

Article

High-Spin Chains and Crowns from Double-Exchange Mechanism

Vijay Gopal Chilkuri, Nicolas Suaud and Nathalie Guihéry *

Laboratoire de Chimie et Physique Quantiques, UMR5626, IRSAMC, Université de Toulouse 3, Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse Cedex, France; vijay.gopal.c@gmail.com (V.G.C.); suaud@irsamc.ups-tlse.fr (N.S.)

* Correspondence: nathalie@irsamc.ups-tlse.fr; Tel.: +33-5-51556098; Fax: +33-5-61556065

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Abstract: This article addresses the question of the possibility of obtaining high-spin chains and crowns of magnetic units $s = 1$ from doped (by a hole) antiferromagnetic architectures. It aims at determining the range of values of the double-exchange model interactions for which these molecules exhibit a high-spin ground state. Several chains and crowns of sizes varying between three to seven magnetic sites have been studied using a refined double-exchange model. It is shown that, for physical values of the parameters, linear chains of three, four and five sites are likely to adopt the highest spin state. For chains of six sites, small values of magnetic couplings are needed to get the highest spin, but it would be easy to get an $S = 3/2$ ground state. For systems of seven (or slightly more) sites, the highest spin state becomes non accessible but $S = 5/2$ states are likely to be obtained. Surprisingly, the physics of crowns is substantially different. The same trends are observed for even-number systems but with a larger double-exchange regime. At variance, odd-number systems do not exhibit a double-exchange mechanism for low values of the magnetic couplings. These observations are rationalized from an analysis of the computed spectra and wave functions.

Keywords: high-spin molecule; double-exchange phenomenon; model Hamiltonian; theoretical chemistry

1. Introduction

Magnetic systems are increasingly important in our daily life. They may be found in data storage devices, energy storage, medical imaging, *etc.* With miniaturization techniques, they are also expected to be of interest in quantum computing for instance and many other technological fields. Several strategies have been used to produce high-spin molecules and materials with magnetic ordering. The simplest idea that comes to mind is to consider a mononuclear complex constituted of a high-spin metal ion. The largest spin that can be obtained is $S = 7/2$ with a lanthanide ion bearing seven unpaired electrons such as Gd(III). Increasing the spin could be achieved by coupling ferromagnetically several metal ions in their non-zero spin ground state. Among the first attempts following this strategy, ferromagnetic interactions could be imposed in a series of Gd(III)Cu(II) complexes, leading to a spin $S = 9/2$ for instance in a complex of Gd(II)Cu(II)₂ [1–3]. The invoked reason for this ferromagnetic interaction is the delocalization of the copper unpaired electron into the unoccupied Gd 6s orbital, which forces all the unpaired electrons to align their spin according to Hund's rule. Ferromagnetism can also be imposed by symmetry, *i.e.*, the magnetic orbitals of nearest neighbor metal ions are orthogonal (or close to be) [4–8]. As a consequence, there is no kinetic exchange and the only contributions to the exchange coupling are the direct exchange, which is always ferromagnetic, and the spin polarization, which may be either positive or negative. As ferromagnetic interactions are usually of weak magnitude and relatively difficult to obtain, antiferromagnetic couplings between magnetic units of different spins (resulting in a ferrimagnet) are an interesting alternative. One can

quote the first structurally characterized regular ferrimagnetic chain, $\text{MnCu}(\text{dto})_2(\text{H}_2\text{O})_3 \cdot 4.5\text{H}_2\text{O}$ with $\text{dto} = \text{dithiooxalato}$. Magnetization studies show a saturation at low temperature indicating a spin $S = 2$ per $\text{Mn}(\text{II})\text{Cu}(\text{II})$ unit resulting from an antiferromagnetic coupling between the two metal ions [9,10].

Besides the use of inorganic metal complexes, large efforts have been made to synthesize stable organic high-spin molecules. The simplest idea consists in getting a magnetic building block that might play a role similar to that of the magnetic transition metal ion in inorganic metal chemistry. A first strategy has been introduced by Longuet Higgins [11] and further developed by Higuchi [12] and Mataga [13]. The main idea consists in exploiting the topological degeneracy of magnetic molecular orbitals to generate magnetic organic spin carriers with a high-spin multiplicity. Strategies to induce ferromagnetic interactions between organic radicals have been developed since the 1960s. Following the McConnell strategy [14] based on spin polarization effects, several authors could synthesize high-spin organic compounds exhibiting a ferromagnetic interaction between carbenes [15]. A similar approach consists in choosing the connectivity between the magnetic building blocks such that it results in a high-spin ground state. This can easily be achieved using the Ovchinnikov's rule [16], also proposed by Klein [17], which enables one to predict the spin ground state multiplicity of any alternant hydrocarbons from topological arguments. This strategy, firstly exploited by several groups [18–21], is still used to conceive magnetic compounds and 2D materials with ferro-, ferri- and antiferromagnetic properties [22–25]. It has been exploited both in a bottom-up and top-down philosophy. In the latter approach, it has been possible to conceive magnetic 2D materials by introducing molecular holes in graphene, *i.e.*, the removal of magnetic units in appropriate positions from the graphene leads to a magnetic material with controlled properties. An exhaustive presentation of the various proposed strategies to conceive magnetic systems is of course out of the scope of the present article but let us also mention the first pure organic *p*-nitrophenylnitronylnitroxide molecular compound exhibiting a ferromagnetic transition, which was reported in 1991 by Kinoshita [26] and the impressive work performed by Rajca [27–29] who has been able to generate huge spin in organic architectures.

