrons still avoid each other but they can move because now there is one empty site. The wave functions corresponding to situations of lower energy will be $|ab\rangle$, $|ac\rangle$, $|bc\rangle$, $|a\bar{b}\rangle$, $|a\bar{c}\rangle$, $|b\bar{c}\rangle$, $|\bar{a}b\rangle$, $|\bar{a}c\rangle$, $|\bar{b}c\rangle$, $|\bar{a}\bar{b}\rangle$, $|\bar{a}\bar{c}\rangle$, $|\bar{b}\bar{c}\rangle$, with different spin orientations. What must be the effective Hamiltonian in this case? The answer has been given in several reports.[15–17] We use here our result which has a simple formulation[18]:

$$H_{\text{eff}} = H_e + H_t + H_{et} \tag{4}$$

with

$$H_t = \beta \sum_{\substack{i<j \\ innj}} t_{ij}, \tag{5}$$

$$H_e = J_0 \sum_{\substack{i<j \\ innj}} \left(\frac{1}{4} - s_i \cdot s_j\right) n_i n_j, \tag{6}$$

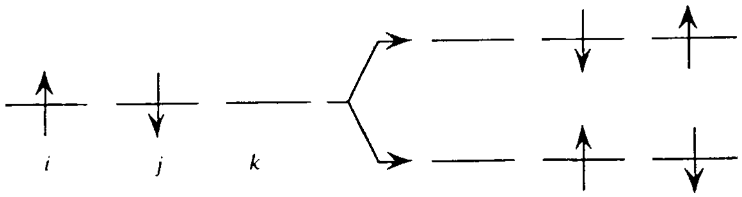
$$H_{et} = J^{et} \sum_{\substack{i<k \\ innj \\ jnnk}} \sum_{j} t_{ik} \left[\left(\frac{1}{4} - s_i s_j\right) n_i n_j + \left(\frac{1}{4} - s_j s_k\right) n_j n_k\right]. \tag{7}$$

H_{eff} works only on wave functions with no double occupation. It is valid for any nuclearity n_i in the occupation operator of site i.

H_t is a transfer Hamiltonian which takes an electron from i to the neighbouring site j without changing the spin. One has $t_{ij} | i\sigma_i, k\sigma_k \ldots \rangle = | j\sigma_i, k\sigma_k \ldots \rangle$ if the site j is empty and zero if j is occupied.

H_e is the usual exchange interaction for two neighbouring electrons.

H_{et}, the exchange-transfer Hamiltonian, is an interesting term which is operational only when two neighbouring electrons have opposite spins: then one of those two electrons (site i) can go to site j to give a doubly occupied site and shift to the empty site k as illustrated below:



This term appears in the construction of H_{eff} at the same order of perturbation as H_e and we see no reason to ignore it other than simplicity of calculation (which is a good reason!).

We found[18]

$$J_0 = -\frac{4\beta^2}{U_0}, \tag{8}$$

$$J^{et} = -\frac{2\beta^2}{U_0}. \tag{9}$$

In this case the energies are $-2\beta(^3A)$, $-(\beta + J^{et}) + J_0(^1E)$, $\beta(^3E)$, $2(\beta + J^{et}) + J_0(^1A)$.

Solutions of H_t have been given by Takahashi[20] and solutions of $H_t + H_e$ by Belinskii.[19]

Exchange transfer in this case is just additive to β. This is a peculiarity for the triangular lattice. In a square lattice, exchange transfer occurs between sites which are not related through β.

Important first order effects are found and the magnetic properties will be quite different from the ones computed for electron exchange situations. For β positive a ground spin triplet will be found and a spin singlet for $\beta < 0$. So for β positive, despite the sign of the exchange interaction a ground spin triplet will be found. This is the expected result using molecular orbitals with $\beta > 0$:

The very striking result is that even at first order there is a strong dependence of energy gained by delocalization on the spin state. This problem has been studied for different types of finite clusters by Takahashi.[20]

A $W(V)_2W(IV)_2$ which represents an example of a d^1-d^1-d^0-d^0 square has been studied.[32] Fascinating V(V)V(IV) clusters with a variable number of unpaired electrons have been prepared by Müller *et al.*[33] Study of such magnetic mixed valence systems with one orbital per center would be very valuable to test the theory.

Wave functions can be written with focusing on the spin problem as $|m_{S_A}, m_{S_B}\rangle$, $|m_{S_A}, m_{S_C}\rangle$, $|m_{S_B}, m_{S_C}\rangle$, but it is imperative to remember the antisymmetric nature of those functions and we prefer to write $|m_{S_A}, m_{S_B}\rangle^{AB}$, $|m_{S_A}, m_{S_C}\rangle^{AC}$, $|m_{S_B}, m_{S_C}\rangle^{BC}$. Any transposition in the superscripts will lead to a change of sign in the wave function.

