

Research:

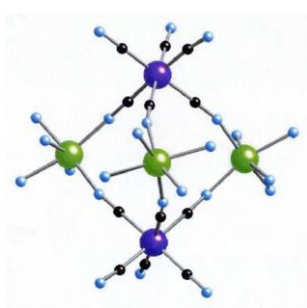
I. Molecular magnetism and single-molecule magnets

The research in the area of molecular magnetism is focused on molecular assemblies containing a finite number of exchange coupled magnetic ions (metal clusters). These kind of molecular nanomagnets, so-called single molecule magnets (SMMs) can be placed on the border line between the object of quantum and classical physics. Indeed, from one side they show slow relaxation of magnetization and magnetic hysteresis as a bulk magnet and on the other side they are still small enough to show important quantum effects.

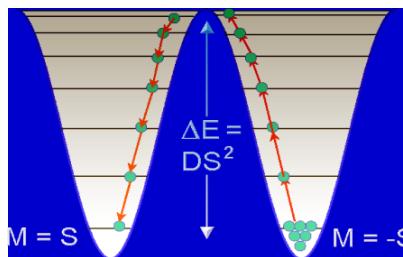
The main topics of research: molecular magnetic materials, SMMs exhibiting magnetic bistability and quantum tunneling of magnetization that is expected to allow to use them as the memory storage of molecular size and quantum bits of information (qubits).

1. Exchange interactions in molecule-based materials

Elaboration of the general approach to the problem of the orbitally-dependent kinetic exchange and its application to the interpretation of the magnetic behavior of compounds comprising metal

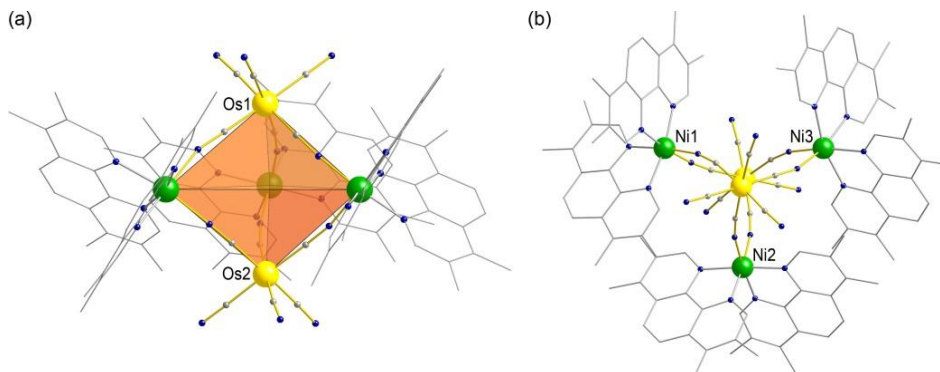


Mn₅-cyanometalate fragment



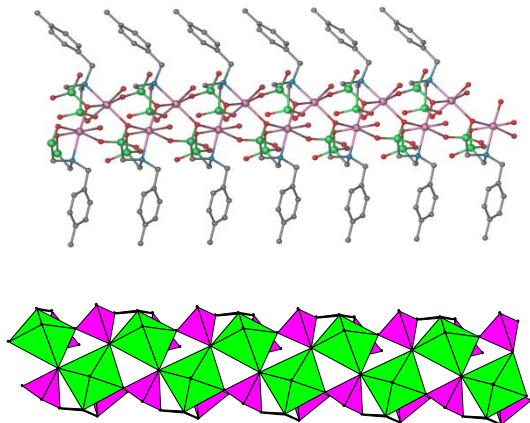
Scheme for the magnetic bistability in a SMM

ions with unquenched orbital angular momenta. Under the condition of orbital degeneracy the conventional Heisenberg-Dirac-Van Vleck model is inapplicable and the theoretical approach is based on the developed orbitally dependent exchange Hamiltonian. Exchange interaction in these compounds is strongly anisotropic and therefore they are shown to exhibit a higher barrier for the

