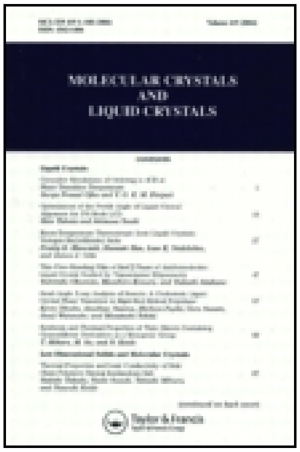

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ELECTRON DELOCALIZATION AND MAGNETIC INTERACTIONS IN MAGNETIC MOLECULAR SYSTEMS. THEORY AND APPLICATIONS

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Abstract. Using the general computational approach based on the angular momentum theory we discuss here the magnetic properties of large magnetic clusters (polyoxometalates) and mixed-valence chains (diphtalocyanine-based materials). The interplay between electron delocalization, magnetic exchange and Coulomb interaction is examined in detail.

INTRODUCTION

The systems formed by localized magnetic moments and itinerant "extra" electrons that can undergo a rapid hopping over the magnetic sites are becoming of increasing interest in Molecular Magnetism. The main effect of this electron transfer is to couple two localized magnetic moments through a specific kind of exchange interaction known as double exchange[1-3].

Till now the quantum evaluation of this coupling has been restricted to comparatively simple mixed valence (MV) systems comprising one or two electrons (or holes) delocalized over a restricted number of exchange-coupled metal sites (dimers[4,5], trimers[6,7] and tetramers[8-11], basically). However, even for these simple cases the role of the electron delocalization proved to be different in each particular case. Thus, while in MV dimers the electron transfer process results always in a strong stabilization of the ferromagnetic state, in higher nuclearity systems this process can also favor the stabilization of other spin states different from the ferromagnetic one, depending on the sign of the electron transfer integral and on the topology of the MV cluster. A second important difference between dimers and higher nuclearity systems comes from the fact that in the later some additional electronic processes should be also considered for the correct evaluation of the electron delocalization effects. For example in clusters containing more than one delocalized electron, the two-electron transfer processes can be also important when the ground state is degenerate and the one-electron processes increase Coulomb energy of the system.

The previous remaks show that the conclusions obtained for the relatively simple clusters can not be extended to higher-nuclearity systems involving localized and delocalized spins in a complicated molecular and crystal structures.

On the other hand a variety of high-nuclearity systems exists in which localized and delocalized electrons coexist and interact. We can mention in this context the polyoxometalate clusters[12,13, 14] which are molecular metal oxides of high nuclearity that resemble discrete fragments of extended metal oxide structures. The ability of polyoxometalates to accept various numbers of electrons, which are delocalized over a significantly large number of metals, and to accommodate magnetic clusters[14], provide us with ideal model systems to study the interplay between electron transfer and exchange interactions in structures with different topologies and symmetries. The problem of the interaction between localized and delocalized electrons can be also found in the area of MV chain compounds [16,17].

Till now the progress in the interpretation of the magnetic properties of these kind of systems was strongly restrained due to the absence of an apropriate theoretical approach. Recently we have proposed a general approach to the problem of the electronic interactions in the arbitrary nuclearity systems possessing arbitrary number of localized spins and itinerant electrons[15]. We present here the results obtained with the use of this approach for both localized and delocalized magnetic clusters and chains.

SHORT DESCRIPTION OF THE THEORETICAL APPROACH

In the framework of the proposed computational scheme magnetic exchange as well as one-electron transfer, two-electron transfer and all three-center interactions (so-called exchange-transfer) are taken into account. The new approach is based on the successive (chain-like) spin coupling scheme and takes full advantages of the angular momentum technique. The use of the angular momentum theory allowed us to derive the explicit analytical dependence of the matrix elements of the above electronic interactions in terms of 6j-symbols for arbitrary MV systems. In order to reduce the dimensions of the energy matrices obtained in this way point symmetry arguments were taken into account.