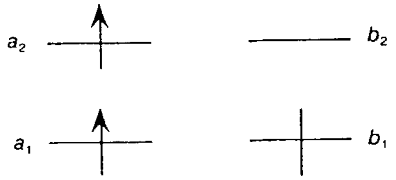
In Fig. 1 we give an illustration of the difference in H_{eff} between a square lattice made of single valent metal ions with one unpaired electron on each site and the same lattice in a mixed valent state obtained by oxidation of some sites. In the first case (Fig. 1(a)), the only interaction is the electron exchange and in the second case (Fig. 1(b)), there are three types of energies: transfer, exchange and exchange-transfer.

The Hamiltonian $H = H_t + H_e$ in which H_{et} is neglected is actively studied under the name of *t-J* model, by specialists of high T_c copper oxide superconductors.[21] Spalek has developed a model for those systems taking into account the three components of H_{eff}.[16]

Several Magnetic Orbitals Per Site. Double Exchange

Electron delocalization can also occur between two metal ions which both have non-zero spin, like Fe(III) ($S_A = 5/2$) – Fe(II) ($S_B = 2$) or Mn(III) ($S_A = 2$) – Mn(IV) ($S_B = 3/2$).

A simple picture is the following



Electrons are parallel on the first site because we suppose that ion A is in a high spin ground state.

The basic idea is that the extra electron is delocalizing from one site to the other but that it is coupled (ferromagnetically) to the unpaired internal electron. This internal electron defines the core

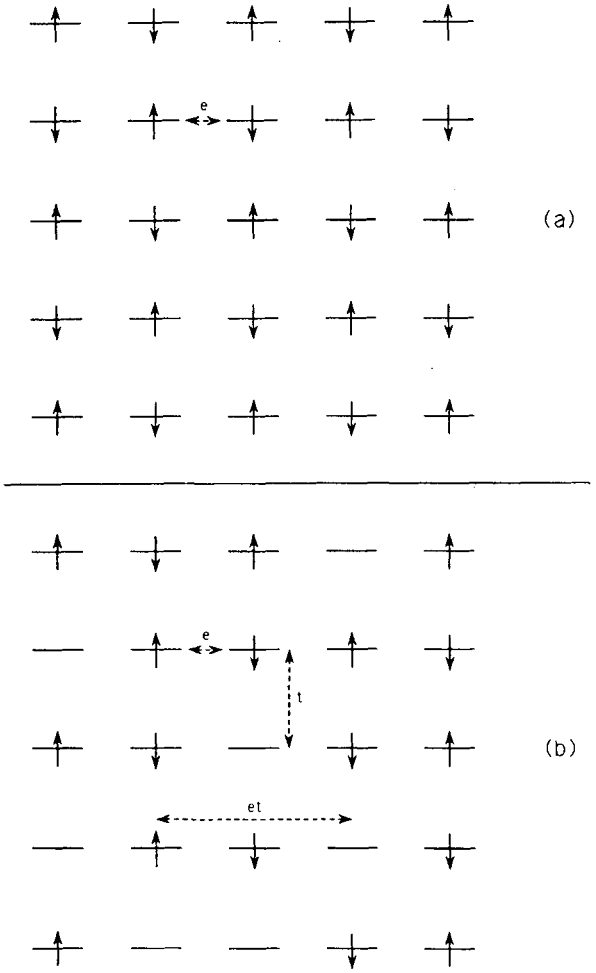


FIGURE 1 Comparison of components of H_{eff} for a square lattice in the cases of one unpaired electron per site (a) and of less than one electron per site (b). For (a) H_{eff} contains only exchange terms; for (b) H_{eff} consists of three terms: transfer, exchange and exchange-transfer.

spin (S_0). Depending on the orientation of the core spins, the walk of the extra electron will be more or less easy.

The theory of this problem has been made by Zener, Anderson and Hasegawa in the 1950's and the term double exchange has been coined for it.[22,23] In chemistry, this effect was studied almost simultaneously by different groups.[24–28]

The effective Hamiltonian for such a situation has been proposed[1,2,29,30]:

$$H_{\mathrm{eff}} = H_t + H_e \tag{10}$$

with

$$H_t = \beta \mathrm{P}_0 t_{\mathrm{AB}} P_0,$$

$$H_e = (-J_0 S_{\mathrm{A}} \cdot S_{\mathrm{B}} \mathrm{O}_{\mathrm{A}} - J_0 S_{\mathrm{A}} \cdot S_{\mathrm{B}} O_{\mathrm{B}})$$

where β is the interaction between the two orbitals which contain the moving electron, t_{AB} is the transfer operator from A to B,[31] P_0 is the projection operator in the subspace of wave functions obeying local Hund's rule, O_i is an occupation operator which keeps track of the position of the extra electron.

One of us has developed[26] a different effective Hamiltonian, called the generalized Anderson–Hasegawa Hamiltonian, which works not only in the subspace of highest spin (S_0 + 1/2) states but also in the (S_0 − 1/2) subspace. Hamiltonian (10) is simplier but is limited to the hypothesis that Hund states are much more stable than non-Hund ones.

