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High-Nuclearity Mixed-Valence Clusters and Mixed-Valence Chains: General Approach to the Calculation of the Energy Levels and Bulk Magnetic Properties

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A general approach to the problem of electron delocalization in the high-nuclearity mixed-valence (MV) clusters containing an arbitrary number of localized spins and itinerant electrons is developed. Along with the double exchange, we consider the isotropic magnetic exchange between the localized electrons as well as the Coulomb intercenter repulsion. As distinguished from the previous approaches dealing with the MV systems in which itinerant electrons are delocalized over all constituent metal sites, here, we consider a more common case of systems exhibiting partial delocalization and containing several delocalized domains. Taking full advantage of the powerful angular momentum technique, we were able to derive closed form analytical expressions for the matrix elements of the full Hamiltonian. These expressions provide an efficient tool for treating complex mixed-valence systems, because they contain only products of 6*j*-symbols (that appear while treating the delocalized parts) and 9*j*-symbols (exchange interactions in localized parts) and do not contain high-order recoupling coefficients and 3*j*-symbols that essentially constrained all previous theories of mixed valency. The approach developed here is accompanied by an efficient computational procedure that allows us to calculate the bulk thermodynamic properties (magnetic susceptibility, magnetization, and magnetic specific heat) of high-nuclearity MV clusters. Finally, this approach has been used to discuss the magnetic properties of the octanuclear MV cluster $[Fe_8(\mu_4\text{-}O)_4(4\text{-}Cl\text{-}pz)_{12}Cl_4]^-$ and the diphthalocyanine chains $[YPc_2]\cdot CH_2Cl_2$ and $[ScPc_2]\cdot CH_2Cl_2$ composed of MV dimers interacting through the magnetic exchange and Coulomb repulsion.

1. Introduction

Mixed-valence (MV) magnetic clusters are of current interest in areas as diverse as solid-state chemistry, molecular chemistry, biochemistry, and especially in molecular magnetism. These clusters contain ions of the same transition metal in different oxidation states. Under some conditions (equivalent metal sites, nonvanishing intercenter hopping integrals, weak vibronic trapping, etc.), the extra electrons in these clusters can be delocalized over the network of metal sites. This delocalization gives rise to the so-called double exchange that couples the localized magnetic moments through an itinerant electron that can travel between the magnetic centers. Since the itinerant electron keeps the orientation of its spin in the course of transfer, double exchange results in a strong spin polarization effect which favors a ferromagnetic spin alignment in the system. First, this mechanism of electron-spin interaction was suggested by Zener[1] to explain the ferromagnetism observed in the mixed-valence manganites of perovskite structure, such as $(La_{1-x}Ca_x)MnO_3$. Presently, these MV oxides are an active focus of research in solid-state chemistry, as they exhibit colossal magnetoresistance.[2] Anderson and Hasegawa[3] suggested a solution of the double-exchange problem for an MV

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pair deducing the spin dependence of the double-exchange parameter. Finally, De Gennes[4] demonstrated how these ideas can be applied to the study of the extended systems.

Until recently, the calculation of the energy pattern formed by the double exchange and Heisenberg exchange has been restricted to comparatively simple MV systems comprising one or two itinerant electrons (or holes) delocalized over a restricted number of exchange-coupled metal sites (dimers,[5−9] trimers,[9−12] and tetramers,[9,13−17] basically). However, even for these simple cases, the role of the electron delocalization has proved to be different in each particular case. Thus, while in MV dimers, the double exchange always results in a strong stabilization of the higher spin (ferromagnetic spin alignment); in MV systems of higher nuclearity, the double exchange can also favor the stabilization of the spin states different from the ferromagnetic one, this effect being dependent on the sign of the electron-transfer integral and on the overall symmetry of the MV system. As a consequence, the conclusions obtained for the relatively simple clusters cannot be, in general, extended to MV systems of higher nuclearity which involve localized and delocalized spins in complicated molecular and crystal structures.

The previous remarks allow us to justify the need for developing a general approach to the problem of the calculation of the energy spectrum of MV systems containing an arbitrary number of the localized magnetic moments and itinerant electrons, taking into account all relevant electronic interactions. But, besides these reasons, one can mention at least two more reasons why such an approach is required.

The *first reason* is related to the existence of two classes of high-nuclearity MV systems that are of current interest in molecular magnetism and magnetochemistry, namely, large MV clusters and MV chains. As the representatives of the first class of MV systems, one can mention the hexanuclear−octahedral clusters $[Fe_6(\mu_3\text{-}X)_8(PEt_3)_6]^+$ ($X = S$, Se).[18−20] Other important representatives of this class are the so-called polyoxometalates.[21−31] These inorganic complexes present discrete cluster-like highly symmetrical structures of definite sizes and shapes formed by a large number of MO_X polyhedra (usually octahedra and tetrahedra; $M = V$, Mo, W), which resemble discrete fragments of metal oxide structures. Polyoxometalates have a remarkable electron storage capacity that has attracted considerable interest in catalysis and other interrelated areas, including applications in materials and solid-state chemistry and biomedical applications. Typical examples of MV polyoxovanadates are $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ and $[V_{12}As_8O_{40}(HCO_2)]^{3-,5-}$ (see refs 28−30). The polyoxotungstates and polyoxomolibdates are represented by the anions with Keggin and Wells-Dawson structures. These anions can be reversibly reduced to mixed-valence species (heteropoly blues and browns) by addition of various specific numbers of electrons, which are delocalized over a significantly large number of atoms of the heteropoly framework (see ref 21 and refs therein). An additional possibility of accommodation into these structures of paramagnetic metal atoms, which contain localized magnetic moments, yields to MV clusters in which localized and itinerant electrons can coexist and interact.[21,22,28−31] In the theory of mixed valence, these polyoxometalate complexes are very suitable as model systems to study electron delocalization and magnetic interactions in high-nuclearity clusters. As an example of a large MV cluster, one can mention the fulleride anion C_{60}^{2-}, which contains two electrons delocalized over 60 equivalent carbon sites.[32] The interest in the electronic structure and magnetic properties of this system was generated by the discovery of superconductivity[33,34] and ferromagnetism[35] in fulleride salts. Finally, recently an octanuclear MV iron cluster with partial electron delocalization has been reported.[36] Another class of high-nuclearity MV systems contains the chain MV compounds in which we also face the problem of the interaction between localized and delocalized electrons. The representatives of this class are the diphthalocyanine chains $[YPc_2]\cdot CH_2Cl_2$ and $[ScPc_2]\cdot CH_2Cl_2$.[37,38]

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The *second reason* is the challenge to overcome the limitations imposed by the conventional approach to treating the problem of the electronic interactions in high-nuclearity MV systems. Such limitations precluded from the successful theoretical study of the magnetic and spectroscopic properties of complex MV systems. Consideration of these limitations led us to develop a new efficient approach[39−41] suitable for the calculation of the energy patterns formed by the electronic interactions in MV systems containing large numbers of spin cores and itinerant electrons. This allowed us to explain the magnetic properties of hexanuclear octahedral iron−sulfur MV clusters[20] and also properties of higher nuclearity MV systems, including polyoxometallates[42−46] and fulleride anion[32] (see also review article[47] and references therein).

In spite of its high efficiency, the approach developed in refs 39−41 was still based on some simplifying assumptions concerning the structure of the compound, which significantly limit the applicability of the approach to complex MV systems. First, in refs 39−41 all metal sites in the cluster are assumed to be equivalent. The second assumption is that all extra electrons are allowed to be delocalized over all constituent metal sites; that is, all ions can change their oxidation states in the course of electron transfer. These restrictions preclude from consideration an important class of MV clusters exhibiting partial electron delocalization. In such clusters, only part of the metal ions are involved in the electron delocalization (double exchange), whereas the spins of other ions remain constant. In this Article, we go beond these simplifying assumptions and consider the most general case of the MV system, which contains several delocalized domains as well as the localized one, with the electron transfer between different domains being forbidden. We develop a quite general theoretical approach for the calculation of the energy levels and bulk thermodynamic properties (magnetic susceptibility, magnetization, and magnetic specific heat) of high-nuclearity MV clusters exhibiting partial electron delocalization. The first part of this paper is devoted to present this new approach. In the second part, the potentialities of this approach are illustrated with two examples: the first of them representing the octanuclear MV cluster $[Fe_8(\mu_4\text{-}O)_4(4\text{-}Cl\text{-}pz)_{12}Cl_4]^-$ and another one being the diphthalocyanine chains $[YPc_2]\cdot CH_2Cl_2$ and $[ScPc_2]\cdot CH_2Cl_2$ composed of mixed-valence dimers interacting through the magnetic exchange and Coulomb repulsion.

