Electronic and Vibronic Problems of Nanosized Mixed Valence Clusters: Advances and Challenges

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Abstract. Here we discuss the electronic and vibronic problems of mixed valency (MV) in molecular clusters which are of current interest in areas as diverse as solid-state chemistry, biochemistry, and molecular magnetism. Modern research in these areas is focused on the nanosized clusters at the border between classical and quantum scales and for this reason they are particularly difficult to study. First, we describe a general approach to the evaluation of the energy pattern of MV systems containing arbitrary number of localized spins and itinerant electrons with due account for the double exchange and other relevant interactions, like interelectronic Coulomb repulsion in instantly localized configurations. Then we present a symmetry adapted approach to the dynamic vibronic problem in large scale multimode Jahn-Teller (JT) systems, in particular, molecular MV clusters. The developed techniques are applied to the analysis of nanosized MV systems with emphasis on the 2e-reduced MV Keggin anion in which the electronic pair is delocalized over twelve sites (1T2d) giving rise to the (1T2 + 1E + 1A1) ⊗ (e + t2) and (3T1 + 3T2) ⊗ (e + t2) combined JT/pseudo JT problems for the spin-singlet and spin-triplet states. The delocalization of the two itinerant electrons in this remarkable systems was shown to lead to an effective spin paring. We study the energy pattern of this MV system and show that the vibronic interaction results in the ferromagnetic contribution.

1. Introduction

Modern trends in the molecular electronics and spintronics gave strong impact on the development of the synthetic, experimental and theoretical studies of large magnetic clusters and especially MV systems exhibiting double exchange [1]. These systems contain mobile itinerant electrons that provide unique opportunities for the control of quantum states through the action of external fields. The problem entire can be subdivided into two parts, namely, evaluation of the electronic levels (will be referred to as “electronic problem”) and consequent consideration of the vibronic states (“vibronic problem”). For a binuclear MV system the problem of the double exchange [2] was solved by Anderson and Hasegawa [2c] and the ferromagnetic effect of the double exchange in MV dimers was elucidated. Since the solution of the double exchange problem has been essentially attributed to the case of an electron shared between pair of ions (spin cores) the results of Ref. [2c] should be generalized for more complicated high nuclearity systems [3a-c].

On the other hand, evaluation of the energy levels and JT /pseudo JT effects lead to a complicated dynamic vibronic problem [4-6]. The difficulties are aggravated for the multimode systems when the energy pattern contains several low-lying levels mixed by the active JT vibrations. This especially refers to the large scale MV systems, like biologically important systems such as iron-sulfur proteins [7], polynuclear metal-oxide clusters in which several electrons are delocalized over
metal network (for example, reduced polyoxometalates (POMs) with Keggin and Wells-Dawson structures) [3,8], impurity metal ions in crystals [9-11], etc. In these cases the dimension of the truncated vibronic matrices to be diagonalized becomes very high due to sizeable electronic basis and multiple degeneracy of the excited vibrational levels.

Many efforts have been applied to get an accurate solution of the dynamic problem (see refs [3-6]). A significant progress has been achieved by the exploration of the Lie symmetries of the JT Hamiltonians [12]. Nevertheless, the vibronic Hamiltonian exhibits unitary symmetries only providing some essential restrictions, like linear vibronic coupling and special interrelations between the coupling constants which significantly reduces the area of practical applicability of these extremely elegant approaches.

The goal of this article is to describe a general solution of the electronic problem of mixed valency and a symmetry adapted approach aimed to an accurate solution of the dynamic JT/ pseudo JT problem in large MV systems. We introduce the mathematical procedure through the consideration of the MV POM with Keggin structure reduced by 2e [13]. This dodecanuclear MV system belongs to a large class of POMs, the so-called “heteropolyblues”, which are attracting considerable interest in solid state chemistry, biomedical applications, catalysis and materials science in view of their unique electronic properties [14]. In terms of mixed-valency, the Keggin anion can be viewed as a high-nuclearity cluster belonging to Class II in Robin and Day classification and a complicated example of the JT system for which the dynamic problem seems to be actual for the adequate description of the non-trivial magnetic and optical (intervalence bands) properties. In this article we will focus on the elaboration of the theoretical approach, while the associated computer program with the detailed discussion of the experimental data on the Keggin anion will be published elsewhere [3d,15].

