I. INTRODUCTION

The interplay between electron delocalization and magnetic interactions play a crucial role in the properties of many mixed-valence (MV) compounds of current interest in areas as diverse as solid state physics (bulk magnets, superconductors\(^5\)), inorganic chemistry (mixed-valence clusters, heteropolyblues\(^2–5\)), and biology (iron–sulfur proteins\(^6–15\)). These kinds of systems are formally formed by localized magnetic moments and itinerant “extra” electrons that can undergo a rapid hopping over the magnetic sites. The main effect of this electron transfer is to couple two localized magnetic moments through a kind of exchange interaction namely double exchange. Since the itinerant electron keeps the orientation of its spin in course of transfer, double exchange results in a strong spin polarization effect which favors a ferromagnetic spin alignment in the system.

This mechanism of electron-spin interaction was first suggested by Zener\(^16\) to explain the ferromagnetism observed in MV dimers deducing the spin dependence of the double exchange splitting. Since the itinerant electron transfer process results always in a strong stabilization of the higher spin (ferromagnetic) states, in higher nuclearity systems this process can also favor the stabilization of other spin states different from the ferromagnetic one, depending on the sign of the electron transfer integral and on the topology of the MV cluster. That is why the conclusions obtained for the relatively simple clusters can not be extended to high-nuclearity systems involving localized and delocalized spins in a complicated molecular and crystal structures.

A second important difference between dimers and higher nuclearity systems comes from the fact that in the later some additional electronic processes, should be also considered for the correct evaluation of the electron delocalization effects. One of these processes is associated with the so called exchange-transfer interaction involving three centers. The parameters of the magnetic (Heisenberg) exchange and exchange transfer are of the same order of magnitude and thus the exchange transfer cannot be neglected so far as the magnetic exchange is taken into account. In clusters containing more than one delocalized electron, two-electron transfer can be also important when the ground state is degenerate and the one-electron processes increase Coulomb energy of the system.

The previous remarks allows us to justify the need to...
develop a general approach to treat the problem of double exchange in multinuclear MV magnetic clusters containing several delocalized electrons. But besides this reason, we can find at least two more reasons of interest. The first reason is related to the existence of a variety chemical systems of large nuclearities in which localized and delocalized electrons coexist and interact. That includes large magnetic MV clusters and MV magnetic chains, which are systems of current interest in molecular magnetism and magnetoochemistry. We can mention in this context the polyoxometalate clusters which are molecular metal oxides of high nuclearity that resemble discrete fragments of extended metal oxide structures. The ability of polyoxometalates to accept various specific numbers of electrons, which are delocalized over a significantly large number of metals, and to accommodate at specific sites magnetic metal ions provide us with ideal model systems to study the interplay between electron transfer and exchange interactions in structures with different topologies and symmetries. The problem of the interaction between localized and delocalized electrons can be also found in chains compounds. Numerous examples of this kind are found in the area of molecular conductors and charge transfer salts which are usually formed by stackings of planar π-electron donor organic molecules in a MV state. The coupling between the magnetic moments through the delocalized electrons can be approached by assuming that the magnetic properties of the infinite MV chain are obtained from the extrapolation of the results obtained on finite chains of increasing length. Such a procedure requires the exact computation of finite chains having the maximum number of sites in order to approach to the infinite chain behavior.

The second reason faces to the challenge to overcome the limitations imposed by the existing conventional approaches to treat the problem of double exchange in these kinds of high-nuclearity MV systems. The main difficulties in this context may be realized taking as examples the cases of dimeric, trimeric, and tetrameric clusters with one electron delocalized over the spin sites.

Thus, in dimers in order to obtain the energy pattern one should evaluate the matrix element of double exchange, linking the states associated with the two sites of localization of the extra electron [a and b]. The states, belonging to the total spin S, are denoted as: \( |s_a s_b s_a(s_b)SM \rangle \) and \( |s_a s_b s_b(s_a)SM \rangle \), where \( s_a \) and \( s_b \) are the spins of two paramagnetic cores \( s_a = s_b = s_0 \), \( s_c = 1/2 \) is the spin of the migrating electron, \( s_a^\pi \) and \( s_b^\pi \) are the spins of ions a and b with the trapped extra electron. The two localized states of a dimer can be associated to two possible coupling schemes of three spins \( s_a, s_b, and s_c \): namely; \( s_a + s_b + s_c = S \) and \( s_a + s_b + s_c = S \). Spins \( s_a^\pi \) and \( s_b^\pi \) play the role of the intermediate spins in these spin coupling schemes. The matrix element of the double exchange operator turns out to be proportional to the Racah 6j symbols, appearing in the recoupling procedure leading thus to the linear dependence of the energies on the total spin of the dimer where \( t \) is the transfer integral.

The conventionally adopted basis for calculation of the energy spectrum of MV trimeric clusters contains the states of three types: (1) \( |s_a s_a s_a(S_{ab}SM) \rangle \), (2) \( |s_a s_b s_b(S_{ab}SM) \rangle \) and (3) \( |s_a s_b s_b(S_{ac}SM) \rangle \) corresponding to the following three coupling schemes of four spins: (1) \( s_a + s_c = s_a^\pi + s_c = S \), (2) \( s_b + s_c = s_b^\pi + s_c = S \), and (3) \( s_a + s_c = s_a^\pi + s_c^\pi = S \). The wave functions and the corresponding spin addition schemes can be transformed one into the another by means of cyclic permutations of the symbols \( a, b, c \) (corresponding to \( C_3 \) rotations). From this point of view it may be said that each spin-coupling scheme is linked with a certain site of localization of the extra electron and thus the matrix elements of the double exchange in the trimeric systems turns out to be proportional to the 9j symbols appearing in the four spin recoupling.

For more complicated tetrameric systems, we face the recoupling procedure for five spins. In this case the matrix elements of the double exchange operator prove to be proportional to the 12j symbols. It is evident that for systems with more than four centers the use of the spin coupling schemes linked to the extra electron localization results in the appearance of higher order \( nj \) symbols. Because of the lack of knowledge of the properties of higher-order \( nj \) symbols, the theoretical studies of such type polynuclear (oligomeric) systems have not been undertaken till now. The computational procedure is also dramatically complicated when we are dealing with the cases of more than one moving electron.

Here we propose a general approach to the problem of the electronic interactions in the arbitrary nuclearity MV systems possessing arbitrary number of localized spins and itinerant electrons paying particular attention to the double exchange concept. In the framework of the proposed computational scheme two-electron transfer and all three-center interactions are considered along with the double exchange. For the reasons given below electron transfer through three-center interactions can be referred to as potential exchange transfer, the associated parameter being of the same order of magnitude as Heisenberg potential exchange. The new approach is based on the successive (chainlike) spin coupling scheme and takes full advantages of the angular momentum technique. Utilization of the angular momentum theory allows to derive the explicit analytical dependence of the matrix elements of the double exchange, two-electron transfer and exchange transfer, on all relevant spin quantum numbers for an arbitrary MV systems. These analytical expressions contain 6j symbols and do not contain higher order recoupling coefficients. In order to reduce the dimensions of the energy matrices obtained in this way the point symmetry arguments are taken into account.

II. THE MODEL OF THE MIXED-VALENCE SYSTEM

We consider the most general case of MV system of the type \( Pd^{n+1}_1 + (N - P)d^n \). This system contains \( N \) \( d^n \) ions occupying the sites 1, 2, ..., \( N \), and \( P \) extra electrons delocal-
ized over these sites. We start our study by considering ions with less than half-filled d shells (n+1≤5). The case of more than half-filled d shell (n+1>5) will be studied separately in Sec. VII. Each jth site (j=1,2,...,N) has n+1 orbitals in such a way that n of these orbitals φjv (v =1,2,...,n) are supposed to be singly occupied forming high-spin (Hund’s) ions with spins s0=n/2 (spin cores). The remaining (highest in energy) ψj orbital is singly occupied when site j contains a d^{n+1} ion, or empty for a d^n ion (Fig. 1). The d^{n+1} ions are also high-spin ones so the spins of ions will be either sj=s0 for d^n ion or sj=s0+½ for d^{n+1} ion. All orbitals are supposed to be orthogonal (Wannier functions).

III. THE WAVE FUNCTIONS OF THE LOCALIZED SYSTEM

There are N!/[P!(N-P)!] possibilities to distribute P extra electrons among N sites. Let us suppose that we are dealing with the definite electronic distribution D fixing thus the sites occupied by d^n and d^{n+1} ions. The vth spin-orbital of the jth ion with the spin projection σ_j(v) will be denoted as [σ_j(v)]=φ_j(r-R_j)σ_j(v), where R_j is the position vector of the site j, and |σ_j(v)| is the spin function. The wave function of the d^n ion belonging to sj mj state (spin of ion and its projection) is built from Slater determinants in nk−1 steps using the successive coupling of the electronic spins to give total spin s_j:

\begin{equation}
|s_j m_j\rangle = \sum_{\alpha_j} \langle \alpha_j s_j | |s_j m_j\rangle [\sigma_j(1)|\sigma_j(2)]\cdots[\sigma_j(n_j)].
\end{equation}

(1)

where [· · ·] stands for the Slater determinants. The coefficients of the unitary transformation (1) are the following products of Clebsch–Gordan coefficients:

\begin{equation}
\langle \alpha_j s_j | s_j m_j\rangle = C_{1/2|1/2}^{\alpha_{j}1}\sigma_j(2) C_{3/2|1/2}^{\alpha_{j}1}\sigma_j(3) \cdots (\alpha_j \tilde{\alpha}_j)_{n_j-1/2}\sigma_j(n_j-1) (1/2)\sigma_j(n_j),
\end{equation}

(2)

where α_j and \tilde{\alpha}_j are the combined symbols:

\begin{equation}
\alpha_j=\{\sigma_j(1),\sigma_j(2),\ldots,\sigma_j(n_j)\},
\end{equation}

\begin{equation}
\tilde{\alpha}_j=\{\tilde{\sigma}_j(2),\tilde{\sigma}_j(3),\ldots,\tilde{\sigma}_j(n_j-1)\},
\end{equation}

and \tilde{\sigma}_j(2)=\sigma_j(1)+\sigma_j(2), \tilde{\sigma}_j(3)=\tilde{\sigma}_j(2)+\sigma_j(3), etc., are the intermediate spin projections in the successive spin addition.