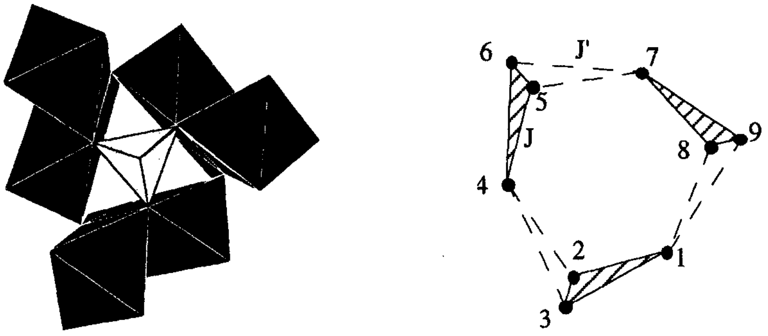
A program able to organize and perform all the required elementary operations (generating of all possible electronic distributions, calculation of the matrix elements of all named interactions, construction of the symmetry adapted basis sets for all types of molecular symmetry etc.) has been developed. This program allows to handle not only with the MV systems but also with magnetic clusters containing big number of localized spins. Formally this kind of system can be viewed as a particular case of MV system in which only one electronic distribution is allowed.

EXAMPLES

Let us consider three examples illustrating the computation abilities of the developed approach and the interplay between different types of electronic interactions in the high nuclearity magnetic systems. One example represents a complex exchange cluster formed by nine Ni(II)-ions, other two examples represent the MV systems, namely, the Keggin polyoxometalate complex with delocalized electronic pair and the diphtalocyanine MV chains.

Nonanuclear nickel (II) cluster

This cluster arise from the union of three tri-substituted Keggin units $\left(PNi_3W_9\right)$ by two PO_4^{-3} tetrahedra (see [14] and refs. therein). Although this system provides no electron delocalization, it exhibits unusual magnetic properties due to the coexistence of both ferro- and antiferromagnetic exchange interactions. Besides this system is large enough to demonstrate the advantages of the developed approach.



(a) (b)

FIGURE 1. (a) Polyhedral representation of the $[M_9O_{36}]$ (M=Ni^{II}, Co^{II}) cluster. The magnetic ions are located in the black octahedra. (b) Exchange network of the M_9O_{36} cluster showing the intra- and inter-triangle exchange constants J and J'.

Nonanuclear Ni_9 cluster can be modellized by a system with nine spins $S_i = 1$ interacting by isotropic Heisenberg exchange. This system is formed by a triangle of triangular Ni_3 clusters. The presence of two types of connections between NiO_6 octahedra (Figure 1-a) should lead to two types of pairwise exchange interactions (J and J′ in Figure 1-b). Thus, the triangular Ni_3 clusters are sharing edges as in the above clusters, while the inter-triangle connections involve corner-sharing octahedra with Ni–O–Ni angles around 120^{o}, which deviate considerably from the ortogonality value. Therefore, an unprecedented magnetic cluster with coexistence of both ferro- and antiferromagnetic couplings is to be expected. The magnetic properties confirm this prediction (Figure 2). The product $\chi_m T$ shows a continuous increase with decreasing temperature, indicating the presence of ferromagnetic exchange interactions within the triangles, but below 25 K it exhibits a sharp decrease as a consequence of the antiferromagnetic inter-triangle interactions. In order to obtain the exchange parameters the diagonalization of the matrix of the Heisenberg exchange has been performed using the elaborated computational procedure based on the irreducible tensor operator techniques (the number of the basis states for the total spin S=9, 8, 7, 6, 5, 4, 3, 2, 1, and 0 are 1, 8, 36, 11, 258, 468, 672, 750, 603, and 232 respectively; the application of symmetry adopted basis reduces significantly these matrices). The exchange parameters providing the best fit to the experimental results are $J = 3.9\ cm^{-1}$ and $J' = -0.97\ cm^{-1}$. Thus, from the magnetic point of view, this cluster provides a very nice example of the system with coexistence of both ferro and antiferro interactions. The same computational procedure allows take into account other types of interactions (biquadratic, anisotropic, antisymmetric) including also the zero field-splitting.

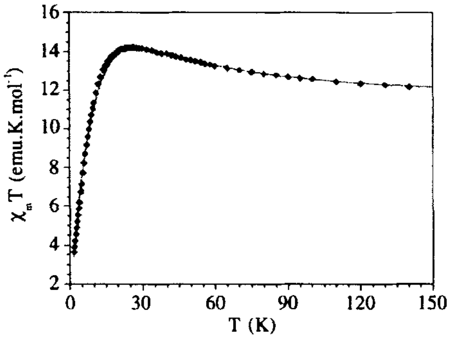


FIGURE 2. Plot of $\chi_m T$ versus T for the three Ni^{II} clusters: Ni_9O_{36} . Solid line are the best fit to the isotropic Heisenberg exchange model.