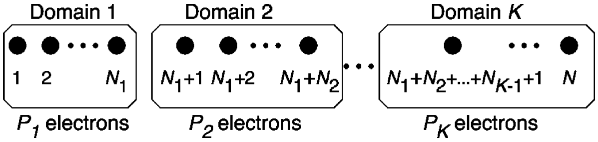

Figure 1. Scheme of the MV system with the indication of the domains.

2. Theoretical Approach

2.1. Model of the High-Nuclearity MV System. An approach to the problem of double exchange in high-nuclearity clusters containing a large number of localized spins and itinerant electrons has been worked out in our article[41] where we consider the MV system comprising one or several extra electrons delocalized over all constituent metal sites. As distinguished from this earlier approach, here we focus on a more common case when the MV system exhibits partial-electron delocalization. The system under the study consists of N metal sites and an arbitrary number P of delocalized electrons as schematically shown in Figure 1. We will consider the case of a strong one-site Coulomb repulsion that usually occurs in the transition metal clusters, so that the configurations with two (or more) electrons on the same site are excluded. In this sense, we imply the restriction $P < N$ that can be removed in the framework of the developed procedure provided that a more sophisticated consideration is required. We assume that under certain reasonable physical conditions the whole system can be divided into K mixed-valence domains each containing N_r ($r = 1, 2,..., K$) metal sites ($N_1 + N_2 +... + N_K = N$). Each domain contains an arbitrary number P_r of delocalized electrons ($P_1 + P_2 +... + P_K = P$), so that the domains are represented by the mixed-valence clusters of the type of $P_r\,\mathrm{d}^{n_r+1} + (N_r - P_r)\,\mathrm{d}^{n_r}$ containing P_r ions in d^{n_r+1} configuration and N_r-P_r ions in the configuration d^{n_r}.

A domain can be identified with a group of spins that are isolated (for example by an appropriate ligand surrounding) from the rest of the molecule. In this case, the transfer processes (double exchange) are confined to the area of the domain, and the exchange interaction is also absent. This limited case of a fully isolated domain is probably uncommon. In a more realistic case, the interdomain transfer processes are not forbidden, but they are strongly constrained, for example, due to the fact that such jumps result in a strong increase of the energy of the system (for example, by the value Δ). In this situation, the interdomain double exchange acts as a second-order perturbation. The result of the action of such second-order double exchange can be understood by taking into account spin dependence of the double-exchange parameter in a simple case of a cluster consisting of two domains: $t(S) \propto t_0(S+1/2)$, where S is a full spin of two coupled domains and t_0 is a biorbital-transfer integral (numerical factors are omitted). Spin dependence of the second-order correction to the energy can be expressed as $t(S)^2/\Delta \propto t_0S(S+1)/\Delta$. This dependence shows that an effective interdomain coupling represents the isotropic-

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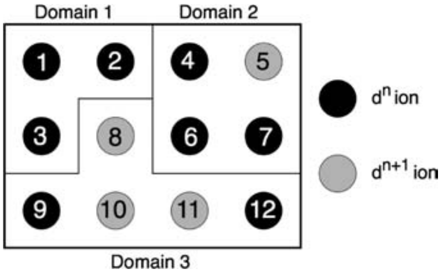

Figure 2. Illustrative example of the complex MV system comprising three domains.

exchange interaction in accordance with the Anderson's mechanism of the kinetic exchange through the virtual jumps of an electron to the adjacent magnetic center and back. An effective kinetic-exchange coupling parameter can be roughly estimated as $J \propto t_0^2/\Delta$. As it follows from this estimate, generally, the double exchange (first-order interaction) is expected to exceed the exchange coupling (second-order interaction). Nevertheless, the exchange interaction can be substantial (especially for high-nuclearity MV systems with large local spins) and gives rise to the important consequences in symmetric spin-frustrated MV systems exhibiting "accidental" degeneracy of many spin multiplets in the ground state.[47] For this reason, the Heisenberg−Dirac−Van Vleck (HDVV) exchange interaction between domains will be taken into account in our calculation procedure (section 2.3).

An interesting and physically important situation occurs when one or several P_r vanish. If $P_r = 0$, we are dealing with a domain consisting of the ions with the definite numbers of the electrons in the unfilled shells (fixed valences). These domains are not involved in the electron-transfer processes, so we will refer to them as localized domains. In general, the localized domains can be heteronuclear; that is, they can contain different ions (spins). The systems containing both localized and delocalized domains can be termed the mixed-valence systems with partial electron delocalization (see, for example, such kinds of polyoxometalates clusters in refs 28−30 and an octanuclear iron cluster in ref 36).

This general scheme of an MV system and the meaning of the notations can be illustrated by considering a particular case that is shown in Figure 2 for an instant distribution of the extra electrons over metal sites. This system comprises twelve sites ($N = 12$) and four itinerant electrons ($P = 4$). We assume that this cluster has such a structure that it can be divided into three ($K = 3$) domains.

The three sites ($N_1 = 3$) with the numbers 1, 2, and 3 (domain 1) are occupied by the localized spins so that the number of the delocalized electrons for this domain is zero ($P_1 = 0$). Domain 2 contains one excess electron ($P_2 = 1$) delocalized over four sites ($N_2 = 4$) with the numbers 4, 5, 6, and 7. Finally, in domain 3, three electrons ($P_3 = 3$) are delocalized over five ($N_3 = 5$) sites.

Here, for the sake of definiteness, we describe the case when $n_r + 1 \leq 5$; that is, all ions (with and without an extra electron) within rth delocalized domain possess less than half-filled d-shells. An active orbital space of each ion contains $n_r + 1$ orbitals, with n_r of these orbitals being singly occupied forming the high-spin ions (Hund state) with spins $s_0^r = n_r/2$. Conventionally, these d^{n_r} ions will be referred to as spin cores. The remaining (highest in energy) orbital is singly occupied when the site with the number f contains the d$^{n_r+1}$ ion or empty if the position f is occupied by the d^{n_r} ion. The d$^{n_r+1}$ ions are also assumed to be the high-spin ones, so the spins of the constituent ions in the rth delocalized domain will be either $s_f = s_0^r$ for the d$_f^{n_r}$ ion or $s_f = s_0^r + 1/2$ for the d$_f^{n_r+1}$ ion. Both kinds of ions (d^{n_r} and d$^{n_r+1}$) are supposed to possess orbitally nondegenerate ground terms that means that the low-symmetry crystal field removes the orbital degeneracy in both d^{n_r} and d$^{n_r+1}$ ions, and the excited states are much higher in energy than the effective electron-transfer integrals. We consider a common case assuming that the domains can be physically different (different ions, local crystal fields, etc.). In our notations, the number n of the core′s electrons are allowed to depend on the symbol r, and hence the core′s spin can be different for different domains. There are $N_r!/[P_r!(N_r - P_r)!]$ possibilities to distribute P_r extra electrons among N_r sites in the rth domain. Then, the total number of the electronic distributions in the whole cluster is calculated as follows:

$$\prod_{r=1}^{K} N_r![P_r!(N_r - P_r)!]^{-1} \tag{1}$$

2.2. Matrix Elements of the Double Exchange. The electron hopping from the i site to the k site is described by the following transfer (double exchange) Hamiltonian:

$$H_{\mathrm{tr}}(i \rightarrow k) = t_{ik} \sum_{\sigma} c_{k\sigma}^{+} c_{i\sigma} \tag{2}$$

where the operator $c_{k\sigma}^{+}(c_{i\sigma})$ creates (annihilates) an electron on the site $k(i)$ with the spin projection σ and t_{ik} is the transfer integral. Such Hamiltonian connects the states belonging to different electronic distributions. It is worthy to give a general view of spin functions that are used for the diagonalization of the double-exchange Hamiltonian:

$$|(s_\beta, \beta \neq i, k)(s_i = s_0^r + {}^1/_2, s_k = s_0^r)(\tilde{S})SM_S\rangle$$

In this representation of the vectors, the following notations for the quantum numbers are used:

(1) It is supposed that the extra electrons are instantly distributed over sites having spin cores s_0^r, i.e., belong to a definite distribution D.

(2) One of the sites in the domain r, namely, i, contains an extra electron that is explicitly indicated ($s_i = s_0^r + 1/2$).