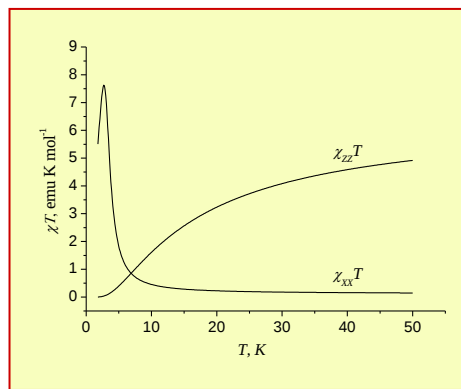


Molecular structure of the Ni^{II}₃Os^{III}₂ complex: (a) a side view emphasizing the NiN₆ and OsC₆ coordination environments; (b) a view along the axis of the trigonal bipyramid Color scheme: Ni = green; Os = yellow; N = blue; C = gray.

reversal of magnetization. The main factors controlling the magnetic anisotropy in SMMs, are studied: magnetic bistability in Mn_5 based SMMs, barrier for the reversal of magnetization in the octanuclear $\text{Re(II)}_4 \text{Mn(II)}_4$ cluster exhibiting SMM behavior, $\text{Ni}^{\text{II}}_3\text{Os}^{\text{III}}_2$ complex (Kramers doublet problem).