Heteropoly complexes with Keggin and Wells-Dawson structures

As other example of the application of the developed approach we consider so-called heteropoly complexes with Keggin structure (Figure 3). The reduced species (heteropoly blue) contains electronic pairs delocalized over a large number of metal atoms (M=Mo, W) yielding multi-nuclear mixed-valence systems. Experiments show that electronic spins are always completely paired (see Baker et al.[12]). Let us elucidate the conditions leading to the stabilization of an antiferromagnetic ground state due to the delocalization of the electronic pair in absence of magnetic exchange.

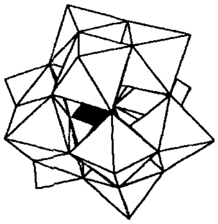


FIGURE 3. Structure of a Keggin polyoxometallate.

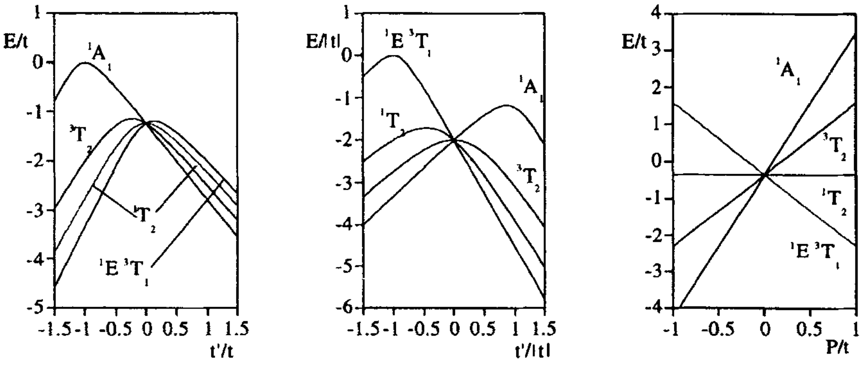
The following interactions are taken into account:

(i) the interelectronic Coulomb repulsion in the electronic pairs, which depends on the different distributions of the electronic pairs over the available metal sites, and

(ii) one-electron and two-electron transfer processes, which promote the delocalization of the electronic pairs and converts one into another.

The developed approach allows to perform group theoretical classification of the delocalized pair states, and calculate the energy matrices involving various single and double transfer parameters as well as the Coulomb energy terms U. Thus, the different electronic pairs are split in five groups, according to the intermetallic distances in such a way that the ground group of levels is separated from the first excited one by about 2000 cm^{-1}(see [13]). This corresponds to the situation in which the two electrons are in non-adjancent MO_6 octahedra, occupying opposite positions of the Keggin structure (the corresponding intermetallic distance is about 7Å). On the other hand, the fact that two adjacent octahedral sites share edges or corners, restrict the number of transfer processes to two: t (transfer through corners) and t′ (transfer through edges). These transfer processes split the ground level only through the mixture with the excited states. When both t and t′ are nonvanishing, the ground level splits into the following four levels: $^1A_1$, $^3T_2$, $^1T_2$ and (^1E, $^3T_1$), as shown in Figure 4 a,b. The ground state can be either the singlet $^1A_1$ ($t'/t > 0$) or the degenerate level (^1E, $^3T_1$) ($t'/t < 0$). The splitting of the ground state increases when the ratio t'/t increases from 0 to 1, and remains nearly constant for larger values of this ratio. This splitting is unsymmetric with respect to the sign reversal, being minimal when both t and t′ are positive.

With respect to the two-electron transfer processes only one process proves to be able to split the ground group of levels. This process can be viewed as two successive one-electron transfers considered above (actually it is proportional to the product $t \cdot t'$). If the associated two-electron transfer parameter P<0, the $^1A_1$ singlet is stabilized, whereas the (^1E, $^3T_1$) mixture is stabilized if P>0 (Figure 4-c).



(a) (b) (c)

FIGURE 4.- Pattern of the low-lying energy levels of the electronic pair for the Keggin unit: One-electron transfer with (a) t>0 and with (b) t<0. Two-electron transfer (c).

Summarizing we can say that electron delocalization is able to stabilize a singlet ground spin state when both t and t′ have the same sign, or when P<0. It should be emphasized that these processes are operative even when the two moving electrons are widely separated in the structure due to the Coulomb repulsion. In this case the spin pairing via a antiferromagnetic superexchange coupling is hardly possible and the electron delocalization remains the only origin of the spin pairing.