Combining inorganic metal chemistry and organic chemistry has led to new advances in the conception of high-spin molecules. This approach has first been proposed by Gatteschi and coworkers and is known as the metal-radical approach. It relies on the direct coordination of transition metal ions to free radicals. As the coupling is direct, the simple use of the Goodenough–Kanamori rule enables one to predict the nature of the magnetic coupling. The aim of this strategy was to synthesize molecules with strong magnetic couplings [30–33].

Another milestone in order to conceive high-spin molecule consists in exploiting the double-exchange phenomenon. The double-exchange mechanism rationalizes the appearance of a high-spin ground state in mixed valence systems with several unpaired electrons per magnetic unit. It is also at the origin of the magnetoresistive effects observed in doped manganites [34,35]. As rightly pointed out by Lemaire, little work has been devoted to the synthesis of high-spin molecules with a double-exchange mechanism [36]. However, getting a high-spin state thanks to the double-exchange mechanism would be advantageous in many respects. The existence of two electronic populations, one localized and the other one delocalized, offers the opportunity to combine magnetic and transport properties and would be of wide interest in the domain of molecular spintronics. Another advantage comes from the energetic splitting of the states, which is usually larger than in the case of purely magnetic systems. This feature would be particularly interesting in order to exploit the magnetic anisotropy properties that might be affected by the spin mixing with excited states. Among the various interesting magnetic systems, one may quote single chains magnets and magnetic metallacrowns. Indeed, the discovery of single chains [37,38] opened a new trend of research in the field of molecular magnetism with potential application in one-dimensional information storage and molecular electronics. The metallacrowns, discovered in 1989 [39–41], are actually recognized as an exceptional class of coordination compounds as they combine a variety of beneficial synthetic and structural features [42–44]. Only a few examples of metallacrowns exhibiting a single molecule magnet behavior are known. The reason for this rareness is the presence of a low-spin ground state

due to antiferromagnetic couplings between the metal ions in most cases [45]. One may hope that, for some peculiar values of the interactions between the metal ions, a double-exchange regime can be achieved leading to a high-spin ground state in doped metallocrowns. The present work focuses on this double-exchange regime and aims to gain further insight into the factors controlling spin alignment in doped magnetic chains and doped metallocrowns with a local spin $s = 1$ per magnetic unit. As the size of these correlated systems is too large to allow an *ab initio* study, calculations using the double-exchange model and different values of its interactions will be performed. It is worth noticing that, as shown in many *ab initio* studies [46] devoted to the extraction of model Hamiltonians, the effective interactions of these models account for the orbital order and for the effects of the ligands as well as for the charge and spin polarization effects. The relevance of these models for the description of real compounds is therefore dependent on the reliability of the interaction values used in the calculations. The range of values that correspond to those found in the literature for real compounds will therefore be indicated.

The article is organized as follows. In the next section, the interactions involved in the double-exchange mechanism will be recalled. Keeping the most important interactions in the double-exchange model, model chains and metallocrowns of different sizes will be theoretically studied in Section 3. The main objective is to determine the range of values of the interactions for which a double-exchange regime can be achieved. Finally, the most important results are summarized in the conclusion section where some perspectives will be discussed.

2. Interactions of the Double-Exchange Model

The double-exchange mechanism has been the subject of several theoretical works and the corresponding model is now well established [35,47–59]. In a system of two magnetic sites, each having a local spin larger than $\frac{1}{2}$, for instance an $s = 1$ triplet ground state, the ground state of the binuclear system is a singlet for an antiferromagnetic coupling between the two spin $s = 1$. In the ionized state, obtained for instance by removing one magnetic electron, the ground state is not systematically a doublet state, as occurs for the ionization of a closed shell ground state, but may be a high-spin state, *i.e.*, a quartet state in the considered case. The interpretation of this dramatic effect has been the subject of numerous theoretical analyses. The first one is due to Zener [34,35] who proposed a spin-dependent delocalization mechanism in order to rationalize the magnetoresistive effects observed in manganites. This delocalization is described by a hopping integral t between the orbitals having the largest overlap. Let us call a_1 and b_1 (a_2 and b_2) the local orthogonalized magnetic orbitals of center 1 (center 2, respectively) (see Figure 1). For a larger overlap between the orbitals labeled a , $t_a = t_{a_1 a_2}$ couples determinants of total $M_s = 3/2$ which are product of an $m_s = 1$ local triplet state component ($T^+ = |a_1 b_1 \uparrow\rangle$) on one site and an $m_s = 1/2$ local doublet state component (noted D^+) on the other site:

$$\langle a_1 b_1 b_2 | \hat{H} | a_2 b_1 b_2 \rangle = \langle T_1^+ D_2^+ | \hat{H} | D_1^+ T_2^+ \rangle = t_a \quad (1)$$