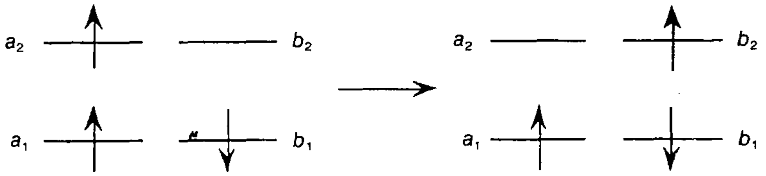
This effective Hamiltonian acts on wave functions which obey the local Hund's rule like $|a_1 b_1 a_2\rangle$ which is a spin triplet on A; on this wave function one will have

$$P_0 t_{\mathrm{AB}} P_0 |a_1 b_1 a_2\rangle = |a_1 b_1 b_2\rangle.$$

As an example of a situation in which the spin of A is not parallel to the spin of B, we can take $|a_1 \bar{b}_1 a_2\rangle$:

$$P_0 t_{\mathrm{AB}} P_0 |a_1 \bar{b}_1 a_2\rangle = P_0 |a_1 \bar{b}_1 b_2\rangle = (1/2)(|a_1 \bar{b}_1 b_2\rangle + |a_1 b_1 \bar{b}_2\rangle).$$

The result corresponds to a spin triplet on center B. The situation can be represented as



We understand that when the spins of A and B are antiparallel, the displacement of the extra electron from A to B creates on B a state which corresponds to a mixture of local triplet and singlet. We keep only the triplet contribution.

One can make the convention that the orbitals involved in the electron transfer are written at the end of the ket (as above); this simplifies the phase evaluation. We can again use a spin notation like $|m_{S_A}, m_{S_B}>^i$ where the superscript stands for the site of the extra electron. A general formula for the action of $P_0 t_{AB} P_0$ on a wave function with a given pair spin has been given by Anderson and Hasegawa[22]:

$$P_0 t_{AB} P_0 | S_A S_B S\rangle^i = \frac{S + 1/2}{2S_0 + 1} | S_A S_B S\rangle^j. \qquad (11)$$

S_0 is the core spin. The solutions of (10) for a dinuclear unit are

$$E = -\frac{1}{2} J_0 S(S + 1) \pm \beta \frac{S + 1/2}{2S_0 + 1}. \qquad (12)$$

This $(S + 1/2)$ dependence of delocalization energy defines "double exchange." In Fig. 2 we show the energy levels predicted in the function of β for J_0 corresponding to antiferromagnetic coupling for a 5/2, 2 pair. The spectacular feature that the theory predicts is that despite antiferromagnetic coupling, a strong enough delocalization is able to force the spins to parallel alignment. This seems to be the case in a recently synthesized Fe(III)Fe(II) tris-μ-hydroxo complex.[8,9]

We have proposed that in the $[Fe_3S_4]^0$ cluster of Ferredoxin II of D. Gigas, the delocalization in one Fe(III)Fe(II) pair explains the stabilization of the $(1/\sqrt{2})(|S_{12} = 9/2, S_3 = 5/2, S = 2\rangle^1 \pm$

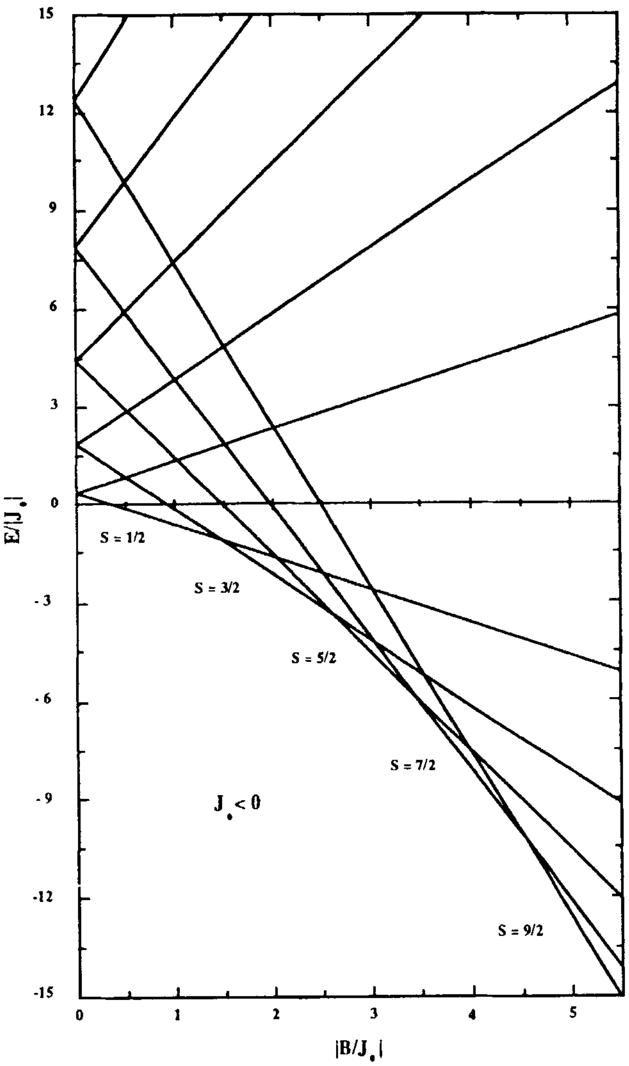


FIGURE 2 Eigenvalues of the transfer + exchange model in units of J_0 as a function of $|B/J_0|$ for a (5/2;2) dinuclear complex with delocalized valences. $B = \beta/5$.