2. Electron transfer and double exchange in nanosized mixed-valence clusters

Until recently the calculation of the energy pattern of MV compounds exhibiting electron delocalization/double exchange has been restricted to comparatively simple systems comprising one or two itinerant electrons delocalized over a small number of exchange-coupled metal sites [1] (basically, dimeric and trimeric clusters). Consideration of nanoscopic MV systems require a more common approach that would allow to solve the double exchange problem for high-nuclearity MV clusters containing arbitrary number of localized spins and itinerant electrons [3]. The electron hopping from the site \( i \) to the site \( k \) is described by the following double exchange Hamiltonian \( H_{\text{Heis}} \) (first term in Eq. (1)) supplemented by the Heisenberg type exchange interaction between localized spins (second term) and intersite Coulomb repulsion (last term):
\[
H_e = \sum_{i,k,\sigma} t_{ik} \left( c_{i\sigma}^+ c_{i\sigma} + h.c. \right) + \sum_{i,j,k,l,\sigma,\sigma'} p_{ij,kl} \left( c_{i\sigma}^+ c_{k\sigma'}^+ c_{i\sigma'} c_{j\sigma} + h.c. \right) + \sum_{i,k} J_{ik} s_i s_k + \sum_{i,k} U_{ik} n_i n_k
\]

where the operator \( c_{k\sigma}^+ (c_{i\sigma}) \) creates (annihilates) an electron on the site \( k \) \((i)\) with the spin projection \( \sigma \), \( t_{ik} \) and \( p_{ij,kl} \) are the one- and two-electron transfer integrals, respectively, \( U_{ik} \) is the intersite Coulomb integrals (the distributions with the two itinerant electrons per site are supposed to be much high in energy and for this reason are neglected). Finally, \( J_{ik} \) are the exchange parameters that depend on the electronic distributions with the set of the local spins \( s_i \) defined by populations of the sites \( n_i \). In particular, the exchange interactions between two spin cores \((s_i = s_j = s_0)\), between spin cores and ions accommodating “extra” electron \( s_i = s_0, s_j = s_0 + 1/2 \) and between two centers with “extra” electrons \( s_i = s_0 + 1/2, s_j = s_0 + 1/2 \) are to be discriminated for each instantly localized electronic distribution. Using the angular momentum technique the matrix element of the double exchange operator \( H_{tr}(i \rightarrow k) \) describing one-electron jump \( i \rightarrow k \) (one contribution in the first term in Eq. (1)) is calculated as follows [3]:

\[
\langle \left( s_{\beta} = s_{\beta}, \beta \neq i, k \right) | \langle s'_i = s'_0, s'_k = s'_0 + 1/2 \rangle | (\tilde{S}') S' M'_S | H_{tr}(i \rightarrow k) | (s_{\beta}, \beta \neq i, k) \rangle \\
\times \left\langle s_i = s'_0 + 1/2, s_k = s'_0 \left| \left( \tilde{S} \right) S M \right. \right\rangle = (-1)^{s'_0} t_{ik} \delta_{S S'} \delta_{M M'_S} \\
\times \left[ Z_{i \rightarrow k} \left[ \left( s'_{\beta} = s_{\beta}, \beta \neq i, k \right) | \langle s'_i = s'_0, s'_k = s'_0 + 1/2 \rangle | (\tilde{S}') S \right] \right],
\]