This interaction generates two quartet states with an energy difference of $2t_a$. In the total $M_s = 1/2$ subspace, the hopping integral generates two doublet states with an energy difference of t_a . As the lowest quartet is stabilized by $|t_a|$ while the energy of the lowest doublet is only lowered by $\left|\frac{t_a}{2}\right|$, this interaction favors a ferromagnetic order. Later, Anderson and Hasegawa [47] derived both classic and quantum models of the spectrum of ionized states. In this derivation, they introduced the effect of the local non-Hund state (singlet $S^0 = (a_1 \bar{b}_1 + b_1 \bar{a}_1) / \sqrt{2}$), which is at the energy $2K$ above the local triplet state; K being the exchange integral between the electrons located on the same center:

$$\langle a_1 \bar{b}_1 | \hat{H} | b_1 \bar{a}_1 \rangle = \langle a_2 \bar{b}_2 | \hat{H} | b_2 \bar{a}_2 \rangle = K \quad (2)$$

for a left-right symmetric compounds. The effect of the non-Hund states stabilizes the doublet states in comparison to the quartets. Finally, Girerd and coworkers [49] have pointed out the fact that the upper

multiplicity ground state loses the energetic benefit of the antiferromagnetic coupling J_b between the electrons occupying the b orbitals. Refined models, combining the Anderson Hasegawa and the Girerd and Papaefthymiou mechanisms at work in the spectrum of the bi-nuclear complexes have been derived by the authors and coworkers [54–59]. The analytical expression of the energies of the two quartet and two doublet states are:

$$\begin{aligned} E(Q_{\pm}) &= \pm t_a \\ E(D_{\pm}) &= K - \sqrt{K^2 + t_a(t_a \pm K)} - \frac{3}{2}J_b \end{aligned} \quad (3)$$

Figure 1 gives a typical spectrum of a binuclear system and the energy differences between the various states as functions of the main interactions. It must be noted that the main antiferromagnetic contribution comes from the non-Hund states. As shown in many theoretical papers in which the various interactions are extracted from *ab initio* calculations, the antiferromagnetic interaction J_b is usually very small. Nevertheless, in most of the works devoted to double-exchange compounds, the model used neglects the non-Hund states, *i.e.*, K is assumed to be infinite. One must pay attention to the fact that the effect of the two different antiferromagnetic contributions (finite K and J_b) can hardly be distinguished from the spectrum only. As a consequence, the values of J_b extracted from the spectra with models that do not explicitly account for the non-Hund states are overestimated. As J_b is usually very small, it will be neglected in the following.

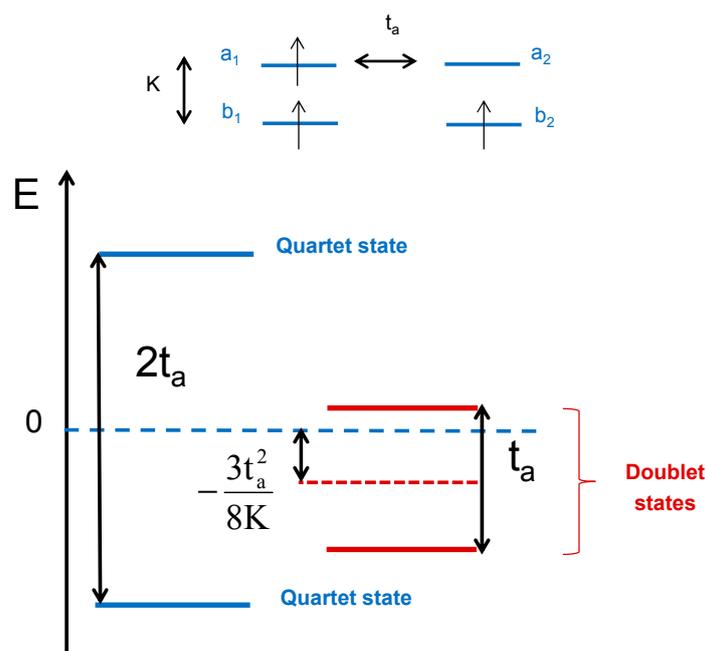


Figure 1. Orbitals and interactions involved in a double-exchange system of two sites (top). Typical low energy spectrum of a two-site system exhibiting a double-exchange mechanism. The splitting energy between the two quartet states is $2t_a$ while that of the two doublets is t_a . The mean energy of the doublet states is lowered by the quantity $-\frac{3t_a^2}{8K} - \frac{3|J_b|}{2}$ (bottom).

In the case of poly (>2) nuclear molecules and a single hole, an additional interaction is needed as two centers bearing 2 electrons (d^2) will interact through a magnetic exchange J such that:

$$J = \langle a_1 \bar{a}_2 | \hat{H} | a_2 \bar{a}_1 \rangle = J_a \quad (4)$$

if one neglects the direct exchange between the two centers (or at least those between a_1 and b_2 and a_2 and b_1). As shown by Coronado and coworkers [52], if the model space is only constituted of products of atomic ground state (*i.e.*, the non-Hund states are not explicitly considered), another interaction known as the exchange transfer has to be taken into account as it is larger than the magnetic coupling J between the centers that do not host the hole. This interaction involves three centers; it couples two determinants $|T_1^+ T_2^+ D_3^{-1/2}\rangle$ and $|D_1^{1/2} T_2^+ T_3^0\rangle$ (where the indices refer to atom labels and the upper indices to the local m_s components) through an outer space determinant involving a non-Hund local singlet state $|T_1^+ D_2^{1/2} S_3^0\rangle$ (T, D and S stand for triplet, doublet and singlet, respectively). The corresponding interaction is t_a^2/K at the second order of perturbations. As K is quite often smaller than t , the perturbative expression is not appropriate and the explicit (variational) account for the non-Hund states is compulsory for the treatment of polynuclear double-exchange compounds. The Hamiltonian writes:

$$\hat{H} = \sum_i 2K \hat{S}_{a_i} \cdot \hat{S}_{b_i} + \sum_{\langle ij \rangle} 2J \hat{S}_{a_i} \cdot \hat{S}_{a_j} \delta_{n_i n_j} + \sum_{\langle ij \rangle} t \left(a_{a_i}^+ a_{a_j} \delta_{n_i(n_j+1)} + a_{a_j}^+ a_{a_i} \delta_{n_j(n_i+1)} \right) \quad (5)$$

where $t = t_a$, \hat{S}_{a_i} is the spin operator acting on the electron localized in orbital a of site i ; a and a^+ are the annihilation and creation operator in second quantization, respectively; δ is the Kronecker symbol; and n_i the number of unpaired electrons on site i . $\delta_{n_i n_j}$ is equal to 1 when the number of electrons on site i is equal to that on site j and zero otherwise.

One may wonder whether a unique t is considered. Indeed orbital order resulting in different t interactions between the magnetic centers often appears in manganites, for which a two-orbital double-exchange model has been proposed [60]. Different values of t can be used in our code but as the considered systems are spin chains and spin crowns with magnetic sites having two magnetic orbitals, real compounds to which our study applies could be made of Ni(II) ions in octahedral environment. In such systems, Jahn-Teller distortions are not likely to occur and quite symmetric architectures are expected. The here-reported study should also apply to systems presenting small chemical distortions. Figure 2 show molecular magnetic orbitals optimized at the Hartree-Fock level for the highest spin state for chains of four sites and crowns (rings) of four and five sites. Due to symmetry reason, these orbitals are linear combinations of atomic d orbitals (e_g -like) having all the same overlap with their first neighbors. As $|t|$ is proportional to the overlap, a single hopping integral is obtained. It is interesting to note that the family of double-exchange states to which the ground state belongs has the hole delocalized in orbitals with the shape of $d_{x^2-y^2}$ in crowns and d_{z^2} in chains.

The qualitative origin of the double-exchange phenomenon is easy to understand (see for instance the text-book of O. Kahn [8]): the delocalization of the hole takes place between the two magnetic orbitals presenting the largest hopping integral and can only play freely when the spins on both sites are aligned. In the low-spin state, where the spins of the different sites are opposite, the delocalization of the hole requires violating the local Hund's rule, and is damped by the preference of the magnetic sites to keep a local high-spin multiplicity.

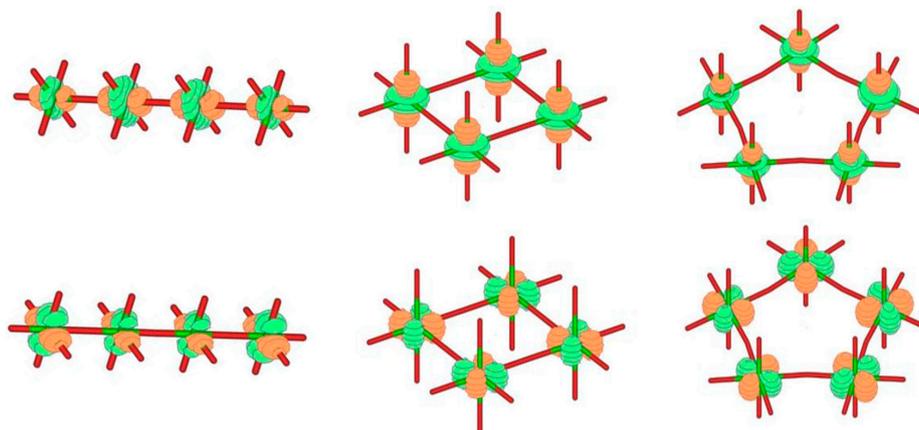


Figure 2. Magnetic molecular orbitals optimized at the Hartree-Fock level for the highest spin state of: single hole doped four-site spin chain (**left**); four-site ring (**middle**); and five-site ring (**right**).

3. Computational Information

A homemade code [61] has been developed in order to build the Hamiltonian matrix of the double exchange model for architectures of any topology. As the Hamiltonian commutes with \hat{S}_Z , separated matrices for each M_S components are computed. A routine of analysis is also available which calculates the expectation value of \hat{S}^2 . We have solved the model Hamiltonian in order to get the low energy spectrum, using exact (but not full) diagonalization methods, either using traditional LAPACK subroutines [62] or, for larger systems, with the SLEPc library [63,64].

Phase diagrams as functions of J and K parameters (in unit of $|t|$) for the various systems have been calculated. In order to be representative of real systems, the following physical parameters ranges for J and K were considered:

$$\begin{aligned} 0.01 |t| &\leq J \leq 0.15 |t| \\ 0.3 |t| &\leq K \leq 1.8 |t| \\ t &< 0 \end{aligned} \quad (6)$$

In order to give an order of magnitude of typical values of such interactions encountered in real compounds for which double-exchange has been observed, one can mention for instance calculated values obtained in doped manganites : $K = 1.28eV$ and $|t| = 1.29eV$ [57] and in the $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^{2+}$ compound: $|t| = 1.4eV$, $K = 1.2eV$ [54]. Values of J and K have also been calculated in non-doped nickelates $K = 0.6eV$ and $J = 30meV$. Much smaller values of $K = 0.3eV$ are observed in organic magnetic systems [22] as the magnetic orbitals are delocalized over several carbon centers.