$|S_{12} = 9/2, S_3 = 5/2, S = 2\rangle^2)$ ground state.[1,2] The theory has been extended to Fe_4S_4 systems by Noodleman.[3-5]

Delocalization can involve more than two centers. For any nuclearity and one particle moving, we have[34]

$$H_{\rm eff} = H_e + H_t + H_{et} \tag{13}$$

with

$$H_t = \sum_{i<j} \beta_{ij} P_0 t_{ij} P_0,$$

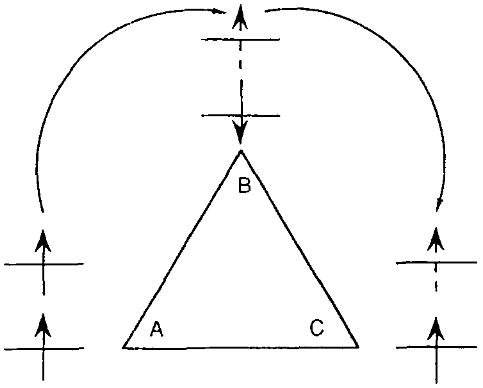
$$H_e = \sum_k \sum_{i<j} J_{ij} S_i \cdot S_j O_k,$$

$$H_{\rm et} = \sum_{i<j<k} J^{et}_{ijk} P_0 t_{ik} \left[\left(S_j \cdot s_i - \frac{1}{2} S_0 \right) O_i + \left(S_j \cdot s_k - \frac{1}{2} S_0 \right) O_k \right] P_0.$$

Here, s_i refers to the spin of the itinerant electron.

For triangles with uniform β and J_0, the first two terms lead to identical results to those obtained in the extensive paper of Belinskii.[19]

The last term includes the exchange-transfer part. In a d^2-d^1-d^1 triangle, exchange-transfer can be illustrated in the following manner:



The extra particle moves from A to C via an excited singlet state on B. This occurs only if the spins of a_2 and b_1 are opposite. The analogy with H_{et} of the preceding section is clear; the only difference lies in the nature of the excited state involved.

In a d^2-d^1-d^1triangle with uniform interactions we obtain: $2\beta - 3J_0(^5A)$, $-\beta - 3J_0(^5E)$, $-\beta + 3J^{et}/2(^1A)$, $\beta/2 - 3J^{et}/4(^1E)$, $-J^{et} - J_0(^3A)$, $-\beta + J^{et}/2 - J_0(^3A)$; the energies for the ^3E are obtained by diagonalization of

$$\begin{bmatrix} \dfrac{J^{et}}{2} - J_0 & \dfrac{\sqrt{6}}{4}(2\beta - J^{et}) \\ \\ \dfrac{\sqrt{6}}{4}(2\beta - J^{et}) & \dfrac{1}{2}\beta - \dfrac{1}{4}J^{et} - J_0 \end{bmatrix}.$$

As said before, the $J^{et} = 0$ solutions have already been given in Ref. 19. Consequences of exchange-transfer are not yet well studied and will be neglected in the next part. Further study of the role of exchange-transfer is underway.

THIRD MOVEMENT: LOCALIZATION BY VIBRATIONS

As said before, the delocalized situation just studied is rarely achieved, and this is due to the coupling of electronic and nuclear movements. This is well understood and is described by the concept of vibronic coupling.[42]

One Magnetic Orbital Per Center

Let us consider again a Cu(II)Cu(III) system. In the preceding part we consider that electron delocalization is easy, i.e., it is equivalent that the extra electron is on site A or site B. In reality this is rarely true even for chemically symmetric systems. When the electron is on one site the coordination sphere of this site is generally more dilated than that one for the other site. So we see that an electron jump will not be possible unless the system receives energy corresponding to this dissymetry. This can be done thermally (activated electron transfer) or with electromagnetic wave (intervalence absorption). For instance, in a Cu(II) Cu(III) case with those ions in a square planar environment, the extra electron is in a magnetic orbital corresponding to the antibonding combination of a $d_{x^2-y^2}$ metal orbital and a σ ligand orbital; then it is clear that the coupling with vibrations is strong.

The important parameter to describe quantitatively this effect reflects the change in bond length when the oxidation state changes and is denoted λ.

Figure 3 shows the well known dependence[35] of the energy of a mixed valence complex with one unpaired electron as a function of a vibration coordinate $q_- = (q_A - q_B)/\sqrt{2}$, which is the antisymmetric combination of local coordinates.