Mixed-valence chains

The last example we consider here represents a chain consisting of equivalent exchange coupled MV dimers. We denote the sites of dimers as $A_1B_1, A_2B_2, \ldots A_nB_n$, where $n = N/2$ is the number of dimers in the chain (N is the number of sites). Each MV dimer is supposed to have one moving electron delocalized over two spin-less cores A_iB_i. Each site is assumed to have only one nondegenerate orbital. The states with two electrons in the dimeric unit are expected to be unaccessible due to the strong intracluster Coulomb repulsion. This system may be viewed as a model of diphtalocyanine chains $[YPc_2]\cdot CH_2Cl_2$ and $[ScPc_2]\cdot CH_2Cl_2$ (see 16 and 17). The extra electron of each $[Pc^- Pc^{2-}]$ MV pair is delocalized over two sites of macrocyclic unit and we arrive at the problem of an infinite chain of the MV dimeric units.

The following three types of interactions are relevant in the system under consideration:

(i) the electron delocalization inside each dimeric unit describing by intracluster transfer parameter $t_{A_iB_i} \equiv t$;

(ii) ferromagnetic exchange interaction between the electrons occupying the adjancent sites of the neighbouring clusters (the associated parameter is denoted as $J_{B_iA_{i+1}} \equiv J$);

(iii) intercluster Coulomb interaction describing by the parameter $U_{B_iA_{i+1}} \equiv U$ (as for the exchange only the shortest distance Coulomb interaction seems to be important).

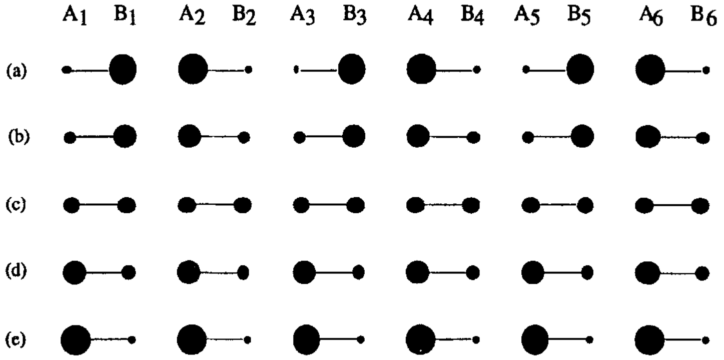
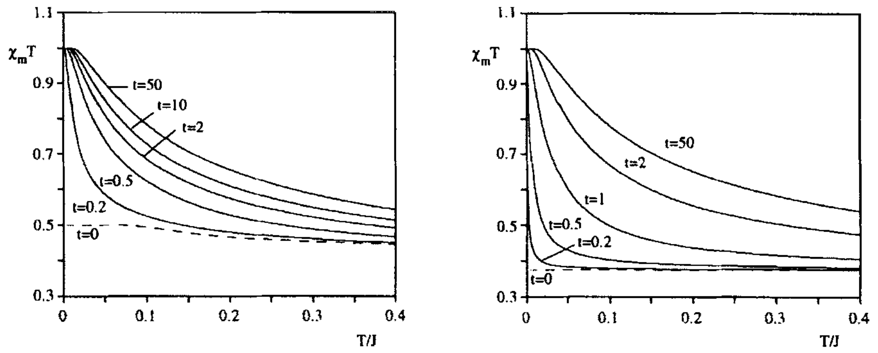


FIGURE 5. Electron density distributions in MV chain.

With the use of developed general approach, the magnetic properties of the chain formed by six MV dimers (twelve sites) have been calculated (full number of states for S=3, 2, 1 and 0 are 64, 320, 576, 320 respectively). This chain lenght seems to be enough to elucidate the main consequenses of the interplay between electron delocalization and Coulomb and exchange interactions. With the aim of better approach to the properties of the infinite chain the closed chain has been considered.

Let us briefly examine the role of the electron transfer on the magnetic properties of this MV system. Depending on the relative values of the parameters J and U we can have two limiting cases which will be referred to as strong exchange interaction limit and strong Coulomb interaction limit.

Provided no electron transfer (t = 0) one can see that in the strong exchange interaction limit the chain adopts an antiferroelectric charge ordered distribution (electric dipole moments of neighbouring MV dimers are antiparallel) in which the electrons of two neighboring MV pairs are located in adjacent sites in order to take advantage of the exchange interaction (Figure 5-a). Antiferroelectric charge ordering apparently eliminates all exchange pathways between exchange pairs so that the magnetic properties will exhibit at low temperatures ($kT \ll J$) the behavior corresponding to the sum of n/2 ferromagnetic dimers with S=1; that is, the behavior of a paramagnet formed by $n/2$ spins S=1 (dashed line in Figure 6-a).