where \( Z_{i \rightarrow k} \) is the function of local spins \( s_i, s_k \) and \( s'_i, s'_k \) for the initial and final electronic distributions, the corresponding sets of intermediate spins \( \langle \tilde{S} \rangle \) and \( \langle \tilde{S}' \rangle \) in the spin coupling schemes for the initial and final electronic distributions, and total spin \( S \). It is to be noted that the function \( Z \) involves 6j-symbols rather than high order recoupling coefficients [2]. The energy levels resulting from the electronic Hamiltonian, Eq. (1), are mixed by the active JT/pseudo JT modes. In most cases of MV compounds this mixing is strong enough due to strong deformation of the ligand surrounding by the “extra” electron. In majority of cases the one-electron transfer (double exchange) is a dominant electronic interaction in MV clusters. However, in some cases, such transfer can give rise to the strongly excited states due to high intersite Coulomb repulsion energy (last term in Eq. (1)). As a result such one-electron transfer appears to be the second order contribution that is comparable (or even smaller) than that arising from the two-electron transfer (second term in Eq. (1)). The 2e reduced MV POM with Keggin structure we consider here provides an example of case when the two-electron transfer contribution proves to be important. The matrix elements of the two-electron transfer operator are expressed in terms of the product of the functions \( Z_{k \rightarrow i} \) and \( Z_{i \rightarrow j} \), see ref.[3] for more details.

3. Jahn-Teller Hamiltonian

The Hamiltonian of a JT (or, in general, pseudo JT) system can be represented as:

\[
H = H_e + \sum_{\pi,\tau} \hbar \omega_{\pi\tau} b_{\pi\tau}^+ b_{\pi\tau} + \left( 1/\sqrt{2} \right) \sum_{\pi,\tau} \nu_{\pi,\tau} O_{\pi,\tau} \left( b_{\pi\tau}^+ + b_{\pi\tau} \right)
\]
where \( b^+_{\nu \Gamma} \) and \( b_{\nu \Gamma} \) are the creation and annihilation bosonic operators for the vibrational modes \( \nu \Gamma \), \( \omega_i \) are the vibrational frequencies so that the second term in Eq. (1) is the harmonic oscillator Hamiltonian. The symbol \( i \equiv \nu \Gamma \) involves active vibrational irreps \( \Gamma \), \( \nu \) numerates the basis functions of the irrep \( \Gamma \) and symbol \( \nu \) is introduced in order to distinguish the repeated irreps \( \Gamma \). The electronic subsystem described by the Hamiltonian \( H_e \) is supposed to consist of a set of the closely spaced electronic levels \( \Gamma_1, \Gamma_2, \ldots, \Gamma_f \) labeled by the irreps of the actual point group (the basis functions are marked by the symbols \( \gamma_1, \gamma_2, \ldots, \gamma_f \)) which are mixed by the active JT/pseudo JT vibrational modes \( \Gamma_1, \Gamma_2, \ldots, \Gamma_f \). The third term in Eq. (1) represents the linear vibronic interaction in which \( \Omega \) are the so-called vibronic matrices defined in the adopted electronic basis and \( \nu_i \) are the dimensionless (in \( \hbar \omega \) units) coupling parameters. Applying the creation operators to the vacuum state \( (0) = \sqrt{n!} n \) one can build the exited states \( |n\rangle \). The computational approach will be illustrated by consideration of the MV 2e-reduced Keggin polyanion.

4. Electronic states and vibrations of the 2e-reduced Keggin polyanion

The Keggin structure [8] consists of the four edge-sharing triads of MO\(_6\) units arranged around the heteroatom X (= B, Si, P, Co, Cu,…) by sharing corners in such a way that the system consisting of the twelve sites possesses overall tetrahedral symmetry \( T_d \). Fig 1b shows the idealized scheme of the metal sites in the Keggin system that consists of the four metal triangles perpendicular to the C\(_3\) axes of the tetrahedron. The Keggin anion can be reversibly reduced by adding one or more electrons, which are delocalized over the metal network. The resulting MV systems usually belongs to Class II in the Robin and Day classification [8,16] exhibiting thus an intermediate vibronic coupling. In this respect the Keggin anion with the delocalized electronic pair is of a special interest due to its unusual magnetic properties. In fact, the 2e-reduced Keggin anion was found to be antiferromagnetic that can not be explained in the framework of the conventional Heisenberg model dealing with the localized spins [8]. It was suggested [13,17] that the delocalization of the electronic pair results in the effective stabilization of the antiferromagnetic spin state of the electronic pair in the Keggin anion [8].