Let us introduce the {Dm} representation with the basis functions of the whole system related to the electronic distribution D and to the definite set of spin projections of ions m={m_1,m_2,...,m_N}. For a given distribution D the basis functions can be represented as antisymmetrized products of the singly ion wave functions of type (1). These wave functions will be denoted as

\begin{equation}
|s_j m_j\rangle|s_{j+1} m_{j+1}\rangle\cdots|s_{j-i} m_{j-i}\rangle(m_j=s_0,m_i)
\end{equation}

(3)

\begin{equation}
|s_{j-1} m_{j-1}\rangle|s_{j} m_{j}\rangle\cdots|s_{j+i} m_{j+i}\rangle(m_j=s_0,m_k)
\end{equation}

(4)

\begin{equation}
|s_{j-k} m_{j-k}\rangle|s_{j-k+1} m_{j-k+1}\rangle\cdots|s_{j+k} m_{j+k}\rangle(m_j=s_0,m_N).
\end{equation}

(5)

(4)

For this given D the site i is assumed to be occupied by an extra electron, meanwhile the site k (k>i) is of the d^n type. This is explicitly shown in Eq. (4) and schematized in Fig. 1. The remaining sites (β≠i,k) can be either of d^n or d^{n+1} type depending on the distribution D. One can consider also the {Dm} state in which the extra electron is transferred from site i to site k. If i<k the corresponding wave function will be

\begin{equation}
|s_j m_j\rangle|s_{j+1} m_{j+1}\rangle\cdots|s_{j-i} m_{j-i}\rangle(m_j=s_0,m_i)
\end{equation}

(3)

\begin{equation}
|s_{j-1} m_{j-1}\rangle|s_{j} m_{j}\rangle\cdots|s_{j+i} m_{j+i}\rangle(m_j=s_0,m_k)
\end{equation}

(4)

\begin{equation}
|s_{j-k} m_{j-k}\rangle|s_{j-k+1} m_{j-k+1}\rangle\cdots|s_{j+k} m_{j+k}\rangle(m_j=s_0,m_N).
\end{equation}

(5)

Finally, we can pass to the {D(S)SM} representation corresponding to the coupled spins of the whole system. In this notation D is the electronic distribution (later on symbol D will be omitted in the notations of the wave functions), S and M are total spin and its projection, S symbolizes the full set of intermediate spins of the N-spin system. There are many possibilities to choose a spin coupling scheme. Further on we will use the successive (“chainlike”) spin-addition scheme which seems to be convenient for the problem under consideration:

\begin{equation}
s_1+s_2=\tilde{S}_2,\quad \tilde{S}_2+s_3=\tilde{S}_3,\ldots,\tilde{S}_{N-1}+s_N=S.
\end{equation}

(6)

In the successive coupling scheme a short notation is used for the chain of intermediate spin values \tilde{S}_2=\tilde{S}_{12}, \tilde{S}_3=\tilde{S}_{123}, etc., \tilde{S}_{12,..N}=S, giving rise to a certain total spin S. The numbers 1,2,...,N are assigned to the constituent metal sites arbitrarily and independently of the geometry of the system but once adopted enumeration is assumed to be fixed for all electronic distributions D. The last determines only the positions of d^n and d^{n+1} ions defining thus the individual (ionic) spins s_j (s_0 or s_0+½) and possible full sets (S)=\{S_2,S_3,..,S_{N-1}\} of intermediate spins.

The wave functions in the {D(S)SM} representation
corresponding to the electronic distribution with $d^m$ ion in the site $i$ and $d^n$ ion in the site $k$ (the remaining sites have definite set of occupation numbers corresponding to the given distribution $D$) can be expressed as follows:

$$\begin{align*}
|s_i s_j (\overline{S}_2) s_3 (\overline{S}_3) \cdots (\overline{S}_{i-2}) s_{i-1} (\overline{S}_{i-1}) (s_i = s_0 + \frac{1}{2}) (\overline{S}_i) s_{i+1} (\overline{S}_{i+1}) \cdots (\overline{S}_{k-2}) s_{k-1} (\overline{S}_{k-1}) (s_k = s_0) \\
(s_{k+1} (\overline{S}_{k+1}) \cdots (\overline{S}_{N-1}) s_N SM) = |(s_{\mu}, \beta \neq i, k) (s_i = s_0 + \frac{1}{2}, s_k = s_0) (\overline{S}) S'M')
\end{align*}$$

$$\begin{align*}
= \sum_{mM} C^{s_2}_{s_2 M_2} s_1 m_1 s_2 m_2 C^{s_3}_{s_3 M_3} \cdots C^{s_{i-2}}_{s_{i-2} M_{i-2}} s_{i-1} m_{i-1} C^{s_{i-1}}_{s_{i-1} M_{i-1}} s_i m_i C^{s_{i+1}}_{s_{i+1} M_{i+1}} \cdots C^{s_{k-1}}_{s_{k-1} M_{k-1}} s_k m_k \\
\times C^{s_{k+1}}_{s_{k+1} M_{k+1}} \cdots C_{S_{N-1} M_{N-1} t' N N} |(s_1 m_1) (s_2 m_2) \cdots (s_i = s_0 + \frac{1}{2}, m_i) \cdots (s_k = s_0, m_k) \cdots (s_N m_N)).
\end{align*}$$

(7)

Here $\overline{M}_i, \overline{M}_{i+1}, \ldots$ are the quantum numbers of intermediate spin projections. The wave function for the cluster with electron transferred from $i$th to $k$th ion has the form

$$\begin{align*}
| (s_{\mu}, \beta \neq i, k) (s'_i = s_0, s'_k = s_0 + \frac{1}{2}) (\overline{S}) S'M')
\end{align*}$$

$$\begin{align*}
= \sum_{mM} C^{s_2}_{s_2 M_2} s_1 m_1 s_2 m_2 C^{s_3}_{s_3 M_3} \cdots C^{s_{i-2}}_{s_{i-2} M_{i-2}} s_{i-1} m_{i-1} C^{s_{i-1}}_{s_{i-1} M_{i-1}} s_i m_i C^{s_{i+1}}_{s_{i+1} M_{i+1}} \cdots C^{s_{k-1}}_{s_{k-1} M_{k-1}} s_k m_k \\
\times C^{s_{k+1}}_{s_{k+1} M_{k+1}} \cdots C_{S_{N-1} M_{N-1} t' N N} |(s_1 m_1) (s_2 m_2) \cdots (s'_i) (s'_2 m'_2) \cdots (s_N m_N)).
\end{align*}$$

(8)

where the quantum numbers of ionic, intermediate and total spins related to the final state are primed. The last two formulas are to be used for the evaluation of the matrix element corresponding to the $i \rightarrow k$ electron transfer.

IV. DOUBLE EXCHANGE HAMILTONIAN

The Hamiltonian of the system can be written as

$$H = h + g,$$

(9)

where one-electron operator $h$ involves kinetic and potential energies of all electrons and $g$ is the interelectronic repulsion term.

Let us pass to the second quantization representation and write down the Hamiltonian acting in the space of the states belonging to the ground manifold [states of the type (4), (5) belonging to all possible electronic distributions $D$ and quantum numbers $s, m_j$ of constituent ions]. This Hamiltonian can be expressed as:

$$H = H_0 + H^e_{ex} + H^{(1)}_{tr} + H^{(2)}_{tr} + H^p_{ex}.$$

(10)

The term $H_0$ includes all interatomic interactions and interatomic Coulomb repulsion. The operator $H^e_{ex}$ is the isotropic potential exchange (the effect of this term as well as the computational procedure are well known$^{40-42}$ and we will not focus our attention on this term). The operator $H^{(2)}_{tr}$ is responsible for the one-electron transfer, which usually is the leading term in the Hamiltonian (10). When this transfer occurs over paramagnetic spin cores we are dealing with the double exchange interaction. The last two terms $H^{(1)}_{tr}$ and $H^p_{ex}$ represent the two-electron transfer and potential exchange transfer correspondingly. These two terms will be considered in detail in Secs. VIII and IX.

In this section we focus on the double exchange Hamiltonian for the case of less than half-filled $d$ shells. One can represent one-electron transfer operator $H^{(1)}_{tr}$ as a sum of two-center contributions:

$$H^{(1)}_{tr} = \sum_{i \neq k} H^{(1)}_{tr} (i \rightarrow k),$$

(11)

where $H^{(1)}_{tr} (i \rightarrow k)$ contains two terms:

$$H^{(1)}_{tr} (i \rightarrow k) = T_{i \rightarrow k} + F_{i \rightarrow k}.$$

(12)

The operator $T_{i \rightarrow k}$ is of the form

$$T_{i \rightarrow k} = \left[ \langle \psi_k | h | \psi_i \rangle + \sum_{j} \langle \psi_k \varphi_j | g | \psi_j \varphi_i \rangle \right.$$

$$\left. + \sum_{j, j' \neq i, \alpha} \langle \psi_k \varphi_j | g | \psi_j \varphi_{j'} \rangle N_{j \alpha} \right] \sum_{\sigma} C^+_{\psi k \varphi \sigma} C_{\psi \varphi \sigma},$$

(13)

where $C^+_{\psi k \varphi \sigma} (C_{\psi \varphi \sigma})$ is the operator of creation (annihilation) of the electron on the $\psi$ orbital of the site $i$ with spin projection $\sigma$, $N_{j \alpha} = \sum_{\sigma} C^+_{\psi j \varphi \sigma} C_{\psi j \varphi \sigma}$ is the operator of the number of the electrons on $\psi$ orbital of $i$th site. The bielectronic integrals in Eq. (13) are defined as

$$\langle \psi_k \varphi_{j'} | g | \psi_j \varphi_i \rangle = \int \int \psi_k (1) \varphi_{j'} (2) g (1.2) \psi_j (1) \times \varphi_i (2) d \tau_1 d \tau_2 \text{ etc.}$$


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The electronic processes described by the operator $H_2^0(i-k)$ in the simple case of $\text{Pd}^{2+}(N-P)\text{d}^1$-system (only the processes with $\sigma=\sigma'=\uparrow$ are shown).