Diagrams are computed as follows. About 200 points covering the full parameter ranges of J and K have been used with 20 points for J and 10 points for K . The Hamiltonian matrix has been built and diagonalized at each point to obtain the low energy spectrum. These energies were used to form the surfaces of the spin subspaces as functions of J and K . The surfaces formed of 200 points alone are not sufficient to get accurate curves of intersection. Therefore, a bi-cubic spline interpolation function was used to get more precise surfaces. The interpolated surfaces were then used to obtain the curves of intersection between the various spin subspaces. These curves of intersection were then used to draw the phase diagrams of the various systems.

4. Results and Discussion

Various linear and cyclic systems of spin $s = 1$ have been considered ranging from three to seven magnetic sites. Real systems involving Ni(II) metal ions, either magnetic chains or magnetic metallacrowns, to which these model systems apply, may be found in the literature [45,65–69]. In order to determine the range of parameters for which the ground state would be a high-spin state, the different parameters of the double-exchange model have been varied, covering a large range of physical values.

4.1. Spin Chains

All studied systems show a low-spin ground state $S = 0$ in absence of impurities (hole) due to an antiferromagnetic coupling J between sites. The presence of a single hole results in a competition between the double-exchange mechanism, which tries to align spin ferromagnetically, and the exchange mechanism (J), which imposes an antiferromagnetic order.

Comparing the phase diagrams (see Figure 3) computed for linear systems of different size leads to the following conclusions.

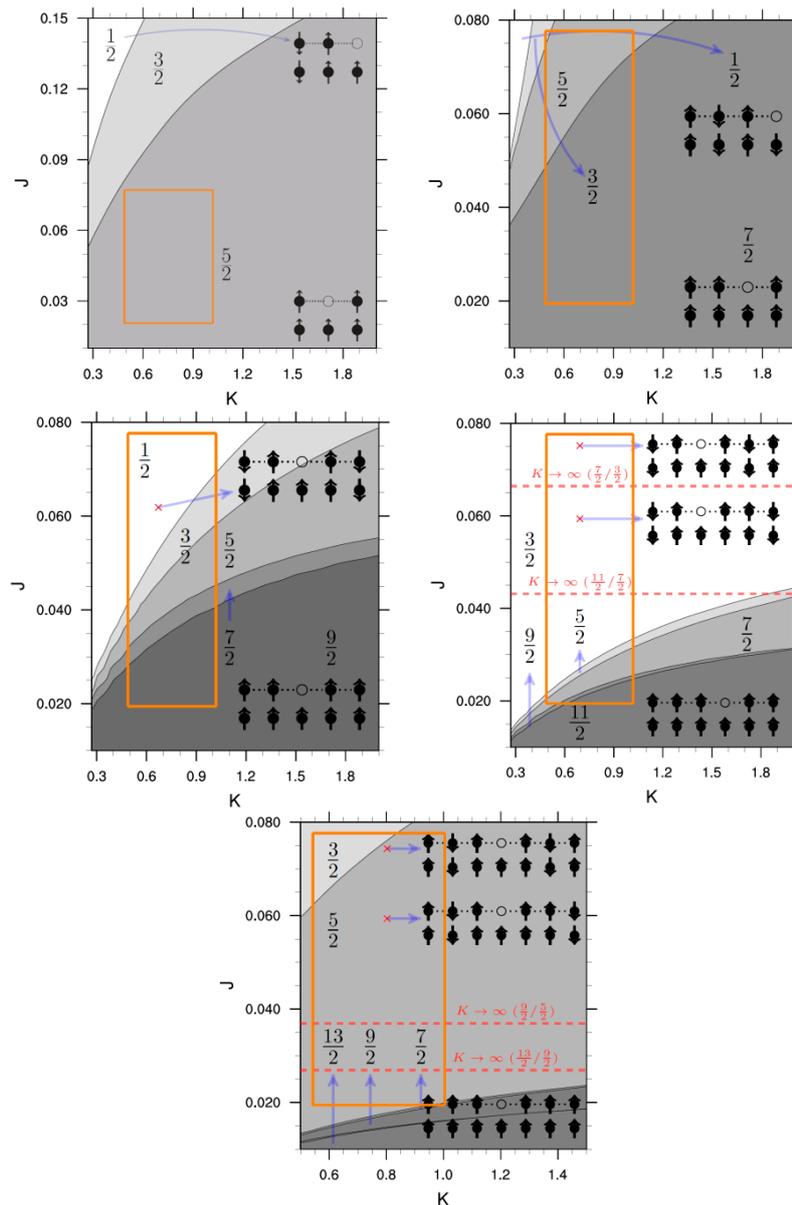


Figure 3. (From top to bottom and left to right) phase diagrams of system of three, four, five, six and seven sites for various values of the antiferromagnetic coupling J and local exchange K . Orange rectangles indicate the values of J and K in units of $|t|$ that are commonly found in magnetic compounds. The nature of the ground state is partially depicted by the determinants having the largest coefficient in the ground state wave function. The dotted red line represents the transition between the indicated spin states for the limit $K \rightarrow \infty$.