The interpretation of the spin pairing in the Keggin anion [13] is based on the model including delocalization of the two electrons over twelve sites (Fig.1b) as well as the Coulomb

![Fig. 1. Two-electron reduced polyoxoanion with Keggin structure: network of the octahedral units (a) and scheme of the metal sites and molecular coordinate frame (b).]
repulsion. The energy levels can be divided into five groups corresponding to the different distances between delocalized electrons in the 66 dispositions. The Coulomb repulsion tends to keep the electrons as far as possible in the ground configuration that is shown to consists of the three spin-singlets $^1A_1$, $^1E$, $^1T_2$ and two spin triplets $^3T_1, ^3T_2$. The low lying energies belonging to the ground Coulomb configuration are formed by the set of states for which the electrons occupy remote sites and the two-electron jumps (transfer parameter $P$) keep the maximal distance between the sites of localization. The energy levels in terms of the bi-electron transfer parameter $P$ are found as:

\[
\begin{align*}
\epsilon(^1A_1) &= 4P, \\
\epsilon(^3T_2) &= 2P, \\
\epsilon(^3T_1) &= \epsilon(^1E) = -2P.
\end{align*}
\]

More common consideration and a more detailed scheme of the levels with the due account for the one-electron transfer processes are given in ref. [13a] and the conditions were elucidated under which spin pairing can occur as a result of competition between the single- and double electron transfer processes and depends also on the interelectronic interaction.

It was emphasized [13c] that the conditions under which the system proves to be antiferromagnetic are strongly affected by the vibronic interactions that tends to localize the electrons and thus effectively reduce the transfer parameters. The degrees of localization prove to be different for the spin-triplet and spin-singlet states that essentially influence the magnetic properties of the reduced Keggin anion. The doubly degenerate ($e$) and triply degenerate vibrations ($t_2$) are found to be active [8a] and hence the potential surfaces are determined by the JT/pseudo JT interactions of the types of $(^1T_2+^3E+^1A_1)\otimes(e+t_2)$ for the spin singlets and $(^3T_1+^3T_2)\otimes(e+t_2)$ for the spin triplets. The adiabatic approximation [13c] provides information about the symmetry of the localized configurations of the electronic pair but it is unable to describe the magnetic characteristics and profiles of the intervalence optical bands for which the quantum structure of the excited vibronic levels is crucially important.

![Pictorial representation of the $E$ and $T_2$ PKS vibrations (one component for each type) in Keggin polyoxoanion; large and small circles symbolize expanded and compressed octahedral sites, intermediate size circles denote undistorted units.](Fig. 2)

It is worthwhile to use the Piepho, Krausz and Schatz (PKS) model [16] that deals with the independent “breathing” displacements of the ions around the sites. Within the PKS model the frequencies of $T_2$ and $E$ vibrations (their pictorial representation is given in Fig. 2) are equal since they simply represent the frequencies of the local “breathing” mode and therefore the electronic system is effectively coupled to a five-dimensional oscillator for which the dimension of the vibrational space $G(N)$ can be found as:

\[
\ldots
\]
\[ G(N) = (1/120) (N + 1) (N + 2) (N + 3) (N + 4) (N + 5), \] (5)

where \( n = n_1 + n_2 + n_3 + n_4 + n_5 \) is the total number of excitation of the five-dimensional harmonic oscillator (label of the energy level), the expression under summation is the total degeneracy of the level with a given \( n \) and \( N \) is the number of the levels included in the basis. The total degeneracy of the electron-vibrational space for spin-singlets is \( 6G(N) \) and the same for spin-triplets, which leads to a very high dimension of the vibronic matrices. At the same time one can see that even a relatively small number of the vibronic levels involved in the evaluation results in a huge size of the matrices in the multimode systems demonstrating thus a necessity of the efficient use of symmetry.

5. Group-theoretical classification for the two- and three-dimensional oscillators

To adapt the vibrational functions to the definite irreps let us first consider the case of a two-dimensional (E) harmonic oscillator. The basis of the irrep \( E \) in \( T_d \) will be chosen in a standard way:

\[ u \propto 3z^2 - r^2, \quad v \propto \sqrt{3} (x^2 - y^2) \] [18]. The functions \( \{ n_u n_v \} \) can be built as:

\[ |n_u n_v\rangle = (n_u^1 n_v^1 !)^{1/2} (b_u^n)^{n_u} (b_v^n)^{n_v} |00\rangle. \] (6)