<table>
<thead>
<tr>
<th>Scheme of the process</th>
<th>Contribution to the parameter $t_{ik}$</th>
<th>Fermion operators</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma_i )</td>
<td>( \langle \varphi_i</td>
<td>h</td>
</tr>
<tr>
<td>( \gamma_i ) ( \gamma_k )</td>
<td>( \langle \varphi_i</td>
<td>\varphi_k \rangle \langle \varphi_k</td>
</tr>
<tr>
<td>( \gamma_i ) ( \gamma_j )</td>
<td>( \langle \varphi_i</td>
<td>\varphi_j \rangle \langle \varphi_j</td>
</tr>
<tr>
<td>( \gamma_i ) ( \gamma_j ) ( \gamma_k )</td>
<td>( \langle \varphi_i</td>
<td>\varphi_j \rangle \langle \varphi_j</td>
</tr>
</tbody>
</table>

The contribution to the transfer (double-exchange) parameter from $T_{i\rightarrow k}$ term is defined as

$$\beta_{ik} = \langle \varphi_i | h | \varphi_i \rangle + \sum_{j\neq i,k} \langle \varphi_i | \varphi_j \rangle \langle \varphi_j | h | \varphi_i \rangle + \sum_{j=i,k} \langle \varphi_i | \varphi_j \rangle \langle \varphi_j | h | \varphi_i \rangle.$$  \hspace{1cm} (14)

The first sum in Eq. (14) involves all core’s orbitals of all centers including centers $i$ and $k$ while the second summation runs over all $d^{n+1}$ centers with the exception of centers $i$ and $k$ which change their oxidation degrees in course of transfer process. The term $\langle \varphi_i | h | \varphi_i \rangle$ arises from the monoelectronic part of the Hamiltonian (9), all the remaining terms describe the influence of the localized electrons on the $i\rightarrow k$ transfer over $\psi$ orbitals. Using definition (14) we can represent operator $T_{i\rightarrow k}$ in the standard form:

$$T_{i\rightarrow k} = \beta_{ik} \sum_{\sigma} C_{\gamma i}^+ \gamma_i C_{\gamma i} \sigma .$$  \hspace{1cm} (15)

Different contributions to the overall transfer process are schematized in Table I for the simple case of two orbitals per center.

The operator $F_{i\rightarrow k}$ is written as

$$F_{i\rightarrow k} = \sum_{j=i,k} \sum_{\sigma} \langle \psi_k | \varphi_{j\sigma} \rangle \langle \varphi_j | \varphi_k \rangle \sum_{\sigma'} C_{j\sigma}^+ C_{k\sigma'} \gamma_k \gamma_i C_{\gamma i} \sigma .$$  \hspace{1cm} (16)

Sum over $j$ involves two terms with $j=i$ and $j=k$. Two bielectronic processes associated with this operator are shown in Table I. Conventionally they are depicted as the two step processes. One step represents the transition between $\psi$ and $\varphi$ orbitals belonging to the same center, another one is the interionic transfer involving core orbital $\varphi$ and orbital $\psi$. The $F_{i\rightarrow k}$ contribution seems to be smaller than that of $T_{i\rightarrow k}$. Latter on we will show that the operator $T_{i\rightarrow k} + F_{i\rightarrow k}$ can be represented as one effective operator of the type (15) in which instead of $\beta_{ik}$ one should write some effective transfer parameter $t_{ik}$.

V. MATRIX ELEMENTS OF THE DOUBLE EXCHANGE IN THE $\langle |Dm| \rangle$ REPRESENTATION (LESS THAN HALF FILLED $d$ SHELLS)

We start with the evaluation of the matrix element of the operator $T_{i\rightarrow k}$ [Eq. (15)] in the $\langle |Dm| \rangle$ representation corresponding to the uncoupled spins of ions. One can easily prove that the matrix element of the operator $T_{i\rightarrow k}$ linking two electronic distributions $D$ and $D'$ is nonvanishing if $D$ and $D'$ differ in occupation numbers of two sites, say, $i$ and $k$ corresponding thus to one-electron transfer. Using the properties of Slater’s determinants and Clebsch–Gordan coefficients one can find the following expression for the matrix element of $i\rightarrow k$ electron transfer (we suppose that $i<k$):

$$\langle s_i m_i | s_k m_k \rangle \cdots \langle s_i m_i | s_i m_i \rangle \cdots \langle s_i m_i | m_i \rangle \cdots \langle s_i m_i | m_i \rangle$$

$$= \beta_{ik} \sum_{\sigma} C_{\gamma i}^+ \gamma_i C_{\gamma i} \sigma \prod_{j=i,k} \delta_{s_j m'_j} \delta_{m_j m_j}$$

$$\times \sum_{\sigma} C_{\gamma i}^+ \gamma_i C_{\gamma i} \sigma \prod_{j=i,k} \delta_{s_j m'_j} \delta_{m_j m_j} .$$  \hspace{1cm} (17)

where $\beta_{ik}$ is the double exchange parameter already defined [Eq. (14)]. Product of $\delta$ symbols in Eq. (17) shows explicitly that only one-electron jump from site $i$ to site $k$ is possible, meanwhile all remaining electrons occupy their initial sites conserving at the same time their spins $(\cdots s_i' \cdots = \cdots s_i' \cdots)$ in course of transfer keeping unchanged their spin projections $(\cdots m_i' \cdots = \cdots m_i' \cdots)$. One can see that only spin projections of two ions participating in the transfer processes are changed. The moving electron keeps its spin projection $\sigma$ and as it is clear from Eq. (17), the conservation law for the full spin projection of two ions involved in transfer is valid $(m_i' + m_k = m_i' + m_k)$. 

Let us calculate now the matrix element of the operator \( F_{i\rightarrow k} \). Two terms of this operator \((j = i \text{ and } j = k)\) generate two processes visualized in the lines 6\( (j = k) \) and 7\( (j = i) \) of Table I. Considering in Eq. (16) term with \( j = k \) we get

\[
\sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} - \sum_{\sigma \sigma'} C_{k \alpha \sigma} C_{-k \beta \sigma'} \sum_{\sigma \sigma'} C_{k \gamma \sigma}^+ C_{-k \delta \sigma'}^-
\]

and hence, we can apply the formula for the matrix element of the product of two operators. Thus we obtain

\[
\left( \sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} \sum_{\sigma \sigma'} C_{k \gamma \sigma}^+ C_{-k \delta \sigma'}^- \right) \sum_{\sigma \sigma'} C_{k \gamma \sigma}^+ C_{-k \delta \sigma'}^-(s_1 m_1)(s_2 m_2) \cdots (s_i = s_0, m_i)(s_k = s_0 + \frac{1}{2}, m_k) \cdots (s_N m_N) \]

\[
+ \frac{1}{2}, m_k) \cdots (s_N m_N) \right)
\]

\[
= \sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} \left( \left( \sum_{\sigma \sigma'} C_{k \gamma \sigma}^+ C_{-k \delta \sigma'}^-(s_1 m_1)(s_2 m_2) \cdots (s_i = s_0, m_i)(s_k = s_0 + \frac{1}{2}, m_k) \cdots (s_N m_N) \right) \sum_{\sigma \sigma'} C_{k \gamma \sigma}^+ C_{-k \delta \sigma'}^-(s_1 m_1)(s_2 m_2) \cdots (s_i = s_0, m_i)(s_k = s_0 + \frac{1}{2}, m_k) \cdots (s_N m_N) \right)
\]

\[
\times \left( \sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} \left( s_1 m_1)(s_2 m_2) \cdots (s_i = s_0 + \frac{1}{2}, m_i)(s_k = s_0, m_k) \cdots (s_N m_N) \right) \right) .
\]

Equation (18) shows explicitly that the whole transfer process is represented as two step process (Table I, line 6). The quantum numbers of the intermediate states are double primed. Symbol \((kv)^0\) indicates that the summation in Eq. (18) involves only those intermediate states in which \(v\)th core orbital of \(k\)th ion is empty and orbital \(\psi\) is singly occupied (the result of the first jump). The second matrix element in the right side of Eq. (18) describes the intrionic transfer \(\psi_{i\rightarrow \psi_k}\) transfer restoring the \(k\)th spin core (second step).

For the second matrix element in Eq. (18) one can obtain the following result:

\[
\left( (kv)^0(s'' \! m''_1)(s'' \! m''_2) \cdots (s'' = s_0 + \frac{1}{2}, m''_i)(s''_k = s_0, m''_k) \cdots (s''_N m''_N) \right)
\]

\[
\sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} \left( s_1 m_1)(s_2 m_2) \cdots (s_i = s_0 + \frac{1}{2}, m_i)(s_k = s_0, m_k) \cdots (s_N m_N) \right) = (-1)^{2s_0 - v} \prod_{j=1}^{N} \delta_{s_j} \delta_{m_j} \delta_{m''}. \tag{19}
\]

One can see that the intrionic transfer does not change the spins and spin projections of all constituent ions. Therefore, only one intermediate state (with all \(s'' = s_j\) and \(m'' = m_i\)) contributes to the matrix element in Eq. (18).