For realistic values of the interactions, the high-spin state is almost always the ground state for systems of three and four sites. The spin dependent delocalization (double-exchange interaction) dominates the physics of low energy in comparison to the exchange coupling. This can be easily rationalized by the fact that winning either one (for three sites) or two (for four sites) J interaction(s) requires to locate the hole on the border and therefore to lose part of the delocalization (kinetic) energy. The determinants having the largest coefficient in the ground state wave function are represented in Figure 3, showing that in the lowest spin state the hole is located on the border atoms. Note that only the determinant where the hole is on the right side is represented, its counterpart with the hole on the left side has of course the same coefficient.

For intermediate sizes, *i.e.*, five and six sites, all the spin states may be the ground state depending on the relative values of the interactions. Of course, the obtaining of the highest spin state requires very small values of J for the six-site system and an $S = 3/2$ ground state would be more probable for physical values of the $\frac{J}{|t|}$ interaction. One may note that the determinants with the largest coefficient show a spin alignment over three sites around the hole in the lowest spin states of the five- and six-site systems.

For larger systems, the highest spin state can hardly be the ground state. However, it is interesting to note that an $S = 5/2$ ground state can easily be obtained for seven-site systems. Looking at the determinant having the largest coefficient, it can be noted that the hole is delocalized over three or four sites and an antiferromagnetic spin wave runs over the other sites. As the delocalization of the hole is restricted to three or four sites and does not strongly depend on the size of the system, this allows us to anticipate that the same logic would apply to system of eight and nine sites (and probably larger), leading to an $S = 5/2$ ground state for reasonable values of the interactions.

In Figure 3, the transition between several spin states obtained for an infinite value of K is represented showing the importance of considering finite values of K . The neglect of the non-Hund states leads to unphysical spin transition in the diagram and could let think that the high-spin states could be reached for physical values of the interactions while it is not the case.

4.2. Spin Crowns

Spin metallocrowns are polymetallic molecules with several transition metals usually bridged by organic ligands. They can be modeled with cyclic chains (rings). In absence of hole, crowns with an even number of magnetic centers would adopt an $S = 0$ spin ground state due to the antiferromagnetic interactions, whereas for odd numbers of magnetic centers, crowns would present an $S = 1$ degenerate ground state due to frustrated antiferromagnetic couplings. Calculations have been performed for the reasonable value of $K = 0.6|t|$ and varying the parameter $\frac{J}{|t|}$. The variation of K around the considered value would not qualitatively change the obtained results. Figure 4 represents the spin of the ground state for both linear and cyclic chains (for comparison) as a function of $\frac{J}{|t|}$. The analysis of these curves leads to the following conclusions.

The behavior of linear chains and cyclic systems with an even number of sites is quite similar: as J decreases the highest spin states are stabilized. As well and expectedly the value of J needed for getting a high-spin ground state decreases with the number of sites. Nevertheless, it should be noted that the regime of double-exchange is larger for cyclic than for linear chains, *i.e.*, the highest spin ground states is kept for larger values of J . Indeed, the absence of border atoms in cyclic systems allows the hole to be delocalized over the full system. As a consequence, the alignment of the spins is expected to occur for larger values of J in comparison to linear open chains. A more detailed explanation is given below where we compare cyclic and open chains.

The systems with an odd number of sites show an unexpected behavior. The three sites cyclic system never exhibits a double-exchange phenomenon: its ground state is always a low-spin state. For systems with a larger number of sites, a high-spin ground state can be observed for

intermediate values of J but the ground state is a doublet state for $J = 0$ (and for small values of J). The double-exchange regime is therefore only observed for a small range of finite values of J . To get further insight on this atypical behavior, several calculations have been performed, leading to the following conclusions.