(a) U/J=0 (b) U/J=5

FIGURE 6. Magnetic susceptibility for a 6 dimers chain: (a) strong exchange interaction, (b) strong Coulomb interaction (t is in J units)

In another limit (strong Coulomb interaction), the electrons tend to be as separated as possible (Figure 5-e) stabilizing thus a ferroelectric charge ordered distribution (all dipole moments are parallel). In such a situation the electrons can not be magnetically coupled and hence the chain will behave at low temperatures ($kT << U$) as a paramagnet formed by n spins $S=1/2$ (dashed line in Figure 6-b). To summarize we can say that these two limiting cases keep the electrons fully localized on one of the two sites of the MV dimer preventing thus the occurrence of long range spin correlations.

When the electron transfer is taken into account the above situation changes since the delocalization within the dimer leads to an electron density different from zero on both sites (Figure 5-b, d). This results in the stabilization of a parallel alignment of all the spins of the chain due to the ferromagnetic exchange interaction between nearest dimers, leading thus to a one-dimensional ferromagnetic behavior (Figure 6). This finding is in agreement with the magnetic behaviour exhibiting by [YPc_2] and [$ScPc_2$] chains[16, 17]. We can see in the Figure 6 that the increase of t leads to an increase in the ferromagnetic coupling between spins (the magnetic curves are shifted towards higher T). In the limit of very strong electron transfer this effective ferromagnetic coupling between delocalized electrons will reach its maximum value since the electron density will be equally averaged over all the sites (Figure 5-c). It can be easily demonstrated that this value is J/4.

The electron delocalization accounts also for the low temperature minimum on the magnetic curve observed for the [$ScPc_2$] chain[16]. As one can see in Figure 7 in the strong Coulomb interaction limit this minimum appears providing weak electron transfer. Indeed in this case in the low temperature region $\chi_m T$ decreases abruptly with the increase of T from its ferromagnetic low temperature limit towards the limit corresponding to paramagnet containing n spins $S = \frac{1}{2}$. This is because the exchange pathways are broken by Coulomb repulsion and the electron transfer is too weak to promote visible one-dimensional ferromagnetism. Thus the system been formally ferromagnetic exchibits the paramagnetic behaviour inherent to n spins $S = \frac{1}{2}$. The further increase of the temperature leads to the population of the excited states corresponding to the electronic distributions with partially restored exchange parthways. Therefore the ferromagnetic coupling becomes more efficient leading thus to the increase of $\chi_m T$. In the case of strong electron transfer the exchange pathways are restored even for very low temperatures and we observe the monotonic ferromagnetic behaviour.

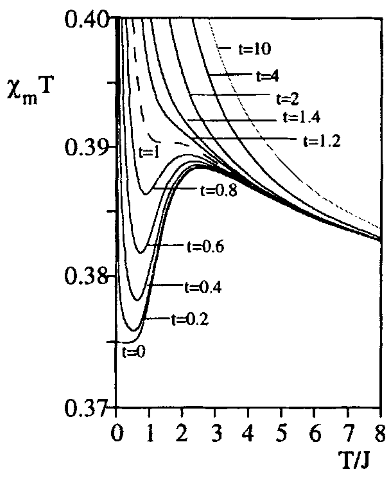


FIGURE 7. Low temperature minima in the case of strong Coulomb (U/J=5) interaction (t in J units)

CONCLUSIONS

The above examples show that the effect of the electron delocalization on the magnetic properties of high nuclearity MV clusters is quite different from that occurring in MV dimers. Very often this effect can not be predicted correctly without accurate quantum mechanical calculation of the energy spectrum of these complex systems. General computational approach applied here takes full advantages from angular momentum theory and group theory and provide comparatively simple and very efficient tool for the theoretical study of high-nuclearity clusters and low dimensional systems. Another advantage of this approach is that it can be applied not only to the MV systems but also to the magnetic clusters including a big number of localized spins. In the next future we plan to exploit the developed computational program for the description of the magnetic behavior of more complex systems, particularly, polyoxometalates containing one ore more paramagnetic centers interacting with delocalized electrons. In these systems we can expect that the nature of the ground state will be the result of an intricate interplay between electron delocalization, magnetic exchange and Coulomb repulsion.

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