Using Eq. (19) and taking into account the properties of Slater determinants and Clebsch–Gordan coefficients one can represent the matrix element in Eq. (18) as follows:

\[
\left( (s' \! m'_1)(s' \! m'_2) \cdots (s' = s_0, m'_i)(s'_k = s_0 + \frac{1}{2}, m'_k) \cdots (s'_N m'_N) \right)
\]

\[
\sum_{\sigma \sigma'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} \left( s_1 m_1)(s_2 m_2) \cdots (s_i = s_0 + \frac{1}{2}, m_i)(s_k = s_0, m_k) \cdots (s_N m_N) \right) = (-1)^{2s_0 - u} \left( (s' \! m'_1)(s' \! m'_2) \cdots (s' = s_0, m'_i)(s'_k = s_0 + \frac{1}{2}, m'_k) \cdots (s'_N m'_N) \right)
\]

\[
\sum_{\alpha \alpha'} C_{k \alpha \sigma}^+ C_{-k \beta \sigma'} (kv)^0(s_1 m_1)(s_2 m_2) \cdots (s_i = s_0 + \frac{1}{2}, m_i)(s_k = s_0, m_k) \cdots (s_N m_N) \right) = (-1)^{1 + 2s_0 + 2(s_1 + s_1 + s_1 + \ldots s_{k-1})} \prod_{j=1}^{N} \delta_{s_j} \delta_{m_j} \sum_{\pi = \pm 1/2} \delta_{s_1 + \pi \frac{1}{2}} \delta_{m_1 + \pi \frac{1}{2}} \sum_{\pi = \pm 1/2} \delta_{s_N + \pi \frac{1}{2}} \delta_{m_N + \pi \frac{1}{2}} . \tag{20}
\]
Comparing Eqs. (20) and (17) we arrive at the following relation of equivalence for the product of Fermion operators:

$$\sum_{\sigma \sigma'} c_{k \alpha \sigma}^+ c_{k \alpha' \sigma'} c_{k \alpha' \sigma'} = - \sum_{\sigma} c_{\bar{k} \bar{\alpha} \sigma}^+ c_{\bar{k} \bar{\alpha} \sigma}.$$  \hfill (21)

Analogously, considering in the operator $F_{i \rightarrow k}$ the term with $j = i$ we get

$$\sum_{\sigma \sigma'} c_{i \sigma}^+ c_{k \sigma} c_{i \sigma} = - \sum_{\sigma} c_{\bar{i} \bar{\sigma}}^+ c_{\bar{i} \bar{\sigma}}.$$  \hfill (22)

Combining Eqs. (21), (22), and (15) one can rewrite the double exchange operator $\mathbf{H}^{(1)}_{it}(i \rightarrow k)$ in the following form:

$$\mathbf{H}^{(1)}_{it}(i \rightarrow k) = t_{ik} \sum_\sigma c_{\bar{k} \bar{\sigma}}^+ c_{i \sigma},$$  \hfill (23)

where

$$t_{ik} = \beta_{ik} - \sum_{j \neq k} \sum_v \langle \psi_k \psi_j | \mathbf{g} | \psi_{jv} \psi_i \rangle$$  \hfill (24)

is the new effective double exchange parameter associated with physical processes resulting in the $i \rightarrow k$ transfer. It should be noted that these processes involve two centers only. Three center processes leading to $i \rightarrow k$ transfer will be considered later on. Since the operator parts of $\mathbf{H}^{(1)}_{it}(i \rightarrow k)$ and $\mathbf{T}_{i \rightarrow j}$ are equivalent the matrix element of $\mathbf{H}^{(1)}_{it}(i \rightarrow k)$ in the $\{Dm\}$ representation can be calculated using Eq. (17) in which $\beta_{ik}$ must be substituted by $t_{ik}$. In this way one can built the matrix of one-electron transfer. Diagonalizing this matrix one can obtain the energies of tunnel states. However, following this way it is hardly possible to handle with the large clusters containing many sites and many electrons. In fact the number of basis states in $\{Dm\}$ representation for $P_d = (N-P)d^n$ cluster is given as $2^P (s_0 + 1)^P (s_0 + 1)^{N-P}! ([P!(N-P)] !)^{-1}$. Taking for example the system $d^2 - d^3 - d^3 (N = 4, P = 2, s_0 = 1)$ we obtain the matrix $864 \times 864$. One can see that even for this comparatively simple system we have to diagonalize a big matrix.

VI. MATRIX ELEMENT OF THE DOUBLE EXCHANGE OPERATOR IN THE $\{D(S)SM\}$ REPRESENTATION

A significant reduction of the dimensions of the matrices can be achieved taking as a basis the states in $\{D(S)SM\}$ representation. Taking the advantage of the angular momentum theory we will show in this section that the matrix element of the double exchange operator may be represented as a simple closed-form expression for the arbitrary nuclearity MV systems. The developed approach will be called angular momentum approach. Using the wave functions in $\{D(S)SM\}$ representation [Eqs. (7) and (8)], and Eq. (17) for the matrix element in $\{Dm\}$ representation, one can represent the matrix element corresponding to the $i \rightarrow k$ transfer ($i < k$) as follows:

$$\langle (s_i = s_i, \beta \neq i, k)(s_i = s_i, \beta \neq i, k) | (s_i, \beta = i, k) | (s_i, \beta = i, k) \rangle = \langle (s_i = s_i, \beta \neq i, k) | (s_i = s_i, \beta \neq i, k) \rangle \delta_{ik}.$$  \hfill (25)

Using the well known properties of Clebsch–Gordan coefficients one can carry out the summations in Eq. (25). Because of the importance of this procedure for the following calculations and for the related electron transfer problems we will consider it in detail. First by using the unitarity property of Clebsch–Gordan coefficients we get

$$\sum_{m_1, m_{1}', m_{1}''} \sum_{m_2, m_{2}', m_{2}''} C_{s_1 M_1 s_2 M_2} C_{s_1 M_1' s_2 M_2'} C_{s_1 M_1'' s_2 M_2''} = \delta_{s_1 s_2} \delta_{M_1 M_2} \delta_{M_1' M_2'} \delta_{M_1'' M_2''}. $$  \hfill (26)

In order to perform further calculations we will employ the formula for the sum of the products of three Clebsch–Gordan coefficients43
\[
\sum_{\alpha \beta \gamma} C_{\alpha \beta \gamma} C_{\delta \varepsilon \phi} C_{\alpha \varepsilon} = (-1)^{b+c+d+f} \sqrt{(2c+1)(2d+1)} \left[ \begin{array}{ccc} a & c & b \\ e & f & d \end{array} \right] C_{\varepsilon \phi},
\] (27)

and the well-known symmetry property
\[
C_{\alpha \beta} = (-1)^{a+b-c} C_{\beta \alpha}. 
\] (28)

In Eq. (27) \( \{a \ b \ c \ d \} \) is a 6j symbol. Using Eqs. (26) and (27) we find
\[
\sum_{m_i M_i - 1} \sum_{s_0 (1/2) m_j} \frac{s_0 + (1/2) m_j}{S_i - 1 (1/2) m_j} C_{\tilde{S}_i \tilde{M}_i} C_{\tilde{S}_i + 1 \tilde{M}_i - 1} \left( \begin{array}{ccc} s_0 & 1/2 & s_0 + (1/2) \\ \tilde{S}_i & \tilde{S}_i - 1 & \tilde{S}_i' \end{array} \right) C_{\tilde{S}_i' \tilde{M}_i} C_{\tilde{S}_i' \tilde{M}_i}'(1/2) \pi.
\] (29)

After that one should perform several successive summations of the same type. The first summation of this series yields
\[
\sum_{\tilde{M}_{i+1} m_{i+1}} C_{\tilde{S}_{i+1} \tilde{M}_{i+1}} C_{\tilde{S}_{i+1} \tilde{M}_{i+1}'} C_{\tilde{S}_{i+1} \tilde{M}_{i+1}} C_{\tilde{S}_{i+1} \tilde{M}_{i+1}'}(1/2) \pi
\] (30)

Using the result of this summation one can perform the second summation of this series
\[
\sum_{\tilde{M}_{i+2} m_{i+2}} C_{\tilde{S}_{i+2} \tilde{M}_{i+2}} C_{\tilde{S}_{i+2} \tilde{M}_{i+2}'} C_{\tilde{S}_{i+2} \tilde{M}_{i+2}} C_{\tilde{S}_{i+2} \tilde{M}_{i+2}'}(1/2) \pi
\] (31)

This series of summations involves \( k - i - 1 \) similar stages. The last one is the following:
\[
\sum_{\tilde{M}_{k-2} m_{k-2}} C_{\tilde{S}_{k-2} \tilde{M}_{k-2}} C_{\tilde{S}_{k-2} \tilde{M}_{k-2}'} C_{\tilde{S}_{k-2} \tilde{M}_{k-2}} C_{\tilde{S}_{k-2} \tilde{M}_{k-2}'}(1/2) \pi
\] (32)

Taking into account the result of the last summation of the series [Eq. (32)] one can perform just one more summation, appearing in the initial Eq. (25), namely
\[
\sum_{\tilde{M}_{k-1} m_{k}} C_{\tilde{S}_{k-1} \tilde{M}_{k-1}} C_{\tilde{S}_{k-1} \tilde{M}_{k-1}'} \left( \begin{array}{ccc} s_0 + (1/2) m_j & 1/2 & s_0 + (1/2) \\ \tilde{S}_{k-1} & \tilde{S}_{k-1} & \tilde{S}_{k-1} \end{array} \right) C_{\tilde{S}_{k-1} \tilde{M}_{k-1}'}(1/2) \pi.
\] (33)

The remaining summations can be easily made by means of the unitarity property of Clebsch–Gordan coefficients and Eq. (28). The result is the following:
\[
\sum_{m_{k+1} \cdots m_N} \sum_{\tilde{n}_{N-1}} \sum_{m_N} \tilde{S}_{M_k}^{i+1} \tilde{S}_{M_k}^{i} = \sum_{m_{k+1} \cdots m_N} \sum_{\tilde{n}_{N-1}} \sum_{m_N} \tilde{S}_{M_k}^{i+1} \tilde{S}_{M_k}^{i} - \sum_{m_{k+1} \cdots m_N} \sum_{\tilde{n}_{N-1}} \sum_{m_N} \tilde{S}_{M_k}^{i} \tilde{S}_{M_k}^{i+1} \times C_{S_{M_k}^{i+1} M_{k+1}} C_{S_{M_k}^{i} M_{k+1}} C_{S_{M_k}^{i+1} M_{k+1}} C_{S_{M_k}^{i} M_{k+1}} \\
= (-1)^{(i+1)+(i+1)} S_{i+1} S_{i+1} - (-1)^{(i+1)+(i+1)} S_{i} S_{i}.
\]

Now we have everything we need for the calculation of the matrix element for \( i \rightarrow k \) transfer in the \( D(\tilde{S})SM \) representation. Substituting Eqs. (26)–(34) into Eq. (25) we obtain the following final result for the matrix element of the double exchange Hamiltonian:

\[
\langle (s'_\beta = s_\beta, \beta \neq i, k)(i'_s = s_0, s'_k = s_0 + \frac{1}{2}) | (S')SM | \mathbf{H}_{ii}^{1}(i \rightarrow k)(s'_\beta = s_\beta, \beta \neq i, k)(i'_s = s_0 + \frac{1}{2}, s'_k = s_0) \rangle.
\]

\[
= (-1)^{2s_0 + 2s_0} Z_{i \rightarrow k}(s'_\beta = s_\beta, \beta \neq i, k)(i'_s = s_0 + \frac{1}{2}, s'_k = s_0, s'_l = s_0 + \frac{1}{2})(S')(S').
\]

In Eq. (35) \( Z_{i \rightarrow k} \) is the function of local spins \( s_i, s_k \) and \( s'_i, s'_k \) for the initial and final electronic distributions, and the corresponding sets of intermediate spins \((\tilde{S})\) and \( (\tilde{S}')\) and total spin \( \tilde{S} \). For the case under consideration \((i < k)\) this function has the form

\[
Z_{i \rightarrow k}(i < k, s'_\beta = s_\beta, \beta \neq i, k)(s_i, s'_i, s_k, s'_k)(\tilde{S})(\tilde{S}') = (-1)^{1 + 2(s_0 + \frac{1}{2}) + (i-k) - s_0 - s_0} \times \left\{ \frac{s_k}{S_{k+1}} \times \frac{s'_k}{S_{k+1}} \right\} \times \left\{ \frac{s_i}{S_{i+1}} \times \frac{s'_i}{S_{i+1}} \right\} \times \left\{ \frac{s_f}{S_{f+1}} \times \frac{s'_f}{S_{f+1}} \right\}.
\]

In the notation of \( Z_{i \rightarrow k} \) corresponding to \( i \rightarrow k \) transfer the remaining spins \( s'_\beta = s_\beta (\beta \neq i, k) \) conserving their values are indicated also. Although they do not enter explicitly in the right side of Eq. (36), these spins determine the sets of intermediate spins \((\tilde{S})\) and \((\tilde{S}')\), i.e., the arguments of the function \( Z_{i \rightarrow k} \).