If β is zero, the system will distort with a contracted site (the oxidized one) and an expanded one (the reduced one). Hush has shown[36] that the activation energy for the thermal electron transfer process (the height of the crossing point) is

$$E_\theta = \frac{\lambda^2}{4k} \tag{14}$$

where k is the harmonic constant.

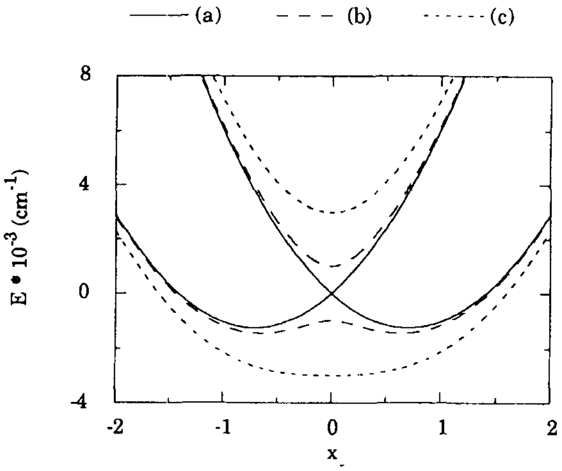


FIGURE 3 Potential energy curves (cm^{-1}) as a function of the antisymmetric reduced normal coordinate $x_- = q_-/(\lambda/k)$ for a two-site, one electron problem. The vibronic coupling parameter $\lambda^2/k = 5000\ \mathrm{cm}^{-1}$. Key: (a) orbital interaction $\beta = 0\ \mathrm{cm}^{-1}$; (b)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

It is well known that when the interaction β between magnetic orbitals becomes non-zero, the activation barrier decreases (Fig. 3) following the relation

$$E_\theta = \frac{\lambda^2}{4k} + \frac{\beta^2}{\lambda^2/k} - |\beta|. \tag{15}$$

This is valid as long as $|\beta| < \lambda^2/2k$ (class II of Robin and Day classification[41]).

When $|\beta| > \lambda^2/2k$ (class III of Robin and Day classification), the activation barrier disappears (Fig. 3) and the system is delocalized: then theories of the preceding paragraphs hold. So in order to observe delocalization, β must be strong enough.

If $|\beta| < \lambda^2/2k$, one has

$$E_{\text{op}} = \frac{\lambda^2}{k} \tag{16}$$

and for $|\beta| > \lambda^2/2k$,

$$E_{\text{op}} = 2|\beta|. \tag{17}$$

The theory of these effects has been made for triangular species in the case of one electron jumping[37,38]: Eqs. (14) and (16) are valid for $\beta = 0$ as can be seen in Fig. 4 which represents a cross section along q_θ (see below) of the potential surfaces. The activation energy is given by the difference in energy between the saddle point and the minimum. Figure 5 represents the lower potential surface for β non-zero as a 3D function of the E coordinates q_ε and q_θ.

$$q_\varepsilon = \frac{1}{\sqrt{2}}(q_B - q_C),$$

$$q_\theta = \frac{1}{\sqrt{6}}(2q_A - q_B - q_C).$$

The three minima are easily identified: each one describes the

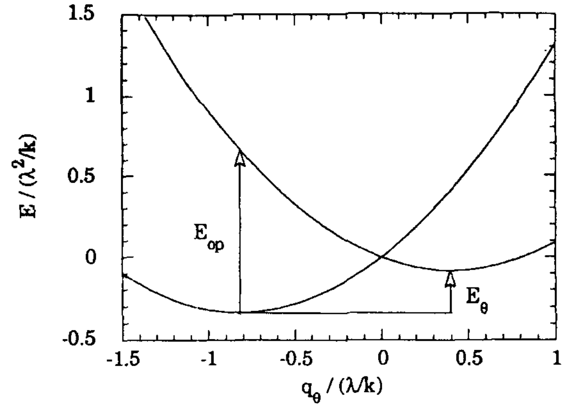


FIGURE 4 Section along q_θ of the potential energy surface for a three-site, one electron problem for $\beta = 0$. The activation barrier is given by the difference in energy between the saddle point and the minimum.

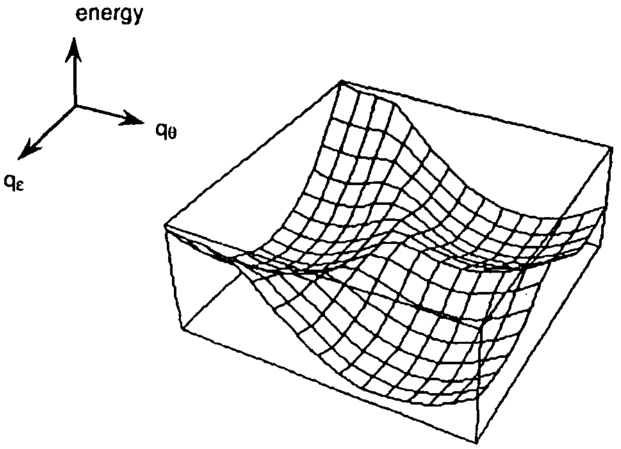


FIGURE 5 3D representation of the energy surface in the $(q_\theta, q_\varepsilon)$ coordinates for β non-zero. Three minima are observed which correspond to localization of the extra electron on site A, B or C.

electron localized on one site. One goes from one minimum to the other through a saddle point.