(3) The site k in the domain r is empty ($s_k = s_0^r$).

(4) All remaining sites β of the full system (except two already indicated, $\beta \neq i, k$) can be either occupied by extra electrons or be empty according to the distribution D. This determines the set of spins s_β.

(5) Within an instant distribution D spins are coupled to give a set of intermediate spins ($\tilde{S}$) and a full spin S. The meaning of the quantum number $\tilde{S}$ can be clarified by a simple example of three coupled spins s_1, s_2, s_3. In this case, the spins s_1 and s_2 are to be coupled to give intermediate

spin $S_{12} \equiv \tilde{S}$, and then spin s_3 is added to give full spin S. In more complicated systems, there is a certain set of intermediate spins (for example, for four spins they can be chosen as S_{12} and S_{123}). The full set of intermediate spins is designated as $\tilde{S}$ in the notation of a spin function.

The method of derivation of the matrix element of the double-exchange Hamiltonian is described in detail in our article.[41] The calculations are rather tedious, so here we will only mention the main steps of this derivation. First, the wave functions $|s_f m_f\rangle$ of the constituent metal $d_f^{n_r}$ and $d_f^{n_r+1}$ ions are built. These wave functions represent, in general, the linear combinations of Slater determinants. Then, the wave functions of the whole cluster in the spin-uncoupled representation are constructed. In this representation, each wave function corresponds to a definite electronic distribution D (this distribution defines the set of the spins of the constituent metal ions $s_1, s_2,..., s_N$) and re-represents a symmetrized product of single-ion wave functions. The matrix element of the electron transfer connecting two states which differ in the position of one electron are simply calculated with the aid of the properties of Slater determinants and creation and annihilation operators. At the next step, using the Wigner coefficients, we build the wave functions in the spin-coupled $\{D(\tilde{S})\, S\, M_S\}$ representation, in which the spins of the individual ions (for a given D) are coupled in a successive way to give the total spin S of the cluster; $(\tilde{S}) \equiv \{\tilde{S}_2, \tilde{S}_3,..., \tilde{S}_{N-1}\}$ are the possible sets of the intermediate spins ($\tilde{S}_2 \equiv S_{12}$, $\tilde{S}_3 \equiv S_{123}$, etc.). Finally, M_S is the total spin projection. Note that the intermediate spins and total spin depend not only on the local spins within the delocalized domains but also on the set of local spins belonging to the localized domain. Using the expression for the matrix element in spin-uncoupled representation, one can express the matrix element in spin-coupled representation through the sum of products of Wigner coefficients. By applying the angular momentum theory,[48,49] one can reduce this sum to a product of 6*j*-symbol. In this way, we obtain the expression for the matrix element of the operator $H_{tr}(i \rightarrow k)$ given in Appendix I (see eqs AI.1 and AI.2). This expression represents the generalization of the results obtained in ref 41 to the case of the systems exhibiting partial delocalization and containing several delocalized domains. In contrast to the expressions deduced in early theories of the double exchange, eqs AI.1 and AI.2 contain the products of 6*j*-symbols only and do not include higher-order *nj*-symbols and also Clebsch−Gordan coefficients. From a general symmetry concept, the latter should not appear in the physical values in a properly designed theory that involves isotropic interactions only. This advantage reduces essentially the time required for the calculation and therefore allows to efficiently treat high-nuclearity systems.

Although eq AI.1 relates to the case of less than half-filled d-shells, it can also be used for the case of more than half-filled d-shells, because the matrices of the double exchange for the "complementary" systems $P_r\, d^{9-n_r} + (N_r - P_r)\, d^{10-n_r}$ and $P_r\, d^{n_r+1} + (N_r - P_r)\, d^{n_r}$ differ only in sign.[41]

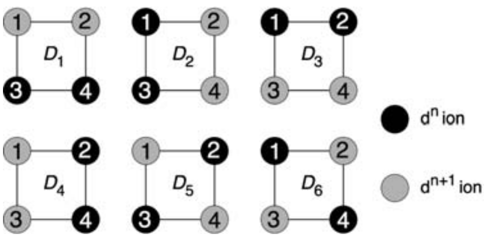

Figure 3. Electronic distributions for a square planar $2d^{n+1}-2d^n$ cluster.

2.3. Matrix Elements of the Isotropic-Exchange Interaction. As it was already mentioned along with the double exchange, one should take into account the HDVV-exchange interaction. This interaction can couple both the spins located in the same domain and those belonging to different domains. As a matter of fact, the HDVV exchange couples localized spins, which means that the HDVV Hamiltonian acts within each localization (electronic distribution) and therefore does not connect the states belonging to different distributions. For this reason, the exchange Hamiltonian, i.e., local spins and exchange parameters, should be defined for each electronic distribution separately. For a certain electonic distribution D, the Hamiltonian is given by

$$H_{ex}(D) = -2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} J_{ij}(D)\mathbf{s}_i\mathbf{s}_j \qquad (3)$$

where $J_{ij}(D)$ are the exchange integrals defined for a certain electronic distribution D. In this sense, the sets of the exchange parameters are dependent on the electronic distribution, and for this reason, the symbol D is explicitly indicated in the notation of the exchange integral. The dependence of the exchange parameters on the distribution D can be illustrated by considering a square planar $2d^{n+1}-2d^n$ cluster (two itinerant electrons per four sites) for which six electronic distributions are possible as shown in Figure 3 from which one can see also the values of the local spins. One can see that depending on the electronic distribution, the exchange integral J_{12} can take three different values related to the following three physically different kinds of interaction: $d^{n+1}-d^{n+1}$ (distribution D_1), d^n-d^n (distribution D_3), and $d^{n+1}-d^n$ (distributions D_2, D_4, D_5, D_6). The remaining exchange integrals can be classified similarly.

The matrix element of $H_{ex}(D)$ can be calculated with the aid of the irreducible tensor operator technique.[48,49] In this calculation, we use the same basis as that in eq AI.1. The expression for the matrix element of $H_{ex}(D)$ is given in Appendix II (eq AII.1).

Formulas AI.1, AI.2, and AII.1−AII.3 form a set of equations providing a theoretical background for the design of the computer program that is able to calculate the energy pattern of complex MV systems.

2.4. Contributions of Intercenter Coulomb Repulsion. Along with the HDVV exchange and the electron transfer, the Coulomb intercenter repulsion should also be included in the Hamiltonian. This contribution, that is in general strong, arises from the fact that different electronic distribu-

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(49) Bencini, A.; Gatteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled Systems*; Springer-Verlag: Berlin, 1990.

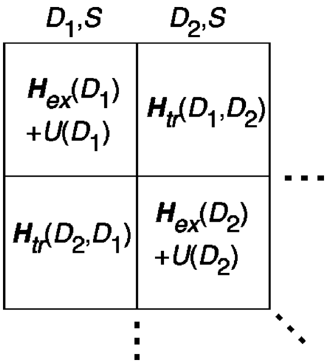

Figure 4. Scheme of the structure of the matrix of the Hamiltonian $H_{tr} + H_{ex}$ (D_1 and D_2 are different in the position of one electron).

tions possess, in general, different intercenter interelectronic Coulomb repulsion energies. Thus, when we turn back to the case of the square planar system shown in Figure 3, one can see that the Coulomb repulsion between the extra electrons located at the nearest sites (edge of the square) is stronger than that in the case when they are located on the remote sites (diagonal of the square). Therefore, there are two different Coulomb energies $U(D_1) = U(D_2) = U(D_3) = U(D_4) \equiv U_e$ and $U(D_5) = U(D_6) \equiv U_d$ with $U_e > U_d$.

2.5. Contributions Arising from the Inequivalence of Metal Sites. Finally, an additional contribution into the Hamiltonian appears if the metal sites belonging to the delocalized domains are nonequivalent, for example, due to a difference in the local crystal fields. Then, the sum of the orbital energies of the extra electrons becomes dependent on the electronic distribution *D*. The full orbital energy of the system corresponding to a certain distribution *D* can be simply added to the intercenter Coulomb energy for this distribution to get an effective parameter $U(D)$, which includes both contributions. This additional contribution as well as the full effective Coulomb energy are spin independent and for this reason appear as diagonal elements of the energy matrix.