One can prove that the result (35) is valid also providing \( i > k \) but \( Z_{i \rightarrow k} \) in this case should be taken as follows:

\[
Z_{i \rightarrow k}(i > k, s'_\beta = s_\beta, \beta \neq i, k)(s_i, s'_i, s_k, s'_k)(\tilde{S})(\tilde{S}') = (-1)^{1 + 2(s_0 + \frac{1}{2}) + (i-k) - s_0 - s_0} \times \left\{ \frac{s_k}{S_{k+1}} \times \frac{s'_k}{S_{k+1}} \right\} \times \left\{ \frac{s_i}{S_{i+1}} \times \frac{s'_i}{S_{i+1}} \right\} \times \left\{ \frac{s_f}{S_{f+1}} \times \frac{s'_f}{S_{f+1}} \right\}.
\]

Some remarks should be made concerning the use of Eq. (35). First of all, for the values \( S_0, S'_0, \tilde{S}_0, \text{ and } S'_0 \) one must use the following rules: \( S_0 = s_1, S'_0 = s_{1/2}, S_N = S = S' \). Besides, in the particular case \( k=i+1 \) (or \( k=i-1 \)) the products in Eq. (36) or Eq. (37)) should be substituted by 1.

Equation (35) shows that the following conservation rules occur for the \( i \rightarrow k \) transfer:

(1) The total spin and its projection are conserved \((S' = S, M' = M)\).

(2) All intermediate spins remain unchanged in the \( i \rightarrow k \) transfer process with the exception of \( S_{i+1}, S_{i+1}, \cdots S_{k-1} \) for the case \( i < k \) and \( S_k, S_{k+1}, \cdots S_{i-1} \) for the case \( i > k \). Using the triangle rules for 6j symbols we obtain the following relation between these intermediate spins in the initial and final states providing \( i < k \): \( S_i = S_{i+1} = S_{i+1} = \frac{1}{2}, \cdots S_{k-1} = S_{k-1} = \frac{1}{2} \). Similarly for the case \( i > k \) we can write: \( S_k = S_{k+1} = \frac{1}{2} \).

Figure 2 illustrates three domains of intermediate spins behavior in course of \( i \rightarrow k \) transfer for the case \( i < k \). There
are two domains of the intermediate spins conservation. The first one includes the set of sites with the numbers 1, 2, ..., i−1 in the initially adopted enumeration scheme. The second domain involves the sites k, k+1, ..., N. The sites with the numbers i, i+1, ..., k−1 forms active domain in which intermediate spins are changed in the transfer process. It should be noted that the final site k is out of the active domain.

One can see that as distinguished from the case of less than half-filled d shells the extra electron is hopping over the dotted box show inactive zone, dashed boxes show spin cores: (a) n=5, (b) n=7.

**FIG. 2.** The domains of different behavior of the intermediate spins for i→k transfer (i<k) in chainlike coupling scheme.

This relation can be easily proved using the definitions (36) and (37).

**VII. MATRIX ELEMENTS OF THE DOUBLE EXCHANGE (MORE THAN HALF-FILLED d SHELLS)**

Let us proceed to elucidate how the developed theory should be modified in the case of the cluster \( Pd^9-n + (N-P)d^{10-n} \) with more than half-filled d shells (n=4). This system contains \( N-P \) extra electrons or \( P \) extra holes. Providing \( n=4 \) the extra electron is hopping over the lowest \( \varphi_{1} \) orbitals forming thus double occupied \( \varphi_{1}^2 \) states of \( d^9 \) ions. Spin cores in the system \( Pd^9 + (N-P)d^6 \) are formed by \( d^9 \) ions, i.e., by the ions without extra electrons as in the case of less than half filled d shells. These spin cores and the scheme of transfer process \( (d_i^d, d_k^d) \rightarrow (d_i^d, d_k^d) \) are schematized in Fig. 3(a). Provided that \( n<4 \), all ions \( d^{9-n} \) and \( d^{10-n} \) possess double occupied d orbitals as shown in Fig. 3(b). The lowest equivalent orbitals [denoted by \( \chi_i \) in Fig.3(b)] are doubly occupied in both \( Pd^{9-n} \) and \( (N-P)d^{10-n} \) subsystems and do not participate in the transfer processes. These orbitals form an inactive zone framed in the dotted box in Fig. 3(b). The extra electron jumps from the doubly occupied \( \varphi_{1} \) orbital (lying above the box) to the singly occupied \( \varphi_{1} \) orbital. In this case, the spin cores are formed by the half-filled orbitals of the \( d^{9-n} \) ions and the \( d^{10-n} \) residues of the \( d^{10-n} \) ions as shown by the dashed boxes in Fig. 3(b). Denoting the spin cores as \( s_0 \) one can see that for more than half-filled d-shells \( n=4 \)

\[
s(d^{9-n}) = s_0 + n/2, \quad s(d^{10-n}) = s_0 - n/2.
\]

We will use the double-exchange operator \( \mathbf{H}_{ex}^{(1)}(i \rightarrow k) = t_{ik} \sum_{\sigma} \mathbf{C}_{i1}^\dagger \mathbf{C}_{k1} \) adapted to the case of more than half-filled d shells. The transfer parameter \( t_{ik} \) in this case contains one-electron integral \( \langle \varphi_{1} | \mathbf{h} | \varphi_{1} \rangle \) and two-electron integrals like in the case of less than half-filled d shells (see Sec. V).

The calculations of the matrix element of \( \mathbf{H}_{ex}^{(1)}(i \rightarrow k) \) are quite similar to those described in Sec. VI. With the use of the properties of Slater determinants and Clebsch–Gordan coefficients one can obtain the matrix element of the double exchange in the \( \{Dm\} \) representation. In the case of \( i<k \) the result has the form

\[
Z_{k \rightarrow i}(s'_b = s_b, \quad \beta = k, i) (s_k, s_k', s_i, s_i')(\bar{S}(i)S) = \left[ \frac{(2s'_b + 1)(2s'_k + 1)}{(2s_b + 1)(2s'_b + 1)} \right]^{1/2} Z_{i \rightarrow k}(s'_b = s_b, \quad \beta = i, k) (s_i, s_i', s_k, s_k')(\bar{S}(i)S).
\]

This relation can be easily proved using the definitions (36) and (37).
\[
\langle s_i' \rangle (s_2m_2') \cdots (s_i' = s_0, m_i' = \cdots (s_k = s_0 - \frac{1}{2}, m_k') \cdots (s_Nm_N) = (s_0, m_k) \cdots (s_Nm_N) = (-1)^{2s_0 + 2(s_{i+1} + s_{i+2} + \cdots + s_{i+k})} t_{ik} \frac{2s_0 + 1}{2s_0} \delta_{s_i'f} \delta_{m_i'm_i} \sum_{\pi = 0}^N c_{s_0m_0(1/2)} c_{s_0m_0(1/2)} c_{s_0m_0(1/2)}. \tag{39}
\]

Using this expression and following the method described in the previous section one can calculate the matrix element associated with the \(i \rightarrow k\) transfer in the \(\{D(S)SM\}\) representation. Omitting the details of the calculations we give the final result only
\[
\langle s_i' = s_0, s_k' = s_0 - \frac{1}{2}, (S')SM | H^{(1)}_{tr}(i \rightarrow k) | (s_\beta, \beta \neq i, k) \rangle = (s_\beta, \beta \neq i, k) \rangle = (s_\beta, \beta \neq i, k) \rangle.
\]
\[
(-1)^{2s_0 + 1} t_{ik} Z_{i-k} \delta_{s_i'f} \delta_{m_i'm_i} \sum_{\pi = 0}^N c_{s_0m_0(1/2)} c_{s_0m_0(1/2)} c_{s_0m_0(1/2)}. \tag{40}
\]

One can see that this expression contains the function \(Z[\cdots]\) already defined, the local and intermediate spin values being specific for the case under consideration.