Similar calculations are underway for two electrons moving on a triangle. Preliminary results show that vibrations affect much more drastically the electron transfer than exchange or exchange-transfer.[39] This suggests that the effective Hamiltonian $H_{\text{eff}} = H_e + H_{et}$ could be the valid one for some range of the parameters β, U_0, λ^2/k. It is easy to check that such a Hamiltonian leads, for instance for a square with two electrons, to a correlated movement of an antiferromagnetically coupled pair.

Several Magnetic Orbitals Per Center

For a dinuclear delocalized magnetic mixed valence system, we saw that the adapted effective Hamiltonian is given by Eq. (10). It is easy to modify this Hamiltonian to take into account trapping effects by vibrations (or by any static assymetry). Let us introduce E_A and E_B, the energy of the pair when the extra electron is on A or B. We then have[30]

$$H_{\text{eff}} = \beta P_0 t_{AB} P_0 + (-J_0 S_A \cdot S_B + E_A) O_A + (-J_0 S_A \cdot S_B + E_B) O_B. \tag{18}$$

Using the usual theory for coupling with vibrations in mixed valence dinuclear systems we end up with a family of curves (Fig. 6): two curves per spin state.[25,30]

An important apparent effect is that the activation barrier is now spin dependent since the interaction is spin modulated following

$$\beta(S) = \beta \frac{S + 1/2}{2S_0 + 1}. \tag{19}$$

We can ask for each spin state if it belongs to class II or class III. For the highest pair spin ($S = 2S_0 + 1/2$) the delocalization energy is just β and for the lowest ($S = 1/2$), we have $\beta/(2S_0 + 1)$.

Let us suppose that the vibronic coupling is strong and that the pair with electron on A is at the energy minimum; we have $E_B - E_A = \lambda^2/k$ whatever S is, if each spin state belongs to class II. It

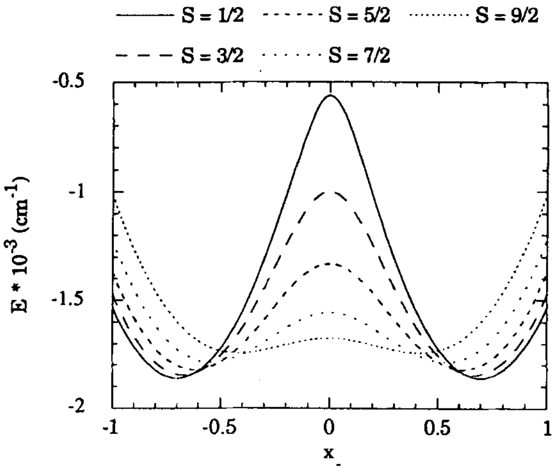


FIGURE 6 Energy curves for a Fe(II)Fe(III) unit as a function of the antisymmetric reduced normal coordinate $x_- = q_-/(\lambda/k)$ with $\lambda^2/k = 7420\ cm^{-1}$; $B = \beta/5$ has been set to $600\ cm^{-1}$; $J_0 = -107\ cm^{-1}$ such that $J_{eff} = -10\ cm^{-1}$.

is easy to show then that[25,30] the energy minima are given by Eq. (1) with

$$J_{eff} = J_0 + \frac{2\beta^2}{(2S_0 + 1)^2\, \lambda^2/k}. \tag{20}$$

Localization restitutes the Heisenberg Hamiltonian with a modified exchange parameter. The contribution of vibrations to this parameter is ferromagnetic.

It is clear that the activation energy is now spin dependent; it is given by Eq. (15) using Eq. (19) for the transfer energy. The activation energy is the lowest for the highest spin.

We have proposed[30,40] that in fact vibrations have to be taken into account in dinuclear systems like the $[Fe_2S_2]^+$ of iron-sulfur proteins or models and in the Fe(II) Fe(III) tris-μ-hydroxo complex synthesized by K. Wieghardt.[8,9]

We must mention that the preceding treatment of vibronic coupling is a semi-classical one and that a more exact one is to take properly into account the quantum aspect of vibrations. The comparison of both approaches nevertheless justifies the treatment given here, for strong enough vibronic and exchange couplings.[43]

As for trinuclear systems, one of us has shown[7] that vibrations for a Fe(III)$_2$ Fe(II) triangle with uniform J_0 and β can induce a ground state with delocalization in one pair only. This is of interest for the understanding of the iron-sulfur cluster of Ferredoxin II of D. Gigas in which Mössbauer has identified one delocalized pair. In Refs. 1 and 2, this was taken as an experimental fact.