2.6. Structure of the Total Hamiltonian Matrix. The structure of the matrix of the Hamiltonian that includes the electron transfer, HDVV exchange, and an effective Coulomb repulsion (that includes required orbital contributions) is schematically shown in Figure 4. The exchange interaction and Coulomb terms form the diagonal blocks with respect to the basis functions belonging to the definite electronic distributions, whereas the electron transfer gives rise to the off-diagonal blocks connecting the electronic distributions, which are different in the position of one extra electron. As far as the full Hamiltonian is isotropic, it is also diagonal with respect to the value of the total spin *S* that allows to additionally reduce the sizes of the matrices to be diagonalized as shown in Figure 4.

2.7. Calculation of the Magnetic Properties. Once we have the energy levels, we can evaluate different thermodynamic properties of the system as magnetization, magnetic susceptibility, and magnetic specific heat. Since anisotropic interactions are not included, the magnetic properties of the MV system do not depend on the direction of the magnetic field. For this reason, one can consider the magnetic field directed along the arbitrary axis *Z* of the molecular coordinate frame that is chosen as a spin quantization axis. In this case, the energies of the system will be $E_\mu(S) + g_e\beta M_S H_Z$, where $E_\mu(S)$ are the eigenvalues of the Hamiltonian containing magnetic-exchange and double-exchange contributions (index μ runs over the energy levels with given total spin *S*). Then, the partition function in the presence of the external magnetic field is given by

$$Z(H_Z) = \sum_{S\mu} \exp[-E_\mu(S)/(kT)] \sum_{M_S} \exp[-g_e\beta M_S H_Z/(kT)] \tag{4}$$

Using this expression, one can evaluate the magnetic susceptibility, magnetization, and specific heat using the standard thermodynamical definitions.

The above-described approach is accompanied by a fast and efficient computer program called MVPACK (that will be described elsewhere) for the calculation of the spin levels and derived properties of high-nuclearity MV systems.

3. Application of the Approach to High-Nuclearity MV Systems

3.1. Octanuclear MV Iron Cluster. In this section, we apply the developed approach to the analysis of the magnetic properties of the recently reported[36] octanuclear MV cluster $[Fe_8(\mu_4\text{-}O)_4(4\text{-}Cl\text{-}pz)_{12}Cl_4]^-$, where pz = $C_3H_3N_2^-$. Although the magnetic data for this system are at present unavailable, the developed approach can be used to predict possible types of the magnetic behavior depending on the relative values of the key parameters. The structure of this cluster (hereunder abbreviated as $Fe_4^{11/4+}$ $Fe_4^{3+}O_4$) along with the numeration scheme for iron centers is shown in Figure 5a. The system includes an inner MV iron core $3d^5{-}d^6$ which is valence-delocalized in the NMR, Mössbauer, and IR spectroscopy time scale and four apical Fe^{3+} ions which are coupled with the inner core through the isotropic magnetic exchange. As it follows from the structural data,[36] the heteroligand surrounding of the Fe-sites produces a rather low symmetry crystal field that definitely removes orbital degeneracy of the metal ions. Under this condition, the spin−orbital interaction is also suppressed, and the Hamiltonian of the system can be written as follows:

$$H_{oct} = \sum_{i=1}^{4}\sum_{j\neq i}^{4} H_{tr}(i\rightarrow j) - 2J\sum_{i=1}^{4}\sum_{j>i}^{4} \mathbf{s}_i\mathbf{s}_j - 2J'\sum_{k=1,2,3}\mathbf{s}_5\mathbf{s}_k - 2J'\sum_{k=1,2,4}\mathbf{s}_6\mathbf{s}_k - 2J'\sum_{k=2,3,4}\mathbf{s}_7\mathbf{s}_k - 2J'\sum_{k=1,3,4}\mathbf{s}_8\mathbf{s}_k \tag{5}$$

where *J* represents the isotropic exchange within the $3d^5{-}d^6$ MV core and *J′* represents the isotropic-exchange interaction between each apical iron center and the triangular base of the inner iron tetrahedron to which it lies closest. For the sake of simplicity, we neglect the difference between the exchange parameters for the $d^5{-}d^6$ and $d^5{-}d^5$ pairs provided that both iron ions are of the same type (inner or outer). Under such a simplified assumption, the exchange part of the Hamiltonian does not depend on the electronic distribution. The magnetic measurements and density functional

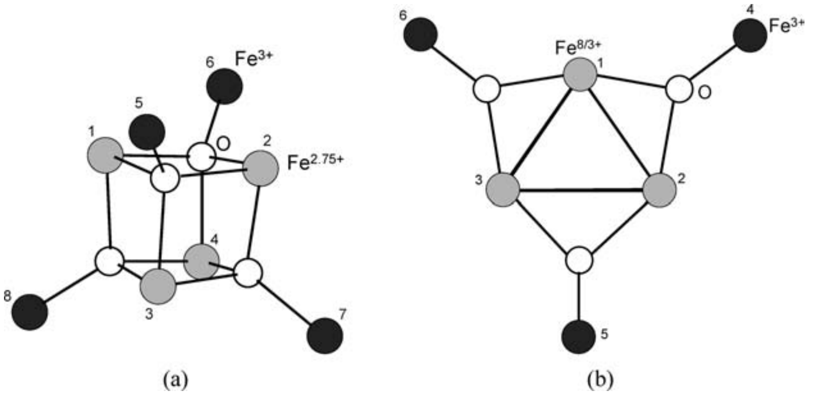

Figure 5. (A) Octanuclear iron−oxo cluster $Fe_4^{11/4+}Fe_4^{3+}O_4$ ([$3d^5-d^6$]−[$4d^5$]) reported in ref 36. (B) Model hexanuclear iron−oxo cluster $Fe_3^{8/3+}Fe_3^{3+}O_3$ ([$2d^5-d^6$]−[$3d^5$]).

theory (DFT) study[50] of the neutral complex $[Fe_8(\mu_4\text{-}O)_4(4\text{-}H\text{-}pz)_{12}Cl_4]$ revealed a strong antiferromagnetic-exchange interaction between the inner and outer iron ions and a weak antiferromagnetic exchange within the inner iron tetrahedron; the corresponding exchange parameters were found to be $J' = -25.5$ cm^{-1} $J = -1.05$ cm^{-1}. Later on, we will use these values in the calculations of the energy levels. It should also be noted that the problem of mixed valency is inherently related to a vibronic pseudo Jahn−Teller interaction that determines both the degree of localization of the moving electron and the shape of the intervalence optical bands. It was argued[36] that the vibronic coupling is intermediate so that the system under consideration belongs to class II according to Robin−Day classification. Nevertheless, in the present consideration, we neglect the vibronic coupling in order to illustrate the developed approach as a tool for the evaluation of spin levels in a fixed configuration of the system. This step of the calculations is required for the full consideration of the vibronic coupling including theoretical description of the intervalence optical absorption bands and magnetic properties.

The largest dimension of the submatrix is 55 640 for $S = 9/2$. Although the exact diagonalization of such a big matrix is feasible with the aid of powerful methods like the Lanczos algorithm, these calculations prove to be too time consuming. For this reason, instead of the octanuclear cluster, we will analyze a more simple model hexanuclear cluster $Fe_3^{8/3+}Fe_3^{3+}O_3$ (Figure 5b) in which the main features of the magnetic behavior of the octanuclear system seem to be retained. The model system contains the inner iron triangular core $2d^5-d^6$ with delocalized extra electron and three outer Fe^{3+} ions, each of them being exchange coupled with two inner iron centers. The Hamiltonian for the hexanuclear cluster is given by

$$H_{\text{hex}} = \sum_{i=1}^{3}\sum_{j\neq i}^{3} H_{\text{tr}}(i\rightarrow j) - 2J\sum_{i=1}^{3}\sum_{j>i}^{3} \mathbf{s}_i\mathbf{s}_j - 2J'\sum_{k=1,2}\mathbf{s}_4\mathbf{s}_k - 2J'\sum_{k=2,3}\mathbf{s}_5\mathbf{s}_k - 2J'\sum_{k=1,3}\mathbf{s}_6\mathbf{s}_k \quad (6)$$

To justify a possibility to consider the hexanuclear cluster instead of the octanuclear one, we performed the calculation of the energy patterns of the double-exchange splittings for the delocalized MV cores $3d^5-d^6$ (tetrahedral) and $2d^5-d^6$ (triangular). It should be noted that in an MV dimer positive and negative t values produce the same double-exchange splittings as it was stated in the pioneer paper of Anderson and Hasegava.[3] In a more general case, the energy patterns of MV systems can be dependent on the sign of t (see review article[47]). These energy patterns for $3d^5-d^6$ (tetrahedral) and $2d^5-d^6$ (triangular) are shown in Figure 6 for the case of a negative t value. If $t > 0$, we obtain the overturned energy patterns. One can see that in both systems, negative ($t < 0$) double exchange stabilizes the ferromagnetic ground state, whereas for $t > 0$ the ground level is highly degenerate (frustrated) and comprises all spin states, with the exception of the state with the maximal spin that proves to be the first excited state. Such similarity of the energy patterns for $3d^5-d^6$ and $2d^5-d^6$ clusters follows from the fact that both systems possess the triangular faces which give rise to the transfer frustration and dependence of the energy levels on the sign of the transfer parameter.[9,10,15−17,20,47] For this reason, the systems $Fe_4^{11/4+}Fe_4^{3+}O_4$ and $Fe_3^{8/3+}Fe_3^{3+}O_3$ are expected to be quite similar from the point of view of their magnetic behavior.