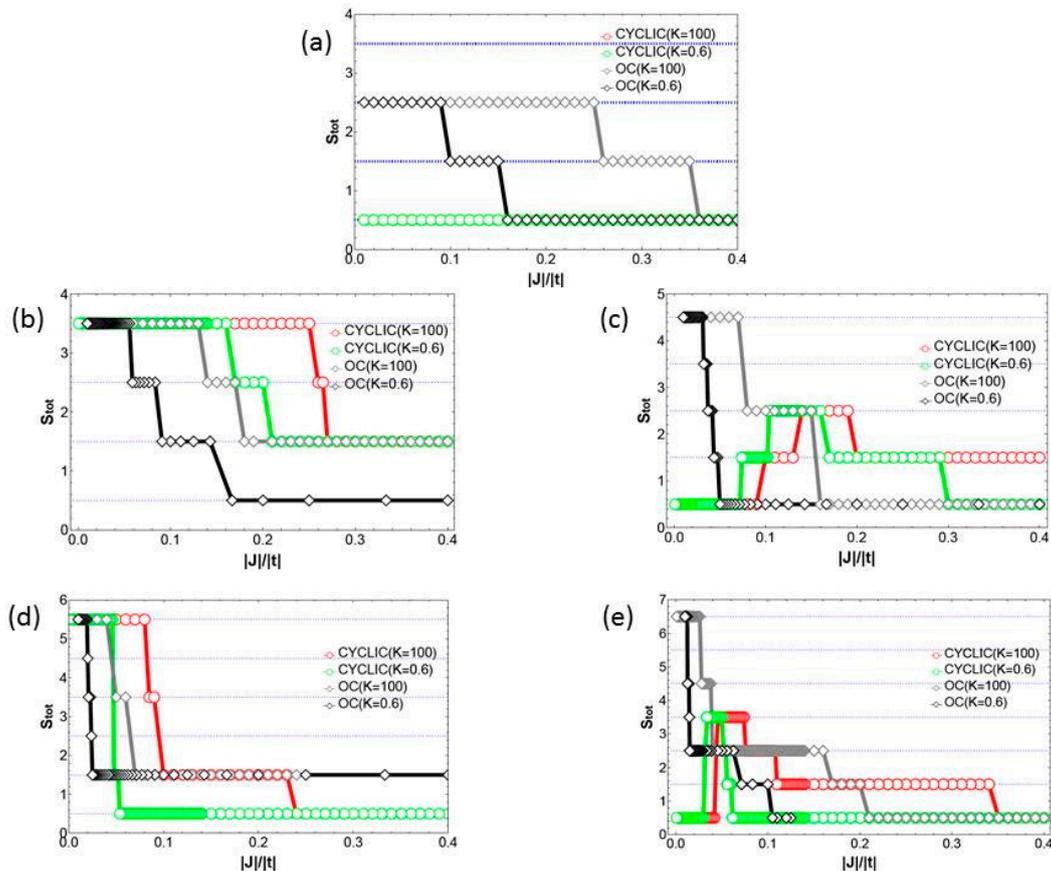


Figure 4. From top to bottom and left to right: Spin of the ground state as a function of the antiferromagnetic magnetic coupling for both open chains (OC) and cyclic chains with three (a), four (b), five (c), six (d) and seven (e) sites.

The curves have been plotted for a larger value of $K = 100 |t|$ (see Figure 4). Even for this huge value of K , the three-site system never has a high-spin ground state. For larger systems, the same behavior as for $K = 0.6 |t|$ is observed but as expected the double-exchange regime is shifted to higher values of J . One should note, however, that the wrong spin ground state is obtained over a very large range of values of J for the five-, six- and seven-site system. This result confirms the importance of the non-Hund states.

In the three-site case, the energies of the lowest doublet, quartet and sextet states have been computed at $J = 0$ and $K = 0.6 |t|$ for both the cyclic and linear chains (see Figure 5). It can be noted that the cyclization is responsible for a complete change in the energetic ordering of the states: the sextet is destabilized, the quartet is stabilized by a small amount of energy and the doublet is greatly stabilized. The destabilizing effect of the sextet state can be mathematically understood when looking at the Hamiltonian matrix of the sextet states. Let us consider that the sites are numbered consecutively, *i.e.*, 1 is linked to 2, 2 to 3 and 3 to 1 (in the cyclic system). The link between the atoms 1 and 3 introduces a hopping integral $|t|$ appearing with a positive sign (due to the Slater rules) in the Hamiltonian matrix. This results in a destabilization of the sextet states of the cyclic system in comparison to that of the open chain for which the corresponding matrix element is zero. The analytical energies of the sextet

states in the cyclic and open chains are respectively: $-2K - |t|$ and $-2K - 1.4142|t|$. As the Slater rule introduces a change in sign depending on the parity, such a destabilization always occurs for systems with an odd-number of sites and rationalizes the occurrence of a low-spin state at $J = 0$ and for small values of J .

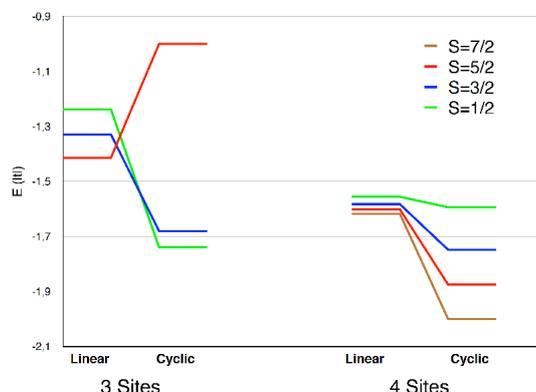


Figure 5. Low energy spectra of the linear and cyclic systems of three sites (**left**) and four sites (**right**) for $K = 0.6|t|$ and $J = 0$. For an even number of sites, the cyclization induces a stabilization of all the states and does not change the energetic ordering of the spin states. For an odd number of sites, the cyclization changes the energetic ordering of the spin states and destabilizes the highest spin state.

In order to understand why the double-exchange regime is larger for cyclic chains than for open chains with an even number of sites, the same calculations were performed for the four-site cases. The calculated spectra (for $K = 0.6|t|$ and $J = 0$) are reported in Figure 5. At variance with the systems with an odd-number of sites, the cyclization does not change the energetic ordering of the states. It leads to a stabilization of all the states and introduces a larger splitting between them. As a consequence, the highest spin state may survive as a ground state for larger values of J and the double-exchange regime is extended in comparison to linear chains. Here again, the solution of the Hamiltonian for the highest $S = 7/2$ spin state can be found analytically. The Hamiltonian matrix here exhibits a negative hopping integral matrix element $-|t|$ for the interaction between atoms 1 and 4, which results in a stabilization of the highest spin state in comparison with the open chain of four sites for which the element is zero. The corresponding analytical energies are $-3K - 2|t|$ and $-3K - 1.618|t|$ for the cyclic and open chains, respectively.

The energies of the lowest and highest spin states which happen to be the ground state for some values of J and the physical value of $K = 0.6|t|$ have been computed as functions of J (see Figure 6) in the case of a five-site system. When J increases one may see that: (i) the decrease in energy of the $S = 1/2$ ground state at $J = 0$ is slower than that of the $S = 5/2$ and $S = 7/2$ higher spin states, explaining the appearance of these high-spin states for intermediate values of J ; and (ii) the decrease in energy of the low-spin $S = 1/2$ ground state at high values of J is faster than that of the high-spin states, explaining the occurrence of a low-spin state at large J values.