Each level with a certain \( n = n_u + n_v \) is \( g = (n + 1) \)-fold degenerate. Before evaluation of the symmetry adapted functions it is worthwhile to classify the resulting irreps for each \( n \) and therefore to find the allowed states. Using correlation between the angular momentum representation for a two-dimensional oscillator [19] and the point group irreps [20-24], one can reach this goal. The results are summarized in Table 1.

| \( n \) | \( g(n) \) | vib. irreps | \( n \) | \( g(n) \) | vib. irreps |
|---|---|---|---|---|---|
| 1 | 2 | \( E \) | 3 | 4 | \( A_1 + A_2 + E \) |
| 2 | 3 | \( A_1 + E \) | 4 | 5 | \( A_1 + 2E \) |

Table 2. Group-theoretical classification of the vibrational states for \( T_2 \) vibrations in \( T_d \)

| \( n \) | \( g(n) \) | vibrational irreps |
|---|---|---|
| 0 | 1 | \( A_1 \) |
| 1 | 3 | \( T_2 \) |
| 2 | 6 | \( A_1, E, T_2 \) |
| 3 | 10 | \( A_1, T_1, 2T_2 \) |
| 4 | 15 | \( 2A_1; 2E, T_1, 2T_2 \) |

The functions of the three-dimensional oscillator \( \{ n_x n_y n_z \} \) in the standard \( T_2 \) basis \( \xi \propto yz, \eta \propto xz, \zeta \propto xy \) for \( T_d \) [18] can be built as:

\[ |n_x n_y n_z\rangle = (n_x^1 n_y^1 n_z^1 !)^{1/2} (b_\xi^n)^{n_x} (b_\eta^n)^{n_y} (b_\zeta^n)^{n_z} |000\rangle. \] (7)
Each level with a given \( n = n_\zeta + n_\eta + n_\xi \) is \( g(n) = (1/2)(n+1)(n+2) \)-fold degenerate. The set of the vibrational states with a given \( n \) can be correlated with a certain value of the angular orbital momentum \( l \) and parity \((-1)^l\) where \( l = 0, 2 \ldots n \) for even \( n \) and \( l = 1, 3 \ldots n \) for odd \( n \) [32]. Then classifying these states one obtains the results listed in Table 2.

6. Symmetry adapted vibrational basis

To create vibrational function \( |n, \Gamma \gamma \rangle \times E \) with a given \( n \) let us introduce the symmetry adapted operators \( T_{n \gamma}^{(n)} \) constructed from operators \( \left( b^+_u \right)^{n_u} \left( b^+_v \right)^{n_v} \) with definite \( n = n_u + n_v \), where \( \Gamma \) is one the irreps \( \left( \Gamma = A_1, A_2, E \right) \) corresponding to the set of the vibrational functions belonging the energy level \( n \). By definition the operator \( T_{n \gamma}^{(n)} \) acts on the vacuum state \( |00\rangle \equiv |n_u = 0, n_v = 0\rangle \) and creates a basis function of the type of \( \Gamma \gamma \) belonging to a certain excited vibrational state \( n \):

\[
T_{n \gamma}^{(n)} |00\rangle = |n, \Gamma \gamma \rangle.
\] (8)

The operators \( T_{n \gamma}^{(n)} \) realize the unitary transformation from the basis \( |n, \nu \Gamma \gamma \rangle \) with a certain \( n \) to the symmetry adapted basis \( |n, \nu \gamma \Gamma \rangle \) where \( \nu \) is a quantum number that distinguishes the states of the system for which an irrep \( \Gamma \) occurs several times in the set \( n \). We will refer \( T_{n \gamma}^{(n)} \) to as multivibronic symmetry adapted creation operators that can be considered as irreducible tensor operators of the type \( \Gamma \gamma \) in the actual point group. This allows one to build up the multivibronic operators with the use of the technique for the manipulation with the irreducible tensor operators in the point groups introduced by Sugano, Tanabe and Kamimura [18] (see refs. [20-22]). For example \( T_{1 \gamma}^{(2)} \) can be found as the irreducible parts of the direct product by the use of the coupling scheme:

\[
\hat{T}_{\Gamma \gamma}^{(2)} = \sum_{\gamma, \gamma_1, \gamma_2} b_{\Gamma_1 \gamma_1}^+ b_{\Gamma_2 \gamma_2}^+ |\Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle \langle \Gamma \gamma \rangle = \left\{ b_{\Gamma_1}^+ \otimes b_{\Gamma_2}^+ \right\} |\Gamma \gamma \rangle, \quad \Gamma \in \Gamma_1 \times \Gamma_2
\] (9)