Note that the sign of the metal−metal electron hopping parameter is governed by the p-orbitals of intervening ligands. Since both σ- and π-type pathways give negative contributions[51,52] the overall t is expected to be negative. Nevertheless, to illustrate the computational procedure, we will present the results for both cases $t < 0$ and $t > 0$. Figure 7 shows the energy pattern of the $Fe_3^{8/3+}Fe_3^{3+}O_3$ cluster for the case of negative double exchange. One can see that the combined effect of the double exchange and isotropic exchange is antiferromagnetic. This result has a clear physical meaning, which is explained by Figure 8. In fact, the effect of double exchange inside the $2d^5-d^6$ triangle is ferromagnetic, so all spins (two spins 5/2 and one spin 2) are coupled parallel, and the state of the $2d^5-d^6$ cluster with the spin $S_{123} = 7$ is stabilized. Strong antiferromagnetic exchange between the 123 triade and the three outer spins 5/2 couple these spins antiparallel to the spin S_{123}, and thus, the total

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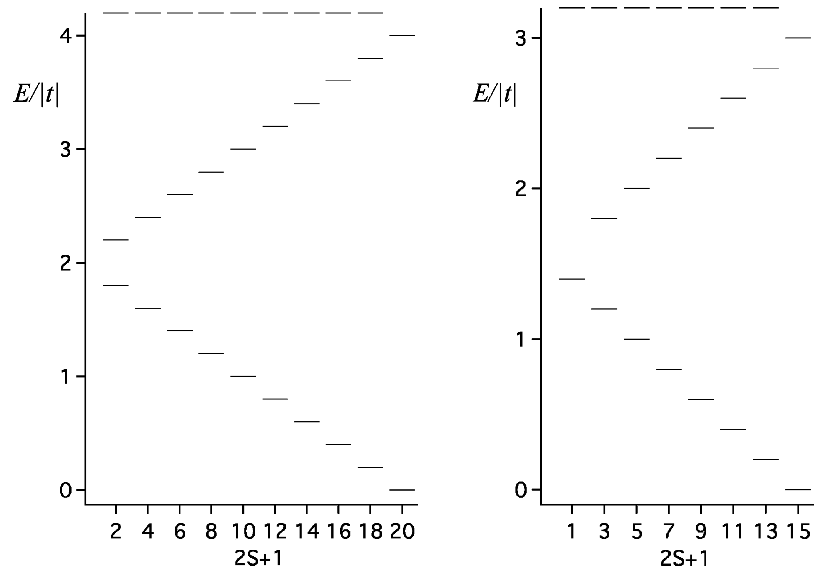


(a) (b)

Figure 6. Energy patterns of tetrahedral $3d^5{-}d^6$ (a) and triangular $2d^5{-}d^6$ (b) clusters calculated with $t < 0$. (The energy patterns for the case of positive t are overturned.)

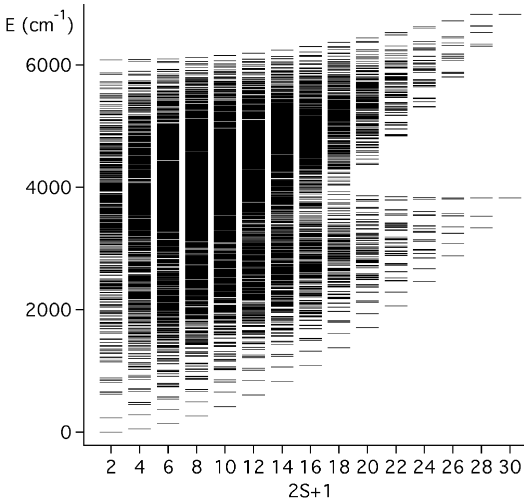


Figure 7. Energy pattern of the MV cluster $[2d^5{-}d^6]{-}[3d^5]$ calculated with $t = -1000$ cm^{-1}, $J = -1.05$ cm^{-1}, $J' = -25.5$ cm^{-1}.

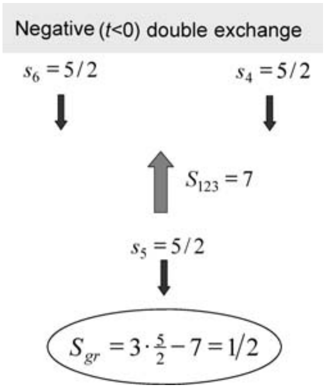


Figure 8. Schematic image of the combined effect of the negative double exchange within the 123 triangle and the antiferromagnetic exchange between the 123 and 456 triangles in the $[2d^5{-}d^6]{-}[3d^5]$ cluster on the spin of its ground state.

spin of the full $[2d^5{-}d^6]{-}[3d^5]$-cluster in the ground state proves to be the minimal one ($S_{gr} = 1/2$).

In the case of positive double exchange ($t > 0$), the spin of the ground state can be either $S_{gr} = 3/2$ (Figure 9a) or $S_{gr} = 1/2$ (Figure 9b) depending on the relative values of the parameters t and J' (J-interaction is weak to produce significant impact on the energy levels). These results can be easily understood by inspecting Figure 6b. We have seen that for $t > 0$ the ground state of the MV core $2d^5{-}d^6$ comprises the states with the spin values $S_{123} = 0, 1, 2, 3, 4, 5$, and 6, and the state with $S_{123} = 7$ is the first excited one. Figure 10 shows the schematic image of the combined effect of the exchange and double exchange. The antiferromagnetic exchange between the spin core and the outer ions 4, 5, 6 couples the spins s_4, s_5, and s_6 antiparallel to the spin S_{123}. The stabilization of the levels with $S = |S_{123} - s_4 - s_5 - s_6|$ (only these levels are shown in Figure 10) is stronger for larger values of S_{123}, so for the level with $S = 1/2$ arising from the first excited state ($S_{123} = 7$) of the $2d^5{-}d^6$ trimer this stabilization is maximal, whereas the levels with $S = 3/2, 5/2, \ldots, 13/2$ arising from $S_{123} = 6, 5, 4, 3, 2$, and 1, respectively, undergo a weaker stabilization which is decreasing with the decrease of S_{123}, finally, the level with $S = 15/2$ arising from the state of MV trimer with $S_{123} = 0$ remains unstabilized. Therefore, the double exchange and magnetic exchange produce competative effects on the spin of the ground state, namely the double exchange tends to stabilize the state with the spin $S = 3/2$ arising from the spin $S_{123} = 6$ of the MV triade, whereas the exchange interaction tends to stabilize the ground state with the spin $S = 1/2$ corresponding to $S_{123} = 7$. For this reason, the interplay between the positive double exchange and antiferromagnetic-Heisenberg exchange gives rise to the ground state with the spin $S = 3/2$ for the case of strong double exchange (Figures 9a and 10a) and spin $S = 1/2$ for the case of weak double exchange (Figures 9b and 10b).