In order to understand the electronic structure of the ground states for the different values of J one may look at their physical content, which is partially depicted by the determinants which have the largest coefficients in the wave functions (see Figure 6). First of all, one should mention that the doublet ground state changes in nature when J varies. For symmetry reason, an avoided crossing occurs between two doublets resulting in a smooth curve. At variance two quartet states cross as can be noticed in the figure at $J \sim 0.14|t|$. For small values of J , the ground states are dominated by determinants that benefit from the delocalization over three sites, are only stabilized by $2J$ (two spin alternant bonds) and have one spin frustration. As J increases, these spin distributions are less favored than others for which the number of spin alternant bonds is larger. For large values of J , the lowest doublet state is dominated by determinants which have three spin alternant bonds

and no spin frustration but have lost part of the delocalization energy over the three sites (as the hole is not surrounded by same spin determinants). The $S = 3/2$ states have large coefficients on two determinants, which form a local $T^0 = (|a_i\bar{b}_i| - |b_i\bar{a}_i|)/\sqrt{2}$ ($s = 1, m_s = 0$); one determinant is plotted. One may note that only one of the two determinants brings a contribution to the exchange coupling energy, *i.e.*, is spin alternant with the surrounding bonds. For the large values of J the $S = 3/2$ state is dominated by determinants in which T^0 is located at the vicinity of the hole and therefore loses part of the delocalization energy, as only one of the two determinants has an up spin in the a orbital.

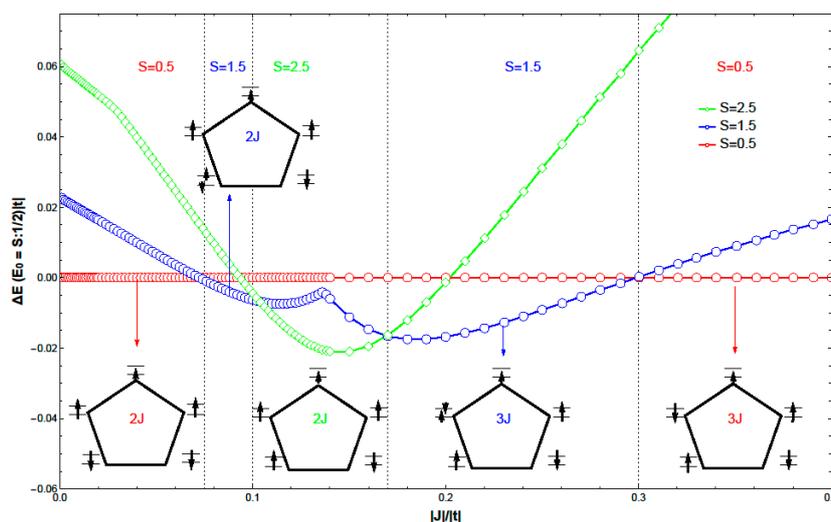


Figure 6. Energy differences between the various ground states and the lowest $S = 1/2$ state for the five-site cyclic system as functions of the antiferromagnetic coupling. The dominant determinants in the various spin ground states for $K = 0.6|t|$ and different values of $|J|/|t|$ are shown. The energetic contribution of the magnetic exchange in each of these determinants is indicated. The determinant having two opposite spins on the same center is combined with another determinant where the two spins are reversed, leading to a local triplet with $m_s = 0$: $T_0 = (a_1\bar{b}_1 + b_1\bar{a}_1)/\sqrt{2}$.

5. Conclusions

This work was devoted to the possible occurrence of a high-spin ground state in magnetic chains and crowns resulting from a double-exchange phenomenon. It has been shown that:

- (i) For systems having three to seven magnetic units and physical values of the double-exchange parameters, the occurrence of a high-spin ground state is possible, either the highest spin state for three, four, five and eventually six sites or an intermediate (between the highest and the lowest) spin state for six and seven sites or larger systems. For all studied model architectures, the regime of double-exchange, *i.e.*, the range of parameters for which the system exhibits a high-spin state has been determined.
- (ii) While the cyclic systems with an even number of sites exhibit a double-exchange regime larger than that of the chains, due to the stabilizing factor of the cyclization, those with an odd number of sites could only have a high-spin ground state for values of the magnetic exchange that are specific, finite and depending on the size of the system.
- (iii) Variational accounting for the non-Hund states is required in order to get reliable values of the parameters for which a double-exchange phenomenon occurs.

In conclusion, the double-exchange mechanism happens to be an interesting alternative to ferro- and ferrimagnetism to create high-spin molecules. Doped spin chains and metallacrowns could be an interesting class of new compounds for which all magnetic properties such as magnetic anisotropy

could be observed. The physics of realistic compounds based on Ni(II) metal ions should be ruled by the above discussed model. Such a study could easily be generalized to highest spin systems, which could serve as a guide for systems involving cobalt, manganese or iron metal ions. Another perspective would be to exploit the presence of two electronic populations, localized and itinerant electrons, to combine magnetic and transport properties in molecular electronics and spintronics.

A further study will be devoted to one- and two-dimensional lattices, with the objective to study the collective properties resulting from the presence of several holes. As such materials should exhibit magnetoresistive effects, the impact of a magnetic field on their electronic structure will be studied.

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