The coupling (Clebsch-Gordan) coefficients \( \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle \Gamma \gamma \rangle \) for all point groups are given by Koster et al [21]. In the case of \( E \) vibrations Eq. (9) gives the following result:

\[
\hat{T}_{A_1}^{(2)} = \frac{1}{\sqrt{2}} \left\{ b_u^+ \right\}^2 + \left\{ b_v^+ \right\}^2, \quad \hat{T}_{A_2}^{(2)} = 0.
\] (10)

\[
\hat{T}_{E_\nu}^{(2)} = -\frac{1}{\sqrt{2}} \left\{ b_u^+ \right\}^2 - \left\{ b_v^+ \right\}^2, \quad \hat{T}_{E_D}^{(2)} = \sqrt{2} \left\{ b_u^+ b_v^+ \right\} E
\]

One can see that the operator \( T_{A_2}^{(2)} \) corresponding to the antisymmetric part \( \{ E \times E \} \) of the direct product \( E \times E \) vanishes in the case of \( n = 1 \) so that the full dimension of the obtained basis is \( g(n) = n + 1 = 3 \). Applying operators \( T_{n \gamma}^{(2)} \) to the vacuum state \( T_{n \gamma}^{(2)} |00\rangle = |2, \Gamma \gamma \rangle \) one obtains the three-dimensional vibrational basis for \( n = 2 \) with \( \Gamma = A_1, E \). Then one has to build the operators \( T_{n \gamma}^{(3)} \) applying the subsequent step of the coupling procedure:
\[
\hat{T}^{(3)}_{\gamma\gamma} = \left\{ \left\{ b_{1,2}^+ \otimes b_{1,2}^+ \right\}_{\Gamma_{12}} \otimes b_{1,3}^+ \right\}_{\Gamma_{12}\gamma_{12}} \left\{ b_{1,2}^+ \otimes b_{1,3}^+ \right\}_{\Gamma_{12}\gamma_{12}} b_{1,3}^+ \left( \Gamma_{12}\gamma_{12} \Gamma_{3}\gamma_{3} \right| \Gamma_{3} \gamma_{3} \right),
\]

(11)

In general the obtained vectors are linearly independent and therefore each step should be supplemented by the Gram-Schmidt orthogonalization within the repeated irreps that takes an arbitrary basis and generates a new orthogonal one excluding thus excessive functions. It should be noted that \(u\)-components of all \(E\) bases are automatically orthogonal to the \(\nu\)-components, and, of course, the orthogonality remains between different irreps and between the functions from the sets arising from different \(n\). Due to this fact the Gram-Schmidt orthogonalization procedure is to be applied only to the corresponding basis functions of the same irreps (let’s say, to the \(u\) type functions belonging to the \(E\) bases) with the same \(n\).

For the three-dimensional oscillator the multivibrionic operators \(T^{(n)}_{\Gamma\gamma}\) are constructed from the products \(\hat{b}_{\gamma}^+ \hat{b}_{\gamma}^+ \hat{b}_{\gamma}^+\) with a definite \(n = n_{\xi} + n_{\eta} + n_{\zeta}\) and with \(\Gamma\) being one the irreps of \(T_{d} (A_{1}, A_{2}, E, T_{1}, T_{2})\) corresponding to the set of the vibrational function belonging to definite \(n\).