We thus arrive at the conclusion that the cluster $Fe_3^{8/3+}Fe_3^{3+}O_3$ (and thus the cluster $Fe_4^{11/4+}Fe_4^{3+}O_4$) possesses either the ground state with $S = 1/2$ (arbitrary negative

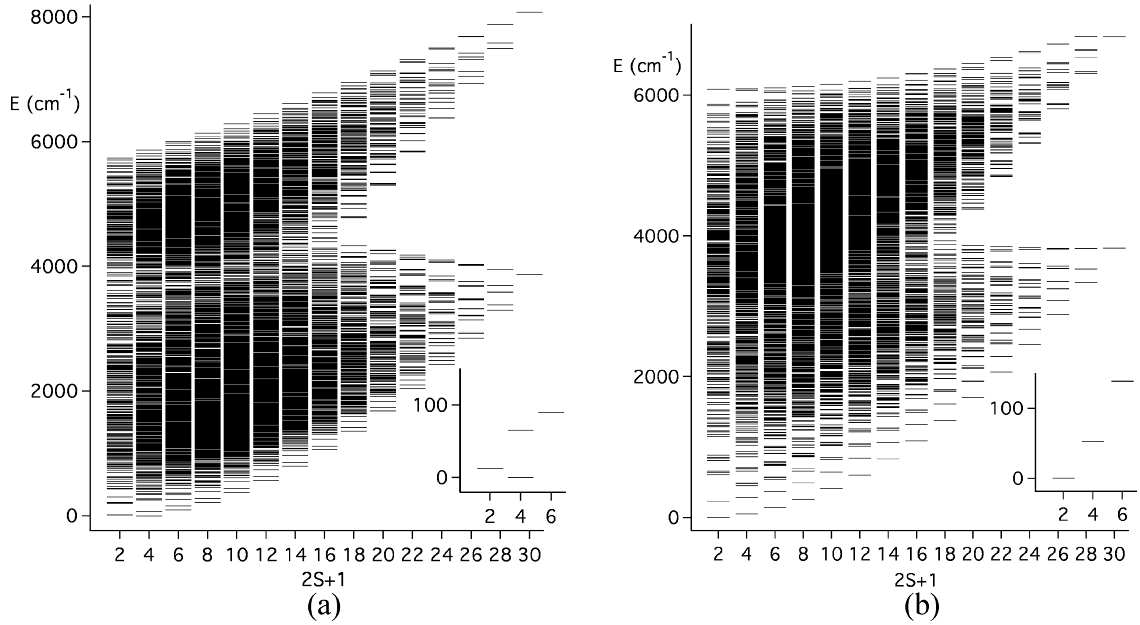


Figure 9. Energy pattern of the MV cluster [2d^5−d^6]−[3d^5] calculated with $J = -1.05$ cm^{-1}, $J' = -25.5$ cm^{-1}, and $t = 1400$ cm^{-1} (a), $t = 1000$ cm^{-1} (b). (Insets show the schemes of the low-lying energy levels.)

or weak positive double exchange) or $S = 3/2$ (strong positive double exchange) spin values.

3.2. Diphthalocyanine MV Chains. Besides the clusters, the developed approach is useful for treating the chain compounds composed of MV fragments interacting with each other through the magnetic exchange and the Coulomb repulsion. In these cases, the behavior of the infinite chain can be obtained by extrapolation of the exact results performed on clusters of increasing size. Just to illustrate the potentialities of the theoretical approach in the case of one-dimentional MV systems, we will focus on the chain consisting of MV dimers. We will enumerate the units of the chain as A_1B_1, A_2B_2,..., A_nB_n, where $n = N/2$ is the number of dimers (number of delocalized domains) in the chain, and N is the number of sites. Each MV dimer is assumed to have one extra electron delocalized over two spinless cores A_iB_i. The states with two electrons in the dimeric unit are expected to be inaccessible due to the strong intracluster Coulomb repulsion. This system can be regarded as a model of the diphthalocyanine chains [YPc$_2$]·CH$_2$Cl$_2$ and [ScPc$_2$]·CH$_2$Cl$_2$.[37,38] In the compound [YPc$_2$]·CH$_2$Cl$_2$, each yttrium atom is sandwiched between two phthalocyanine rings, and the [YPc$_2$] molecules are stacked in columns parallel to the *c* axis (Figure 11). The extra electron of each Pc$^-$ Pc^{2-} MV pair is delocalized over two phthalocyanine rings, so the system does represent an infinite chain of MV dimeric units. The scandium diphthalocyanine chain is isostructural with the yttrium diphthalocyanine one. The magnetic behavior of these compounds indicates the presence of weak ferromagnetic interactions within [YPc$_2$] and [ScPc$_2$] chains.

Three types of interactions seem to be important: (i) electron delocalization inside each dimeric unit, which is described by the intracluster transfer parameter $t_{A_iB_i} \equiv t$ (the hopping parameter does not depend on the index i because all MV dimers are identical), (ii) ferromagnetic-exchange interaction between the electrons occupying adjacent sites of the neighboring dimers (the associated parameter is $J_{B_iA_{i+1}} \equiv J$), and (iii) shortest distance interdimer Coulomb interaction, which is described by the parameter $U_{B_iA_{i+1}} \equiv U$. Using the MVPACK, we have computed the energy levels and the magnetic susceptibility of a finite chain formed by eight MV dimers (sixteen sites). With the aim of a better approach the properties of the infinite chain, the closed chain has been considered. One can expect several types of the electron density distributions in a chain, depending on the relative values of the parameters t, J, and U (Figure 12). Below, we will discuss these distributions together with the computed temperature dependence of the molar magnetic susceptibility per one MV dimer (Figures 13 and 14).

We start the discussion with the simplest case of $t = 0$. We have two limits, which will be referred to as strong exchange limit and strong Coulomb interaction limit, depending on the ratio J/U. In the strong exchange limit, the ground state of the chain corresponds to the antiferroelectric charge-ordered distribution shown in Figure 12a (the electric dipole moments of neighboring 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. Since the antiferroelectric charge ordering eliminates the exchange interactions between the exchange coupled B_i A_{i+1} pairs, the chain at low temperatures ($kT \ll J$) behaves as a set of $n/2$ isolated ferromagnetic dimers with $s = 1$, i.e., as a paramagnet formed by $n/2$ spins $s = 1$ (dashed line in Figure 13a).

In the strong Coulomb interaction limit, the electrons tend to be as separated as possible thus stabilizing a ferroelectric charge-ordered distribution shown in Figure 12e (all the dipole moments are parallel). As a result, the electrons cannot be magnetically coupled and the chain behaves at low temperatures ($kT \ll U$) as a paramagnet formed by n spins $s = 1/2$ (dashed line in Figure 13b). To summarize, one can say that providing $t = 0$ in both limiting cases the electrons are fully localized on one of

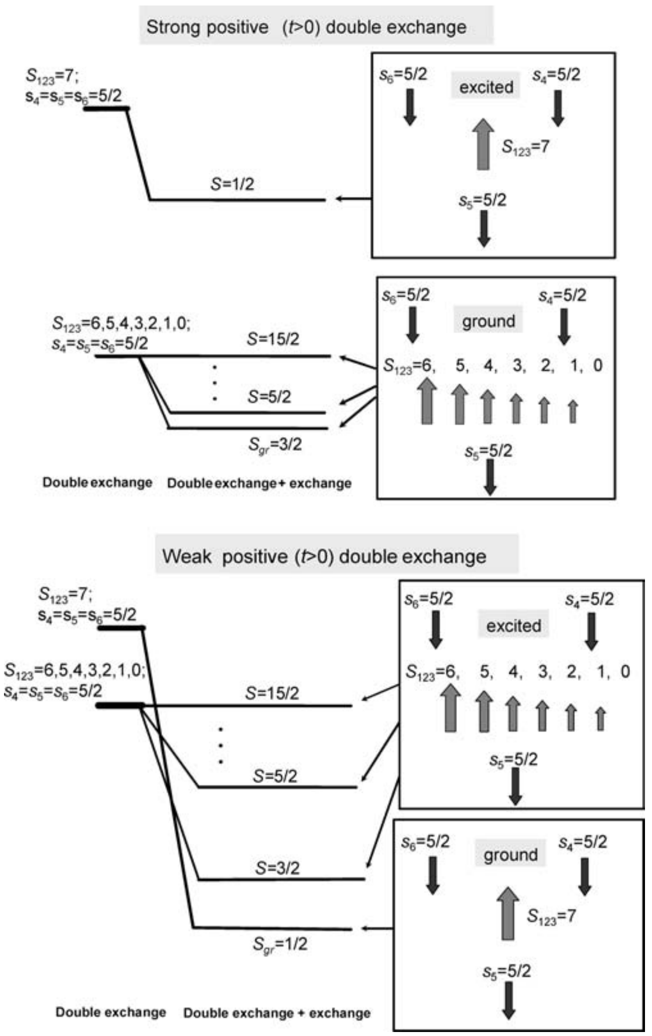


Figure 10. Schematic image of the interplay between the positive double exchange within the 123 triangle and the antiferromagnetic exchange between the 123 and the outer Fe^{3+} ions in the $[2d^5-d^6]-[3d^5]$ cluster on the ground-state spin: (a) strong double exchange, (b) weak double exchange.