Let us compare now the matrices of one-electron transfer for the MV systems of two types \(Pd^{n-n} + (N-P)d^{10-n}\) and \(Pd^{n+1} + (N-P)d^n\) providing \(n \leq 4\). One can see that the ions \(d^n\) and \(d^{10-n}\) possess equal spins (complementary states). The spins for ions \(d^{n+1}\) and \(d^{10-n}\) are also equal. The matrix element of \(i \rightarrow k\) transfer for the system \(Pd^{n-n} + (N-P)d^{10-n}\) [core spin \(s_0 = (n+1)/2\)] is obtained from Eq. (40) as follows:
\[
\left\langle (s_i' = s_0, s_k' = s_0 - \frac{1}{2}, (s_i = n+1/2, s_k = n+1/2) \right) (S')SM | H^{(1)}_{tr}(i \rightarrow k) \right) | (s_\beta, \beta \neq i, k) \rangle = (s_\beta, \beta \neq i, k) \rangle.
\]
\[
(-1)^{n+1} t_{ik} Z_{i-k} \delta_{s_i'f} \delta_{m_i'm_i} \sum_{\pi = 0}^N c_{s_0m_0(1/2)} c_{s_0m_0(1/2)} c_{s_0m_0(1/2)}. \tag{41}
\]

Let us pass now to the system \(Pd^{n+1} + (N-P)d^n\) and consider the matrix element linking the states with the same sets of site spins and intermediate spins as in Eq. (41) [all sites which were occupied by \(d^{10-n}(d^{n+1})\) ions in the previous case now must be occupied by \(d^n(d^{n+1})\) ions]. One can see that this matrix element corresponds to the \(k \rightarrow i\) transfer in the system with less than half-filled \(d\) shells and core spin \(s_0 = n/2\). Changing in Eq. (35) indices \(i\) and \(k\) by places and using the property (38) we get
\[
\left\langle (s_i' = s_0, s_k' = s_0 - \frac{1}{2}, (s_i = n+1/2, s_k = n+1/2) \right) (S')SM | H^{(1)}_{tr}(k \rightarrow i) \right) | (s_\beta, \beta \neq k, i) \rangle = (s_\beta, \beta \neq k, i) \rangle.
\]
\[
(-1)^n t_{ik} Z_{i-k} \delta_{s_i'f} \delta_{m_i'm_i} \sum_{\pi = 0}^N c_{s_0m_0(1/2)} c_{s_0m_0(1/2)} c_{s_0m_0(1/2)}. \tag{42}
\]

Comparing Eqs. (41) and (42) one can see that the matrices of one-electron transfer for the “complementary” systems \(Pd^{n-n} + (N-P)d^{10-n}\) and \(Pd^{n+1} + (N-P)d^n\) differ only in sign. Therefore the double exchange energy pattern of \(Pd^{n-n} + (N-P)d^{10-n}\) system can be viewed as the overturned energy pattern \(Pd^{n+1} + (N-P)d^n\) system and vice versa. The particular cases of this general theorem have been mentioned several times for trimeric24 and tetrameric35 clusters.

The final formulae for the matrix elements of one-electron transfer in the case of less than half-filled \(d\) shells [Eq. (35)] and more than half-filled \(d\) shells [Eq. (41)] give the general solution of the double exchange problem for high-nuclearity MV clusters with the arbitrary number of the moving electrons sharing among the network of spin cores. These formulae are expressed in terms of the products of 6j symbols only and do not contain Clebsch–Gordan coefficients (appearing in the spin-coupling procedures) and high-order recoupling coefficients. Therefore these formulae provide simple and very efficient tool for the theoretical study of the electronic energy spectrum of complex MV systems.

### VIII. TWO-ELECTRON TRANSFER

The one-electron transfer processes (double exchange) so far discussed [the term \(H^{(1)}_{tr}\) in the Hamiltonian (10)] usually play the most important role in the formation of spin levels pattern of MV systems. The total Hamiltonian (10) contains also the term \(H^{(2)}_{tr}\) responsible for the two-electron transfer processes. This term can be represented as
\[
H^{(2)}_{tr} = \sum_{i,j,k,l} H^{(2)}_{tr}(i \rightarrow k, j \rightarrow l). \tag{43}
\]
Considering the case of less than half-filled $d$ shells we can find the contribution corresponding to the jump from the sites $ij$ to the sites $kl$ as

$$
\mathbf{H}^{(2)}_{2}(i \rightarrow k, j \rightarrow l) = \langle \psi_i \psi_j | g | \psi_k \psi_l \rangle \sum_{\sigma \sigma'} C_{i \psi \sigma}^{*} C_{j \sigma} \sigma' C_{k \sigma} \sigma C_{l \psi \sigma'}. \quad (44)
$$

As distinguished from the operator $\mathbf{H}^{(1)}_{1}(i \rightarrow k)$ the operator $\mathbf{H}^{(2)}_{2}(i \rightarrow k, j \rightarrow l)$ changes simultaneously the localization sites of two electrons (Table II).

The contribution of $\mathbf{H}^{(2)}_{2}$ is expected to be smaller than that associated with the one-electron transfer Hamiltonian $\mathbf{H}^{(1)}_{1}$. Nevertheless many physical situations require to take into consideration this smaller contribution. One example represents the 2e-reduced MV polyoxometalates with Keggin and Wells–Dawson structures containing the electronic pair delocalized over the network of the metal ions. In this case two-electron transfer splits the low lying levels meanwhile the one-electron transfer increases the Coulomb energy of the pair giving thus only a second order contribution. Similar situation takes place in complex polyoxovanadates with delocalized electronic pairs. As a second example the high-nuclearity clusters containing triangular faces can be pointed out, particularly, metal skeleton of iron–sulfur proteins $[\text{Fe}_{5} \text{S}_{4}]^{3+}$ $(d^{5} - d^{5} - d^{6} - d^{6} - d^{6})$ system. Strong double exchange in these systems results in the accidentally degenerate ground state comprising a set of different spin states (transfer frustration). In this case the low-temperature magnetic behavior may be determined by the two-electron transfer.

The expressions so far obtained for the matrix elements of one-electron transfer make it possible to evaluate also the matrix elements of two-electron transfer operator $\mathbf{H}^{(2)}_{2}$. Let us consider two-electron transfer $i \rightarrow k, j \rightarrow l$ for the case of less than half-filled $d$ shells (the case of more than half-filled $d$ shells can be considered similarly). The corresponding operator $\mathbf{H}^{(2)}_{2}(i \rightarrow k, j \rightarrow l)$ can be represented as the product of the one-electron transfer operators:

$$
\mathbf{H}^{(2)}_{2}(i \rightarrow k, j \rightarrow l) = \langle \psi_i \psi_j | g | \psi_k \psi_l \rangle \sum_{\sigma} C_{i \psi \sigma}^{*} C_{j \sigma} \sigma' \sum_{\sigma'} C_{k \sigma} \sigma C_{l \psi \sigma'}. \quad (45)
$$

Applying now the formula for the matrix element of the product of two operators we get

$$
\langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | (s', s)_{i} = s_{i} + \frac{1}{2}, s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle = \langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | (s', s)_{i} = s_{i} + \frac{1}{2}, s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle
$$

$$
\times \langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | (s', s)_{i} = s_{i} + \frac{1}{2}, s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle.
$$

One can see that the matrix element of two-electron transfer operator is expressed in terms of the one-electron transfer matrix elements already calculated [see Sec. VI Eq. (35)]. Substituting these matrix elements into Eq. (45) we obtain

$$
\langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | (s', s)_{i} = s_{i} + \frac{1}{2}, s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle = \langle \psi_i \psi_j | g | \psi_k \psi_l \rangle \sum_{\gamma} Z_{ij, \gamma} \langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle
$$

$$
\times \langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle
$$

$$
= \langle \psi_i \psi_j | g | \psi_k \psi_l \rangle \sum_{\gamma} Z_{ij, \gamma} \langle s'_{\beta} = s_{\beta}, \beta \neq i, k, j, l | s'_{\gamma} = s_{\gamma}, \gamma \neq i, k, j, l | s'_{\beta} = s_{\beta} + \frac{1}{2}, s'_{\gamma} = s_{\gamma} + \frac{1}{2} | (S', S)_{\text{SM}} \rangle.
$$

(46)
where \( Z_{j \rightarrow k}[\ldots] \) and \( Z_{i \rightarrow k}[\ldots] \) are given by Eqs. (36) and (37). Sum in Eq. (46) involves all sets of intermediate spins admitted by the given set of spins of the ions indicated explicitly in the notation of \( Z_{j \rightarrow k}[\ldots] \) and \( Z_{i \rightarrow k}[\ldots] \) for the given intermediate (double primed) state.

Let us discuss now briefly the case of more than half-filled \( d \) shells. Two electron jump from double occupied \( \phi_{1j} \) and \( \varphi_{1j} \) orbitals to singly occupied \( \phi_{2j} \) and \( \varphi_{2j} \) orbitals, so the associated two-electron transfer parameter will be \( \langle \phi_{k1} \varphi_{1j} | \phi_{2j} \varphi_{1j} \rangle \). The matrix element of two-electron transfer can be represented in terms of the products of constituent one-electron transfer matrix elements just as in the case of less than half-filled \( d \) shells. Therefore, as distinguished from the energy patterns formed by double exchange (Sec. VII), the energy patterns formed by two-electron jumps will be the same for both “complementary” states \( P \), \( d \bar{n} = n + (N - P) \), \( d \bar{n} = n + (N - P) \).

### IX. POTENTIAL EXCHANGE TRANSFER

Now we consider the last term in the Hamiltonian (10) \( H_{\text{ex-tr}} \). For the reasons given below we will refer the corresponding physical interaction to as the potential exchange transfer. The potential exchange transfer operator can be expressed as

\[
H_{\text{ex-tr}}^P = \sum_{i \neq k} H_{\text{ex-tr}}^P (i \rightarrow k). 
\]  

We consider the case of less than half-filled \( d \) shells, for which each term in Eq. (47) has the form

\[
H_{\text{ex-tr}}^P (i \rightarrow k) = \sum_{j \neq i, k} \left[ H_{\text{ex-tr}}^P (\phi, i \rightarrow j \rightarrow k) + H_{\text{ex-tr}}^P (\varphi, i \rightarrow j \rightarrow k) \right],
\]

where

\[
H_{\text{ex-tr}}^P (\phi, i \rightarrow j \rightarrow k) = \langle \psi_i \psi_j | \mathbf{g} | \psi_j \psi_k \rangle \sum_{\sigma \sigma'} C_{j \rightarrow \sigma} ^+ C_{k \rightarrow \sigma} C_{j \rightarrow \sigma'} C_{i \rightarrow \sigma}.
\]

\[
H_{\text{ex-tr}}^P (\varphi, i \rightarrow j \rightarrow k) = \sum_{\nu} \langle \psi_i \varphi_j | \mathbf{g} | \varphi_j \nu \psi_k \rangle \sum_{\sigma \sigma'} C_{j \rightarrow \sigma} ^+ C_{k \rightarrow \sigma} C_{j \rightarrow \sigma'} C_{i \rightarrow \sigma}.
\]

One can see that exchange transfer operator is expressed in terms of three-center contributions. Each of them can be apparently viewed as the the \( i \rightarrow k \) transfer process via the third center \( j \). Electron transfer occurs through \( \psi_j \) orbital [Eq. (49), Table III, line 1] or through the \( \varphi_j \) orbitals of spin cores [Eq. (50)] of intermediate centers (in Table III lines 2 and 3 correspond to the intermediate \( d^{n} \) and \( d^{n+1} \) centers). Therefore, the operator (48) takes into account all pathways of \( i \rightarrow k \) transfer through the intermediate centers. These processes are quite similar to those involved in the so-called exchange transfer interaction.\(^{19,46–49}\) This interaction arises in the second order of perturbation theory like kinetic exchange, and therefore, it can be referred to as kinetic exchange transfer. The matrices of the kinetic exchange transfer have been recently calculated for the MV clusters of arbitrary nuclearity.\(^{48,49}\) On the contrary, operator (48) acts within the ground manifold and thus appears as a first-order effect like potential exchange. This accounts for the term “potential exchange transfer” introduced here. The detailed discussion of the analogy between potential and kinetic exchange transfer interactions and the differences between their magnetic manifestations is out of the scope of this paper, and will be given elsewhere. It should be noted only that the potential exchange transfer parameter (Table III) and the magnetic (Heisenberg-type) potential exchange parameter may be estimated as the same order parameters. Therefore, as far as the exchange interactions in MV systems are concerned the exchange transfer processes should be taken into account at the same level of approximation.