The general expressions for \(T^{(2)}_{\Gamma\gamma}, T^{(3)}_{\Gamma\gamma}\), etc. can be found as in previous case. For example, one obtains the following result for the \(T^{(2)}_{\Gamma\gamma}\) operators:

\[
\hat{T}^{(2)}_{A_{1}} = \frac{1}{\sqrt{3}} \left( b_{\xi}^+ b_{\xi}^+ + b_{\eta}^+ b_{\eta}^+ + b_{\zeta}^+ b_{\zeta}^+ \right),
\]

\[
\hat{T}^{(2)}_{E_{\xi\xi}} = \frac{1}{\sqrt{6}} \left( -b_{\xi}^+ b_{\xi}^+ - b_{\eta}^+ b_{\eta}^+ + b_{\zeta}^+ b_{\zeta}^+ \right),
\]

\[
\hat{T}^{(2)}_{E_{\eta\eta}} = \frac{1}{\sqrt{2}} \left( b_{\xi}^+ b_{\xi}^+ - b_{\eta}^+ b_{\eta}^+ \right),
\]

(12)

From the direct product of \(\Gamma (n = 2) \times T_{2}\) one finds the following irreps forming the 18-dimensional space for \(n = 3\): \(\left(A_{1} + E + T_{1}\right) \times T_{2} = T_{1} + T_{2} + \left(T_{1} + T_{2}\right) + \left(A_{1} + E + T_{1} + T_{2}\right) = A_{1} + E + 2T_{1} + 3T_{2}\). By comparing these irreps with those predicted by the group-theoretical assignation \((A_{1}, T_{1}, 2T_{2})\) one can conclude that this 18-dimensional space contains linearly dependent vectors and therefore, beginning from this step, the Gram-Schmidt procedure of orthogonalization is to be applied. The next steps are quite similar to those so far described.

7. Symmetry adapted electron-vibrational basis

The evaluation of the vibrational basis for each type of the active modes can be extended to an arbitrary value of \(n\) by the application of the multivibrionic operator of the order \(n\) to the vacuum state with the subsequent Gram-Schmidt procedure at each step \(n\) as described in [3d]. The operator \(T^{(n)}_{\Gamma\gamma}\) can be built by extending the consequent coupling procedure to the order \(n:\)

\[
\hat{T}^{(n)}_{\Gamma\gamma} = \left\{ \left\{ \left\{ b_{1,2}^+ \otimes b_{1,2}^+ \right\}_{\Gamma_{12}} \otimes b_{1,3}^+ \right\}_{\Gamma_{12}\gamma_{12}} \otimes \left\{ b_{1,3}^+ \otimes b_{1,3}^+ \right\}_{\Gamma_{12}\gamma_{12}} \right\}_{\Gamma_{12}\gamma_{12}} \left\{ b_{1,3}^+ \otimes b_{1,3}^+ \right\}_{\Gamma_{12}\gamma_{12}} \left( \Gamma_{12}\gamma_{12} \Gamma_{3}\gamma_{3} \right| \Gamma_{3} \gamma_{3} \right),
\]

(13)

\(\Gamma_{12} \in \Gamma_{1} \times \Gamma_{2}, \quad \Gamma_{123} \in \Gamma_{1} \times \Gamma_{2} \times \Gamma_{3}, \quad \Gamma \in \Gamma_{n-1} \times \Gamma_{n}\).

Then the vibrational functions for the active vibrations can be combined to get the total vibrational basis with the given symmetry. For example, for the two basis sets \(|n_{1}, \nu_{1} \Gamma_{1}\gamma_{1}\rangle\) and \(|n_{2}, \nu_{2} \Gamma_{2}\gamma_{2}\rangle\) one
can directly use the coupling scheme, Eq.(13), within which one obtains the symmetry adapted vibrational functions $\left\{ n, \nu \Gamma_{\nu} \right\}$ ($n = n_1 + n_2, \Gamma_\nu \in \Gamma_1 \times \Gamma_2$). Finally, the vibrational functions $\left\{ n, \nu \Gamma_{\nu} \right\}$ are to be coupled to the electronic ones $\left\{ \alpha \Gamma_{\alpha}, SM \right\}$ that are eigen-functions of the Hamiltonian $H_e$ included in the JT/pseudo JT problem ($SM$ are the quantum numbers of the full spin and its projection, $\alpha$ is the additional quantum number that enumerated the repeated irreps $\Gamma_\alpha$).