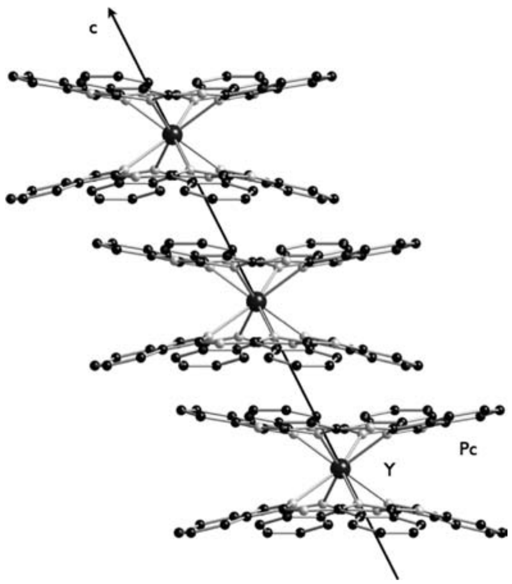


Figure 11. Stacking of the diphthalocyanine units in the $[YPc_2]\cdot CH_2Cl_2$ compound

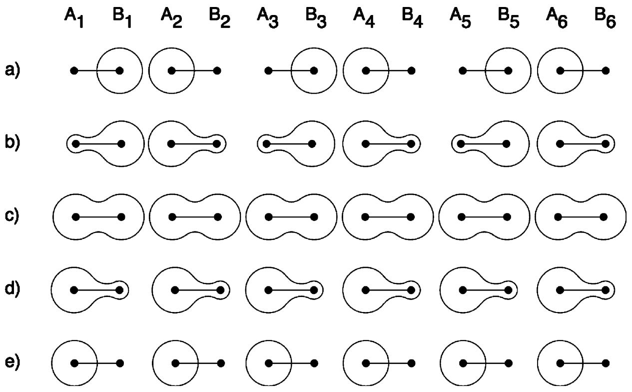


Figure 12. Electron density distributions in a chain of MV dimers: (a) antiferroelectrical paramagnetic, (b) antiferroelectrical ferromagnetic, (c) ferromagnetic with homogeneous electronic density distributions, (d) ferroelectrical ferromagnetic, and (e) ferroelectrical paramagnetic.

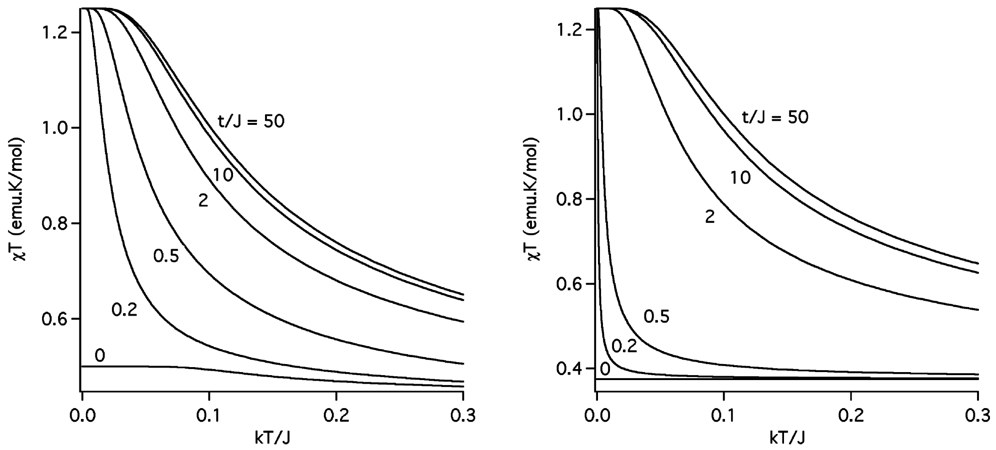
the two sites of the MV dimer thus preventing the occurrence of long-range spin correlations.

When $t \neq 0$, the electron density becomes different from zero on both sites of each MV dimer (Figure 12b,d). This results in the stabilization of a parallel alignment of all local spins due to the ferromagnetic-exchange interaction between nearest dimers. We thus arrive at the conclusion that at $t \neq 0$ the chain will exhibit a one-dimensional ferromagnetic behavior. This finding is in agreement with the magnetic behavior exhibited by $[YPc_2]$ and $[ScPc_2]$ chains. Figure 13 shows that the increase of t leads to an increase in the ferromagnetic coupling between spins (the χT vs T curves are shifted toward a higher T). In the limit of a very strong electron transfer, this effective ferromagnetic coupling between delocalized electrons reaches its maximum, because the electron density will be equally averaged over all the sites (Figure 12c). The maximum value of the effective exchange integral is equal to $J/4$.

The electron delocalization also accounts for the low-temperature minimum on the magnetic curve observed for a $[ScPc_2]$ chain.[37,38] As one can see in Figure 14, in the strong Coulomb interaction limit this minimum appears providing a weak electron transfer. Indeed, in this case in the low temperature region, χT decreases abruptly with the increase of T from its ferromagnetic low temperature limit toward the limit corresponding to a paramagnet containing n spins $s = 1/2$. 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, being formally ferromagnetic, exhibits the paramagnetic behavior inherent to n spins $s = 1/2$. The further increase of the temperature leads to the population of the excited states corresponding to the electronic distributions with partially restored exchange pathways. As a result, the ferromagnetic coupling becomes more efficient thus leading to the increase of χT. In the case of strong electron transfer, the exchange pathways are restored even for very low temperatures and we observe the monotonic ferromagnetic behavior.

Conclusions

Molecular chemists working in magnetism are producing more and more complex MV clusters from elementary building



(a) (b)

Figure 13. Effect of varying t on the low-temperature parts of the χT vs kT/J curves calculated for a chain of eight MV dimers: (a) strong exchange interaction ($U/J = 0$) and (b) strong Coulomb interaction ($U/J = 5$).

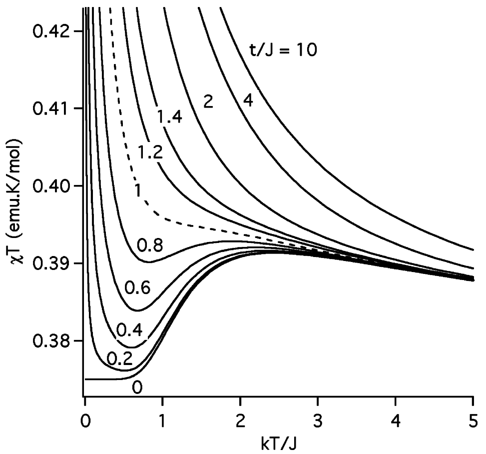


Figure 14. Effect of varying t on the χT vs kT/J curve calculated for a chain of eight MV dimers in the case of strong Coulomb interaction ($U/J = 5$).

blocks. A variety of reasons, already mentioned in the Introduction, justify the multidisciplinary interest for these complex systems. A common central point in this area is that of obtaining as much information as possible on the magnetic structure of the cluster (energies and wave functions of the different spin states), since it determines the peculiar properties of this class of magnetic molecular materials. This requires a development of new theoretical models and approaches adapted to quantatively analyze the magnetic and spectroscopic properties of MV systems. In this paper, we have developed a quite general approach to the electronic problem of electron delocalization in mixed-valence systems of high nuclearity. The spin-coupled representation for the basis has been considered in order to reduce the computational work. We have taken advantage of the successive (chain-like) spin-coupling scheme and used powerful angular momentum technique to derive a closed form expression for the matrix elements of the double exchange, which contains only products of 6*j*-symbols and does not contain neither high-order recoupling coefficients nor 3*j*-symbols. In their turn, the matrix elements of Heisenbertg exchange are expressed in terms of 9*j*-symbols only. This allowed us to build an efficient computational procedure to evaluate the eigenvalues and eigenvectors of high-nuclearity MV clusters with the unique restriction of the computer capacity. The important advantage of this approach in comparison with other related programs is that it is directly applicable to MV systems exhibiting partial-electron delocalization and containing several delocalized domains. The study of the magnetic behavior of the octanuclear iron cluster and diphthalocyanine chains performed in this work illustrates the power of the developed approach in the case of such complex MV systems.