Now we proceed to the calculation of the matrix elements of the potential exchange transfer operator (48). Like the double exchange operator, the operator \( H_{\text{ex-tr}}^P (i \rightarrow k) \) changes the site of localization of one electron while all remaining electrons keep their places.

Using the results of the previous section one can obtain the formula for the matrix element of the operator \( H_{\text{ex-tr}}^P (\phi, i \rightarrow j \rightarrow k) \). In fact this operator can be obviously regarded as a particular case of the two-electron transfer operator so we can write

\[
H_{\text{ex-tr}}^P (\phi, i \rightarrow j \rightarrow k) = H_{\text{ex-tr}}^P (j \rightarrow k, i \rightarrow j).
\]

Applying Eq. (46) and making the necessary modifications we get

<p>| TABLE III. The electronic processes associated with the operator ( H_{\text{ex-tr}}^P (i \rightarrow k) ) (only the processes with ( \sigma = \sigma' = \uparrow ) are shown). |</p>
<table>
<thead>
<tr>
<th>Scheme of the process</th>
<th>Contribution to the parameter term ( \Delta H_{\text{ex-tr}}^P )</th>
<th>Exception operators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processes involved in ( H_{\text{ex-tr}}^P (\phi, i \rightarrow j \rightarrow k) )</td>
<td></td>
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<tr>
<td>1</td>
<td></td>
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<td>3</td>
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</tbody>
</table>

\[ A_{\text{ex-tr}}^P \]

\[ C_{j \rightarrow \sigma} ^+ C_{k \rightarrow \sigma} C_{i \rightarrow \sigma} \]

\[ C_{j \rightarrow \sigma} ^+ C_{k \rightarrow \sigma} C_{i \rightarrow \sigma} \]
\[ \langle (s'_b = s_{\beta, \beta \neq i, k, j}) (s'_i = s_0, s'_j = s_0 + \frac{1}{2}, s''_k = s_0 + \frac{1}{2}) (\vec{S}') \rangle SM | \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) | (s_\beta, \beta \neq i, k, j) \]

\[ (s_i = s_0 + \frac{1}{2}, s_j = s_0 + \frac{1}{2}, s_k = s_0) (\vec{S}) SM \]

\[ = \langle \psi_i \psi_j | \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) | \psi_i \psi_j \rangle \sum (s'_b = s_{\beta, \beta \neq i, k, j}) (s'_i = s_0, s'_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}, s''_k = s_0 + \frac{1}{2}) (\vec{S}') (\vec{S}) S \]

\[ Z_{i \rightarrow j} (s''_b = s_{\beta, \beta \neq i, k, j}) (s''_i = s_0 + \frac{1}{2}, s''_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}) (\vec{S}') (\vec{S}) S. \] (51)

For the calculation of the matrix element of the operator \( \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) \) it is convenient to rearrange this operator in the following way:

\[ \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) = \sum \langle \psi_i \psi_j | \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) | \psi_i \psi_j \rangle \sum C^{+}_{\alpha} C_{i\alpha} \sum C^{+}_{\alpha} C_{j\alpha} \cdot \]

Then one can express the matrix element under consideration in terms of the matrix elements describing two successive one-electron transfers processes. Thus we get

\[ \langle (s'_b = s_{\beta, \beta \neq i, k, j}) (s'_i = s_0, s'_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}) (\vec{S}') SM | \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) | (s_\beta, \beta \neq i, k, j, l) \]

\[ (s_i = s_0 + \frac{1}{2}, s_j = s_0 + \frac{1}{2}, s_k = s_0 + \frac{1}{2}) (\vec{S}) SM \]

\[ = \sum \langle \psi_i \psi_j | \mathbf{H}^{P}_{ex,ij} (\varphi, i \rightarrow j \rightarrow k) | \psi_i \psi_j \rangle \sum (s'_b = s_{\beta, \beta \neq i, k, j}) (s'_i = s_0, s'_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}) (\vec{S}') SM \sum C^{+}_{\alpha} C_{i\alpha} (jv)^0 (s''_b = s_{\beta, \beta \neq i, k, j}) (s''_i = s_0 + \frac{1}{2}, s''_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}, s''_l = s_0 + \frac{1}{2}) (\vec{S}') SM \]

\[ \sum C^{+}_{\alpha} C_{j\alpha} \left( s_\beta, \beta \neq i, k, j \right) (s_i = s_0 + \frac{1}{2}, s_j = s_0 + \frac{1}{2})(\vec{S}) SM , \] (52)

where symbol \((jv)^0\) shows that \( \psi_{jv} \) orbital is empty in the intermediate (double primed) state.

The calculation of the matrix elements of the one-electron transfers involved in Eq. (52) is based on the angular momentum approach developed in Sec. VI. Omitting the details we give the result

\[ \left( s'_b = s_{\beta, \beta \neq i, k, j} \right) (s'_i = s_0, s'_k = s_0 + \frac{1}{2}, s'_j = s_0 + \frac{1}{2}) (\vec{S}') SM \sum C^{+}_{\alpha} C_{i\alpha} (jv)^0 (s''_b = s_{\beta, \beta \neq i, k, j}) \]

\[ (s'_i = s_0 + \frac{1}{2}, s''_k = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2}, s''_j = s_0 + \frac{1}{2})(\vec{S}') SM \]

\[ = (\vartheta I_{ij}(s_j)) Z_{i \rightarrow j} (s''_b = s_{\beta, \beta \neq i, k, j}) (s''_i = s_0, s''_k = s_0 + \frac{1}{2}) \]

\[ = (\vartheta I_{ij}(s_j)) Z_{i \rightarrow j} (s''_i = s_0, s''_k = s_0, s''_j = s_0, s''_j = s_0 + \frac{1}{2}) (\vec{S}') (\vec{S}) S. \] (53)

where \( \vartheta I_{ij}(s_j) \) is a factor defined as

\[ \vartheta I_{ij}(s_j) = \begin{cases} -1, & \text{if } i < j \\ (-1)^{2(j_0+s_j)} & \text{if } i > j \end{cases} \] (54)

We also have
\[
\left((jv)^0(s''_n = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2} s_k = s_0, s_j = \frac{1}{2}) (S^n) SM \right| \sum_{\sigma} C^+_{k,\phi,\sigma} C_{j,\nu,\sigma} \right) \\
(s_{\beta}, \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2} s_k = s_0, s_j = \frac{1}{2}) (S^n) SM \\
\left| \sum_{\sigma} C^+_{j,\nu,\sigma} C_{k,\phi,\sigma} \right) \\
(jv)^0(s''_n = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2} s_k = s_0, s_j = \frac{1}{2}) (S^n) SM \\
\right) = \left((-1)^n \theta_{ij}(s_i) \theta_{kj}(s_j) \sum_{(S')} \langle \psi_k \varphi_j | g | \psi_j \varphi_i \rangle \sum_{(S''')} Z_{k-i} (s''_n = s'_{\beta} = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2}) (S^n) SM \right)
\]

\[
\left| \sum_{\sigma} C^+_{j,\nu,\sigma} C_{k,\phi,\sigma} \right) \\
(jv)^0(s''_n = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2} s_k = s_0, s_j = \frac{1}{2}) (S^n) SM \\
\right) = \left((-1)^n \theta_{ij}(s_i) \theta_{kj}(s_j) \sum_{(S')} \langle \psi_k \varphi_j | g | \psi_j \varphi_i \rangle \sum_{(S''')} Z_{k-i} (s''_n = s'_{\beta} = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2}) (S^n) SM \right)
\]

Comparing this formula with Eq. (54), both formulas give the same dependence on the site spins and on the intermediate spins. Therefore, we can combine Eqs. (56) and (51), taking also into account Eqs. (48)–(50), to obtain the following final result for the potential exchange transfer matrix element:

\[
\langle (s'_n = s'_{\beta} , \beta \neq i,k,j) (s'_i = s_0 , s'_k = s_0 + \frac{1}{2}) (S') SM | \sum_{(S''')} Z_{k-i} (s''_n = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2}) (S^n) SM \rangle = \sum_{j \neq i,k} \theta_{ij}(s_i) \theta_{kj}(s_j) \Lambda^P_{ijk} \sum_{(S''')} Z_{k-i} (s''_n = s'_{\beta} , \beta \neq i,k,j) (s_i = s_0 + \frac{1}{2}) (S^n) SM
\]

Here \( \Lambda^P_{ijk} \) represent the parameters associated with the potential exchange transfer. These parameters depend on the number of the electrons in the center j as follows:

\[
\Lambda^P_{ijk} = \begin{cases} 
\langle \psi_k \varphi_j | g | \psi_j \varphi_i \rangle + \sum_v \langle \psi_k \varphi_{jv} | g | \varphi_{jv} \varphi_i \rangle, & \text{for } d_j^{n+1} \text{ ions} \\
\sum_v \langle \psi_k \varphi_{jv} | g | \varphi_{jv} \psi_i \rangle, & \text{for } d_j^n \text{ ions} 
\end{cases}
\]

Summation in Eq. (57) involves the sites of both types \( d_j^{n+1} \) and \( d_j^n \), possessing spins \( s_j = s_0 + \frac{1}{2} \) and \( s_j = s_0 \), correspondingly.