Let us consider here the effects of vibrations in the d^2-d^1-d^1 triangle with uniform J_0 and β. As said before we will not take into account exchange-transfer. The only parameters of our model are β, J_0 and λ^2/k.

Let us suppose $\beta = 0$ and J_0 and λ^2/k non-zero. We have three spin singlet states, three quintet and six triplet ones. Their potential surfaces in the same coordinates as for the preceding example d^1-d^0-d^0 have each a section like the one in Fig. 4. They are just shifted by amounts proportional to J_0.

Complete solutions can be obtained numerically.

In the limit of strong vibronic coupling can we show that the energy minima follow the Heisenberg law?

We were not able to show this exactly as in the dinuclear case, but it can easily be checked by perturbation theory. Using matrices

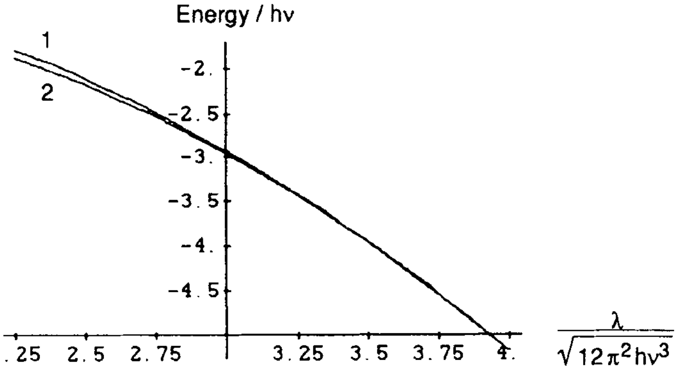


FIGURE 7 Energy (in units $h\nu$) of the minimum for the $S = 2$ state as function of the vibronic coupling parameter for $\beta = -h\nu$. Second order perturbation theory values (curve 1) compared to exact values (curve 2). Note that $\nu = (2\pi)^{-1}\sqrt{k}$.

of H_{eff} in the basis $|S_i, (S_j, S_k)\, S_{jk}, S\rangle^i$ (which are identical with those published in Ref. 19) we can calculate those energy minima:

$$E(S = 2, S_{23} = 1) = -3J_0 - \frac{2\beta^2}{\lambda^2/k},$$

$$E(S = 1, S_{23} = 1) = -J_0 - \frac{\beta^2}{\lambda^2/k},$$

$$E(S = 1, S_{23} = 0) = -J_0 - \frac{3\beta^2}{2\lambda^2/k},$$

$$E(S = 0, S_{23} = 1) = -\frac{\beta^2}{2\lambda^2/k}$$

It is easy to check that these levels are those obtained for an isosceles triangular Heisenberg Hamiltonian with $J_{12} = J_{13} = J_0 + \beta^2/2(\lambda^2/k)$ and $J_{23} = J_0$. This is valid whatever the sign of β is, as long as the perturbation treatment can be used. We can conclude that:

Localization restitutes the Heisenberg Hamiltonian with a modified exchange parameter which has the same expression as in the dinuclear case.

In Fig. 7, we compare the energy for the lowest $S = 2$ state predicted by this modified Heisenberg law with the exact results. We see that the agreement is very good. For lower spin states, the agreement is still better.

What can we say about the activation energies in each spin state?

The activation energy is given by the difference in energy between the minimum and the saddle point. The later is affected by β at first order and this gives a first order contribution to the activation barrier. The dependence on spin state is very easy to get from the preceding matrices and is interesting to interpret. One has

$$E_\theta(S = 2, S_{23} = 3/2) = \frac{\lambda^2}{4k} - |\beta|,$$

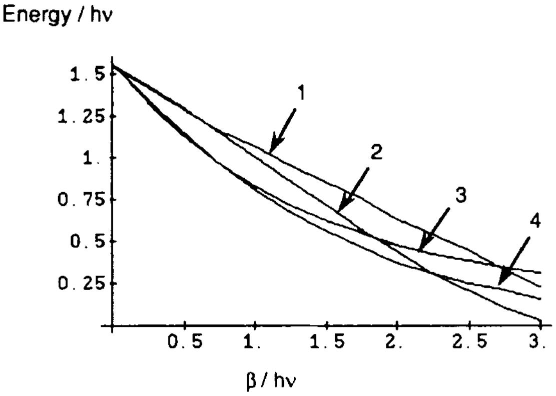


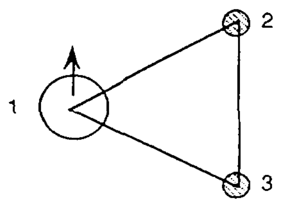
FIGURE 8 Activation energies (in units $h\nu$) for $S = 0$ (curve 1), $S = 1$ (curve 2), $S = 1$ (curve 3), $S = 2$ (curve 4) for $\beta > 0$.