This allows to achieve the final goal of the approach, namely to evaluate the basis in which the full matrix of the JT Hamiltonian is blocked according to the irreps of the point group. Finally, the approach is realized as an efficient computer program [15] that generates the blocks and evaluates required characteristics of the JT systems, like optical spectra, thermodynamic characteristics, etc. The procedure generates the basis assuming only point symmetry of the system without indication of the explicit form of the vibronic coupling, so it is not restricted by the linear terms of vibronic interactions and applicable also when the quadratic and higher order terms are taken into account. Under this condition the approaches based on high symmetries lose their advantages because the actual symmetry is reduced to the point one.

8. Dynamic Jahn-Teller problem for the 2e-reduced Keggin anion

The size of the vibronic matrices $6G(N)$ for the $(^1T_2 + ^1E + ^1A_1) \otimes (e + t_2)$ and $(^3T_1 + ^3T_2) \otimes (e + t_2)$ combined JT/pseudo JT problems in MV Keggin anion is rather large, for example, for $N=10, 11, 12$ the sizes of the matrices are 18018, 26208 and 37128 for spin-singlets and the same dimensionalities for spin-triplets. The sizes of the matrices grow rapidly with the increase of $N$ (Eq. (5)). Table 2 shows the sizes of the blocks (related to different irreps) of the full vibronic matrices for spin-singlet and spin-triplet states. One can see that full exploration of the symmetry essentially simplifies the vibronic problem. In fact, for $N=12$ the full sizes of the vibronic matrices (for $S=1$ and $S=0$) are 37128 while the maximal size of the reduced matrix proves to be only 4676 (for $T_2$ levels in spin-singlets and spin-triplets sets).

![Fig. 3. Calculated vibronic levels for spin-singlet (a) and spin-triplets (b) terms belonging to the ground manifold of the 2e-reduced Keggin anion.](image)

Fig. 3 shows a sample of the vibronic levels for spin-singlet (Fig. 3a) and spin-triplets (Fig. 3b) terms calculated for a rather narrow basis set ($N=8$). At $P=0$ one obtains the electronic levels superimposed
with the unperturbed harmonic oscillator levels. The level $^1A_1$ which is the ground state of spin paired system, is chosen as a reference level for both patterns in Fig. 3. When the vibronic coupling increases the excited levels approach the ground level that corresponds to the multiple degenerate states in the deep wells of the adiabatic potential. Comparing Figs. 3a and 3b one can see that at the same time increase of the PKS coupling decrease the gap between the ground spin-singlet vibronic level $^1A_1$ (Fig. 3a) and the excited spin-triplet level $^3T_2$ (which is the ground level in spin-triplet pattern, Fig. 3b). This leads to the effective increase of the magnetic moment of the system that can be considered as a result of the JT/pseudo JT coupling. From the point of view of the JT theory this is a manifestation of the reduction of efficiency of the electron transfer (Ham effect).

### 9. Concluding remarks

We have presented a theoretical approach to obtain an accurate solution of the electronic and dynamic JT/pseudo JT problems in large scale MV systems. We have shown how to solve the double exchange problem for high-nuclearity MV clusters containing arbitrary number of itinerant electrons shared among arbitrary number of magnetic sites. The algorithm applied to the vibronic problem takes full advantage of the point symmetry arguments and thus allows to reduce the vibronic matrices to full extent. The group-theoretical assignment of the vibronic states allows to predict the symmetry labels for the vibronic levels in advance and thus to get an additional gain in the computational work. This approach is applicable to an arbitrary form of the vibronic coupling, including linear and high order terms. The approach is illustrated by consideration of the 2e-reduced MV dodecanuclear Keggin anion ($T_d$) in which the electronic pair is delocalized over twelve metal sites giving rise (within PKS model) to the ($^1T_2$+$^1E$+$^1A_1$)$\otimes (e+t_2)$ and ($^3T_1$+$^3T_2$)$\otimes (e+t_2)$ combined JT/pseudo JT problems for the spin-singlet and spin-triplet states, correspondingly. The vibronic interaction is shown to increase the magnetic moment of such kind of systems due to partial localization of the electronic pair giving rise to reduction of the electron transfer. The results so far described are expected to open a route to a new level of accuracy in the consideration of large MV systems and to increase the size of the JT systems that can be treated.

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