Equation (57) makes it possible to built the matrix of the potential exchange transfer for the high-nuclearity MV systems containing arbitrary number of moving electrons in the case of less than half-filled \( d \) shells. The case of more than half-filled \( d \) shells can be considered quite similarly.

**X. SYMMETRY CONSIDERATION**

The dimensions of the matrices to be diagonalized increase dramatically with the increase of the number of sites and the number of electrons. That is why the problem of reducing the matrices becomes of crucial importance for the higher nuclearity MV systems. For clusters exhibiting high symmetry the most efficient way to attack this problem is to take advantage of the point symmetry arguments. Let us consider briefly how the symmetry can be added to our general approach.

Since Hamiltonian (10) is isotropic, there will be matrix elements only between states exhibiting the same values for the total spin \( S \) and its projection \( M \), and belonging to the same irreducible representation \( \Gamma \) of the point symmetry group of the cluster. In the angular momentum approach the
Therefore, the set of the wave functions $|D(\tilde{S})SM\rangle$ generates a linear combination of wave functions with the same $S$ and $M$ values but with different distributions $D$ and sets ($\tilde{S}$)

$$|\hat{R}|D(\tilde{S})SM\rangle = \sum_{D'(\tilde{S}')} G_{D'(\tilde{S}'),D(\tilde{S})}(\hat{R})|D'(\tilde{S}')SM\rangle,$$

(59)

where $G$ is the matrix of $\hat{R}$ in the $|D(\tilde{S})SM\rangle$ representation

$$G_{D'(\tilde{S}'),D(\tilde{S})}(\hat{R}) = \langle D'(\tilde{S}')SM|\hat{R}|D(\tilde{S})SM\rangle.$$

(60)

Therefore, the set of the wave functions $|D(\tilde{S})SM\rangle$ for each given $S$ and $M$ can be regarded as the basis of some representation of the cluster's symmetry group. This representation is generally speaking reducible and we denote it as $\Gamma_r$.

The wave functions $|D(\tilde{S})SM\rangle$ can be expressed in terms of a linear combination of Slater determinants (Sec. III). Therefore, applying the symmetry operations to each Slater determinant of these linear combinations one can calculate all matrix elements $G_{D'(\tilde{S}'),D(\tilde{S})}(\hat{R})$ and then find the characters of the representation $\Gamma_r$

$$\chi(\hat{R}) = \sum_{D(\tilde{S})} G_{D(\tilde{S}),D(\tilde{S})}(\hat{R}).$$

(61)

Decomposing $\Gamma_r$ into the irreducible parts one can find all $\Gamma'M\gamma$ terms admitted by the symmetry of the system before finding their energies (an alternative method of group-theoretical classification has been recently proposed based on the properties of the permutation group).

The next step is to construct the $|\Gamma'M\gamma\rangle$ basis belonging to the total spin $\tilde{S}$ and irreducible representation $\Gamma$ ($\gamma$ enumerates the basis functions of $\Gamma$). This can be reached by means of the point group projection operator

$$\hat{P}^{(\Gamma)}_{\gamma\gamma'} = \frac{f_\Gamma}{g} \sum_R G^{(\Gamma)}_{\gamma\gamma'}(\hat{R}) \hat{R},$$

(62)

where $f_\Gamma$ is the dimension of the irreducible representation $\Gamma$, $G^{(\Gamma)}_{\gamma\gamma'}(\hat{R})$ is the matrix element of the matrix of the irreducible representation $\Gamma$ corresponding to the operation $\hat{R}$. The projection operator is to be applied to the arbitrary wave function $|D(\tilde{S})SM\rangle$. Fixing the second index $\gamma'$ we obtain $f_\Gamma$ functions $|\Gamma'M\gamma\rangle$ forming the basis of the irreducible representation $\Gamma$. Since the second index $\gamma'$ can take $f_\Gamma$ values we can obtain $f_\Gamma$ independent basis sets. Using any of these sets one can strongly reduce the dimensions of the matrices to be diagonalized. This is because in the new basis besides the diagonal matrix elements, only those off-diagonal matrix elements linking the states belonging to the repeating irreducible representations can be nonzero.

The symmetry adapted wave functions built in this way are the linear combinations of the wave functions $|D(\tilde{S})SM\rangle$ of the initial set:

$$|\Sigma\Gamma'M\gamma\rangle = \frac{f_\Gamma}{g} \sum_R G^{(\Gamma)}_{\gamma\gamma'}(\hat{R})$$

$$\times \sum_{D'(\tilde{S})} G_{D'(\tilde{S})}|D'(\tilde{S}')SM\rangle|D'\tilde{S}')SM\rangle. \quad (63)$$

This basis set corresponds to a certain fixed $\gamma'$, symbol $\gamma'$ is omitted in the labeling of $\Sigma\Gamma'$ term.

The matrix elements of the Hamiltonian (10) in the symmetry adapted basis can be represented in terms of the matrix elements of the type $\langle D'(\tilde{S}')SM|H|D(\tilde{S})SM\rangle$ that have already been calculated in the previous sections.

The tetrameric cubane-type clusters provide (due to their high symmetry $T_d$) a very good example illustrating the advantages of the symmetry adapted approach. Let us consider, for instance, the tetramer $d^2-d^2-d^2-d^2$ (total spin $\tilde{S} = \frac{7}{2}$, $\frac{5}{2}$). For each $\tilde{S}$ we have reducible representation $\Gamma_r(\tilde{S})$ with the basis $|D(\tilde{S})SM\rangle$. So for $\tilde{S} = 7/2$ the basis set contains 88 states (the dimension of this representation $\Gamma_r(\tilde{S} = 7/2)$ is the biggest one). Following the method described above one can reduce $\Gamma_r(\tilde{S} = 7/2)$ to the irreducible representations of $T_d$ group as follows:

$$\Gamma_r\left(S = \frac{7}{2}\right) = 3A_1 + 5A_2 + 7E + 12T_1 + 10T_2.$$

Since only the matrix elements linking the states with the same $\Gamma$ and $\gamma$ can be nonvanishing, we obtain instead of the initial matrix $88 \times 88$, five matrices of smaller dimensions $(3 \times 3, 5 \times 5, 7 \times 7, 12 \times 12, 10 \times 10)$.

For the distorted cluster of $D_{2h}$ symmetry for the same $\tilde{S} = 7/2$ we get

$$\Gamma_r\left(S = \frac{7}{2}\right) = 10A_1 + 12B_1 + 10B_2 + 12A_2 + 22E.$$

Therefore, now we should diagonalize two matrices $10 \times 10$, two matrices $12 \times 12$, and one matrix $11 \times 11$. One can see that even in this case of comparatively low symmetry, the group theoretical approach provides significant simplifications of the computational procedure. The advantages of the use of symmetry adapted basis set increase with the increase of nuclearity of the system and local spins.

XI. CONCLUDING REMARKS

The evaluation of the exchange interactions effects in localized and delocalized spin systems is quite different. Thus, in the former case it is well known that under some restrictions the full Hamiltonian may be replaced by an effective spin Hamiltonian involving the spin exchange interactions. The required computational procedure (based on the use of irreducible tensors) is well developed and allows one to express the matrix of the spin Hamiltonian in terms of spin exchange parameters and relevant spin quantum numbers. This kind of semiempirical approach can not be applied to the MV systems containing delocalized electrons because the magnetic moments on each site are not well defined. In these
systems besides the usual spin exchange coupling, there is an additional spin coupling due to electron delocalization namely double exchange that can not be expressed in terms of a spin Hamiltonian. Hence, the general form of the effective Hamiltonian for these systems is unknown. As a consequence the resolution of the double exchange problem has required until now a particular procedure for each kind of MV system.

In this paper, we have presented a new efficient and general approach and a computational procedure for the evaluation of the electronic and magnetic properties of MV clusters of arbitrary nuclearity. This approach is based on the angular momentum theory and chainlike spin coupling scheme and avoids the stage to derive a generalized effective Hamiltonian. Thus, starting from the real Hamiltonian that includes all the relevant electronic interactions, we have built directly the energy matrix. This has allowed us to express the matrix elements of double exchange in terms of one-electron transfer parameters (involving all the relevant electronic processes) and the full set of spin quantum numbers in the initial and final localized states of the MV system. In the framework of the developed approach the two-electron transfer processes and three-center interactions (exchange transfer) are considered as well.

The computational procedure is rather simple and consists of the following steps:

1. We define the network of the N active metal sites involved in the transfer processes, and the number of delocalized electrons P;
2. We derive all the localized distributions D of P electrons over N sites, defining at the same time the spin on each site (s0 and s0±½ or s0±½). The N active sites are enumerated (j = 1, 2, ..., N); this enumeration is independent of the electronic distribution;
3. For each electronic distribution D possessing the set of local spins S1, S2, ..., SN (Sj = s0 or s0±½ depending on the distribution D), we build the full set of spin quantum numbers: S1, S2, ..., SN-1 (intermediate spins in the successive spin coupling scheme) and SN = S (total spin of the system);
4. Matrix element of the double exchange can be non-zero if two electronic distributions D and D' differ in the occupation numbers of two sites only (one-electron transfer). To evaluate this matrix element one should use Eqs. (35) and (40) substituting in these equations full sets of spin quantum numbers for the distribution D and D'. Each total spin S (S = S) provides a block of the full double exchange matrix;
5. The matrices of the two-electron transfer and potential exchange transfer are also blocked according to the values of total spin S. The matrix elements are given by Eqs. (46) and (57) correspondingly. The matrix elements of all named interactions are expressed through the universal function Z[···] [Eqs. (36) and (37)] containing products of 6j symbols.

In this paper, we have described the developed approach only. This approach is now being developed to treat some complex MV magnetic systems as the high nuclearity MV polyoxometalate clusters and the diphthalocyanine MV chains. The results will be reported in future papers.

ACKNOWLEDGMENTS

Financial supports by the European Union CHRX-CT92-0080 and the Dirección General de Ciencia y Tecnología DGICYT PB94-0998 are acknowledged. J.M.C. thanks the Generalitat Valenciana for a predoctoral grant. B.S.T. thanks the Universidad de Valencia for a visiting professor grant. A.V.P. thanks the Ministerio de Educacion y Cultura for a postdoctoral fellowship. We also thank the CIUV for its computer facilities.

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