It should be noted that the suggested rather general approach deals with the effective Hamiltonians of the isotropic exchange and double exchange like all model theories. Within this approach, all results are necessarily expressed in terms of the set of adjustable parameters. A microscopic (ab initio) evaluation of these parameters is an independent next step in the study of MV systems. Microscopic calculations of transfer and exchange integrals with the aid of DFT can be found in refs.[53−55] Such kind of evaluations are especially important when the number of adjustable parameters leads to an excessive flexibility in the best-fit procedure. The examples of calculations that are given in this article are aimed to illustrate the computational horizons rather than to study the cited systems in detail, in particular to analyze experimental data. This analysis along with the ab initio calculations will be done elsewhere. It should also be noted that the problem of mixed valency is inherently related to vibronic pseudo Jahn−Teller interaction. Evaluation of the adiabatic potentials and vibronic levels is a rather complicated separate task that is beyond the scope of this Article. The proposed approach provides the basis set of the electronic wave functions and the energy pattern underlying the solution of the vibronic problem. Finally, in

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the proposed approach, we use only the spin symmetry, whereas the point symmetry of the cluster is not exploited. One can expect that the use of point symmetry for high-symmetric clusters could simplify considerably the procedure of diagonalization of large matrices of double exchange (recently essential progress has been reached in the evaluation of the localized systems[56,57]). Such group-theoretical consideration will be reported in forthcoming publications.

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Apendix I. Matrix Element of Double-Exchange Hamiltonian

The expression for the matrix element of the operator $H_{tr}(i\rightarrow k)$ is the following:

$$\begin{aligned}&\langle (s'_\beta{=}s_\beta,\ \beta{\neq}i,k)(s'_i{=}s^r_0,\ s'_k{=}s^r_0{+}{}^1/_2)(\tilde{S}')S'M'_S|H_{\rm tr}(i\rightarrow k)\\ &\quad|(s_\beta,\ \beta{\neq}i,k)(s_i{=}s^r_0{+}{}^1/_2,s_k{=}s^r_0)(\tilde{S})SM_S\rangle =\\ &\quad(-1)^{2s^r_0}t_{ik}\delta_{SS'}\delta_{M_SM'_S}\times Z_{i\rightarrow k}[(s'_\beta{=}s_\beta,\ \beta{\neq}i,\ k)\\ &\quad(s_i{=}s^r_0+{}^1/_2,s'_i{=}s^r_0,s_k{=}s^r_0,\ s'_k{=}s^r_0+{}^1/_2)(\tilde{S})(\tilde{S}')S]\end{aligned}\tag{AI.1}$$

where $Z_{i\rightarrow k}[\cdots]$ is the function of local spins s_i, s_k and s_i', s_k' for the initial and final (primed) electronic distributions, the corresponding sets of intermediate spins $(\tilde{S})$ and $(\tilde{S}')$, and total spin S. It is assumed that the sites i and k belong to the rth delocalized domain. Providing $i < k$ the function $Z_{i\rightarrow k}[\cdots]$ is given by

$$\begin{aligned}&Z^{(i<k)}_{i\rightarrow k}[(s'_\beta{=}s_\beta,\ \beta{\neq}i,k)(s_i,\ s'_i,s_k,s'_k)(\tilde{S})(\tilde{S}')S] =\\ &\quad(-1)^{1+(1/2)(k-i)+2(s_i+s_k)+s'_i+s'_k-\tilde{S}_{i-1}-\tilde{S}_i-\tilde{S}'_{k-1}-\tilde{S}_k}\times\\ &\quad\sqrt{(2s_i+1)(2s'_k+1)(2\tilde{S}'_i+1)(2\tilde{S}_{k-1}+1)}\times\\ &\quad\delta_{\tilde{S}_2\tilde{S}'_2}\delta_{\tilde{S}_3\tilde{S}'_3}\cdots\delta_{\tilde{S}_{i-1}\tilde{S}'_{i-1}}\delta_{\tilde{S}_k\tilde{S}'_k}\delta_{\tilde{S}_{k+1}\tilde{S}'_{k+1}}\cdots\delta_{\tilde{S}_{N-1}\tilde{S}'_{N-1}}\times\\ &\quad\begin{Bmatrix}s'_i & {}^1/_2 & s_i\\ \tilde{S}_i & \tilde{S}_{i-1} & \tilde{S}'_i\end{Bmatrix}\begin{Bmatrix}s_k & {}^1/_2 & s'_k\\ \tilde{S}'_{k-1} & \tilde{S}_k & \tilde{S}_{k-1}\end{Bmatrix}\times\\ &\prod_{f=1}^{k-i-1}(-1)^{-s_{i+f}+\tilde{S}'_{i+f}+\tilde{S}_{i+f-1}}\sqrt{(2\tilde{S}_{i+f-1}+1)(2\tilde{S}'_{i+f}+1)}\times\\ &\quad\begin{Bmatrix}\tilde{S}'_{i+f-1} & {}^1/_2 & \tilde{S}_{i+f-1}\\ \tilde{S}_{i+f} & s_{i+f} & \tilde{S}'_{i+f}\end{Bmatrix}\end{aligned}\tag{AI.2}$$

While applying eqs AI.1 and AI.2, one should use the following rules: $\tilde{S}_0 = \tilde{S}'_0 = 0$, $\tilde{S}_1 = s_1$, $\tilde{S}'_1 = s'_1$, $\tilde{S}_N = S$, and $\tilde{S}'_N = S'$. Besides, in the particular case when $k = i + 1$ the product in eq AI.2 should be substituted by 1.

Appendix II. Matrix Element of Exchange Hamiltonian

HDVV-exchange interaction acts within each localized configuration, so that, this part of the calculation can be done with the use of the developed procedure realized in the MAGPACK program for the systems with localized spins.[58,59] The matrix elements of the HDVV exchange Hamiltonian are calculated as

$$\begin{aligned}&\langle (s_f)(\tilde{S}')S'M'_S|H_{\rm ex}(D)|(s_f)(\tilde{S})SM_S\rangle =\\ &\quad\delta_{SS'}\delta_{M_SM'_S}\times(2S+1)^{-1/2}\sum_{k_1k_2\ldots k_N}\langle s_N\|s^N_{k_N}\|s_N\rangle\times\\ &\quad\sum_{\tilde{k}_2\tilde{k}_3\ldots\tilde{k}_{N-1}}G[k_1k_2(\tilde{k}_2)k_3(\tilde{k}_3)\ldots k_{N-1}(\tilde{k}_{N-1})k_N]\times\\ &\quad\prod_{i=1}^{N-1}\sqrt{(2\tilde{k}_{i+1}+1)(2\tilde{S}_{i+1}+1)(2\tilde{S}'_{i+1}+1)}\times\\ &\quad\begin{Bmatrix}\tilde{k}_i & k_{i+1} & \tilde{k}_{i+1}\\ \tilde{S}'_i & s_{i+1} & \tilde{S}'_{i+1}\\ \tilde{S}_i & s_{i+1} & \tilde{S}_{i+1}\end{Bmatrix}\langle s_i\|s^f_{k_i}\|s_i\rangle\end{aligned}\tag{AII.1}$$

where the set (s_f) of the local spins corresponds to the electronic distribution D. The values $\tilde{k}_2$, $\tilde{k}_3$,... obey the same addition rules as the spin quantum numbers, that is, $|k_1 - k_2| \leq \tilde{k}_2 \leq k_1 + k_2$, $|\tilde{k}_2 - k_3| \leq \tilde{k}_3 \leq \tilde{k}_2 + k_3$,..., $|\tilde{k}_{N-1} - k_N| \leq k \leq \tilde{k}_{N-1} + k_N$. Only the following coefficients $G\ [\cdots]$ are nonvanishing:

$$G[k_i = k_j = 1(i \neq j), k_f{=}0(f{\neq}i, j),\ k = 0] = 2\sqrt{3}J_{ij}\tag{AII.2}$$

The condition $k = 0$ has appeared in eq AII.2, because only isotropic-exchange interaction is considered. In eq AII.1, the rules $\tilde{S}_1 = \tilde{S}'_1 \equiv s_1$, $\tilde{S}_N = \tilde{S}'_N \equiv S$, $\tilde{k}_1 \equiv k_1$, and $\tilde{k}_N = k$ are assumed to be fulfilled. Only the one-center reduced matrix elements with $k_f = 0$, 1 are present in eq AII.1, they are given by

$$\langle s_f\|s^f_0\|s_f\rangle = \sqrt{2s_f+1},\ \langle s_f\|s^f_1\|s_f\rangle = \sqrt{s_f(s_f+1)(2s_f+1)}\tag{AII.3}$$

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