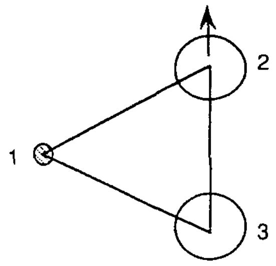
$$E_\theta(S = 1, S_{23} = 3/2) = \frac{\lambda^2}{4k} - |\beta|,$$

$$E_\theta(S = 1, S_{23} = 1/2) = \frac{\lambda^2}{4k} - \frac{|\beta|}{2},$$

$$E_\theta(S = 0, S_{23} = 1/2) = \frac{\lambda^2}{4k} - \frac{|\beta|}{2}.$$

The pair spin S_{23} is a good quantum number and has a half-integer value since the extra electron is delocalized between sites 2 and 3 (see below). As expected, the decrease in the activation barrier due to β is more important for high spin states. It takes the values for double exchange in a d^2-d^1 pair. This can be quite clearly understood if one realizes that the nuclear coordinate for the saddle point is one with two identical dilated coordination spheres contrary to that of the minimum where there exist two contracted spheres and a dilated one:





In Fig. 8 we compare the activation energies for the different spin states for $\beta > 0$. We see that they are lower for higher spin states. At low values of β, they follow the preceding equations.

At higher values of β, they depend also on the sign of β as already found for triangles with one unpaired electron.

CONCLUSION

In Table I, we summarized the results reviewed in this paper.

We recalled first that systems with electrons localized by interaction with other electrons present the phenomenon of electron

TABLE I

Different effective Hamiltonians reviewed in this paper

	H_{eff} $N = 2$[a]	H_{eff} $N > 2$
systems localized by electron–electron repulsion	H_e	H_e
delocalized mixed valence systems (class III)[b]	$H_e + H_t$	$H_e + H_t + H_{et}$ (see note c)
mixed valence systems with strong vibronic coupling (class II)[d]	H_e	$H_e + (H_{et}?)$[c]

[a] N is the number of sites.

[b] The expressions of H_e, H_t, H_{et} depend on the number of orbitals per site (see text).

[c] For one orbital per site and when H_{et} is neglected, H_{eff} corresponds to the *t-J* model (see text).

[d] The indicated H_{eff} describes the energy minima. In the saddle points, $H_{\mathrm{eff}} = H_e + H_t$ (see text).

[c] The role of H_{et} in the presence of vibrations is under study.

exchange: the only degree of freedom is spin orientations and the associated energetics is expressed by the Heisenberg Hamiltonian. For those systems the double exchange Hamiltonian is of no use. We did not speak here of spin-orbit effects, like zero-field splitting, which are very important in the treatment of anisotropy.

Then we explained that delocalized mixed valence systems with several unpaired electrons have one more degree of freedom: electron position. The Heisenberg Hamiltonian is no longer valid.

In the case of one orbital per center, the effective Hamiltonian contains three terms: $H_{\text{eff}} = H_e + H_{et} + H_t$. The transfer part is spin dependent. The approximation $H_{\text{eff}} = H_e + H_t$ is studied by physicists interested in high T_c superconductivity under the name of the t-J model.

When several orbitals per center are involved, we are dealing with delocalization of an electron on a core spin lattice, this electron being coupled ferromagnetically to each core spin. Again the transfer part is spin dependent following Eq. (19). This equation gives the $(S + 1/2)$ dependence typical of double exchange. For nuclearity higher than two, H_{eff} contains three terms as in the one orbital per center case.

In the last part we explained that localization by vibronic coupling can restitute Heisenberg-like behaviour as intuitively expected. Vibronic coupling is well known in mixed valence chemistry: it has been suggested as the origin of valence trapping in $[Fe_2S_2]^+$ clusters in proteins and models[40]; it is likely very strong in high T_c copper oxide superconductors due to the orbital topology.

In the case of one orbital per center, we do not yet have definite results. Preliminary calculations show that the transfer is much more affected by vibrations than by exchange and exchange-transfer. One can imagine situations where H_{eff} is reduced to $H_{\text{eff}} = H_e + H_{et}$. This Hamiltonian seems very interesting to study.

When several orbitals per center are involved, we showed, in the limit of strong coupling and ignoring H_{et}, that the energy minima correspond to the Heisenberg law with a new exchange parameter. The expression of this parameter is transferable from dinuclear systems to trinuclear ones. This is for the spin degree of freedom. As far as electron delocalization is concerned we found that its activation energy is spin dependent: it is easier for highest spin states and needs the double exchange concept to be understood.

To the two degrees of freedom mentioned above, there correspond two kinds of experiments: magnetic susceptibility, neutron inelastic scattering can give information on the energy spectrum and in the case of strong vibronic coupling can be explained without the double exchange concept; movement of the extra electron can be detected by different techniques like Mössbauer, EPR, NMR, absorption spectroscopy and they need the double exchange concept to be interpreted. So it seems to us that future studies of magnetic mixed valence systems must be accomplished keeping in mind this intrication of phenomena.

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