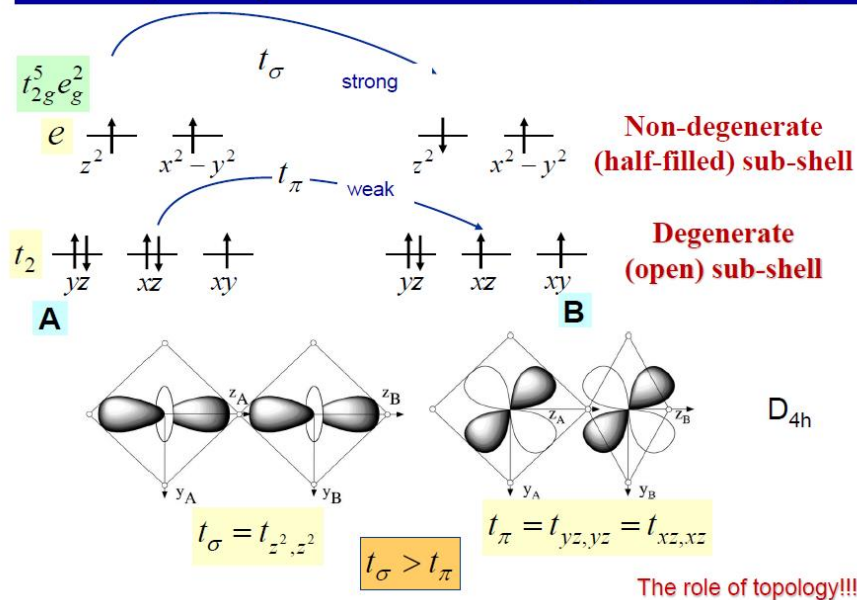


A highly anisotropic Cobalt (II) based Single Chain Magnet



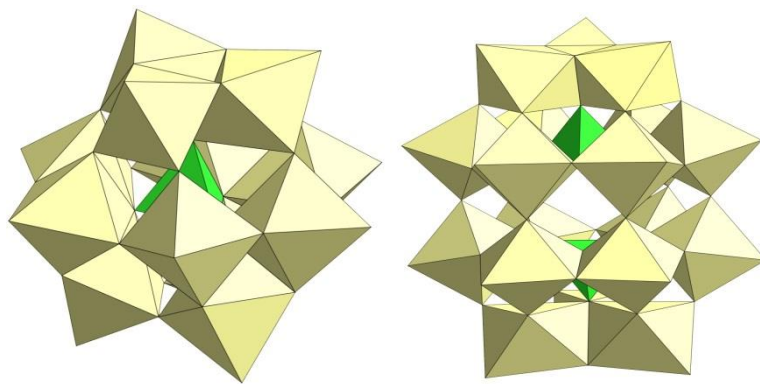
Calculated magnetic susceptibility

Transfer pathways in the kinetic exchange in a Co (II) pair

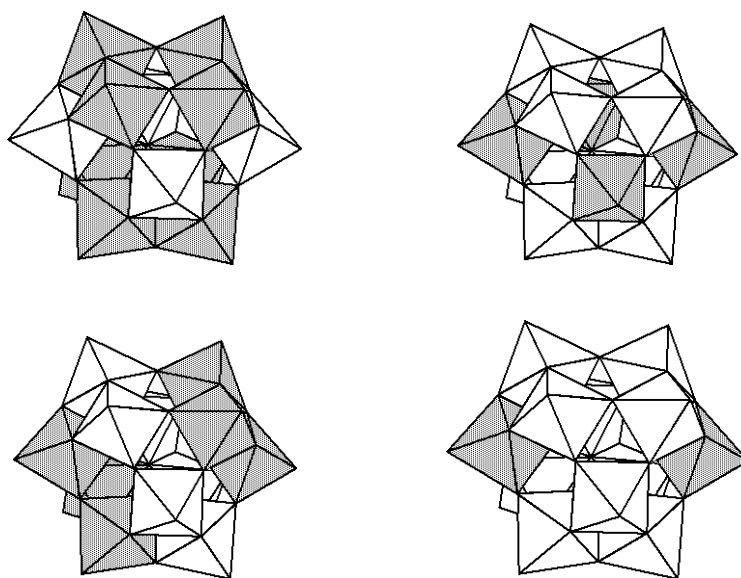


2. Mixed valence and double exchange in metal clusters

Development of the microscopic electronic theory of mixed valency (MV) and double exchange, elaboration of the efficient approach to the evaluation of the energy pattern and



Two-electron-reduced polyoxoanions with Keggin and Wells-Dawson structures

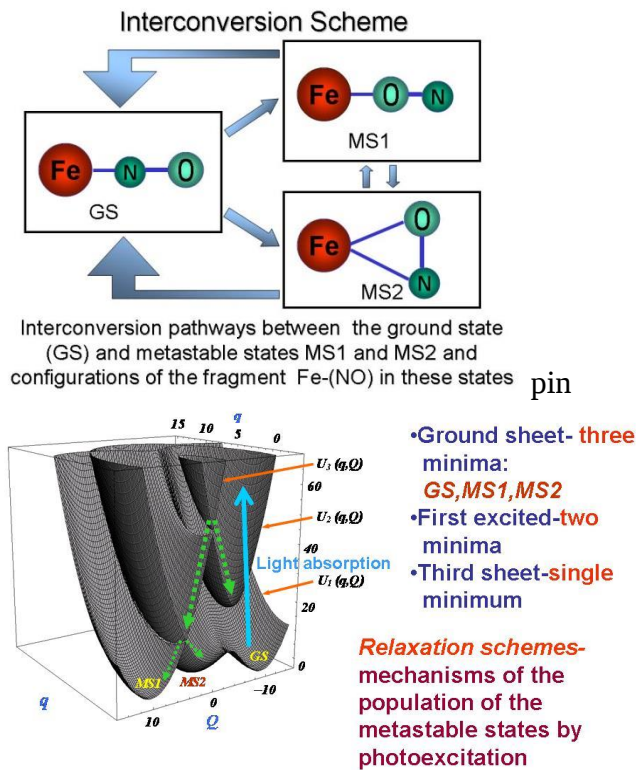


Possible types of the vibronic localization in the “broken symmetry states” of the electronic pair in the Keggin structure

magnetic properties of complex polynuclear MV metal clusters (iron-sulfur clusters, two-electron-reduced polyoxoanions with Keggin and Wells-Dawson structures, diphtalocyanine based MV chains). Anisotropic double exchange in orbitally degenerate MV clusters. Vibronic approach to the problem of localization-delocalization phenomenon and hyperfine interactions in MV clusters.

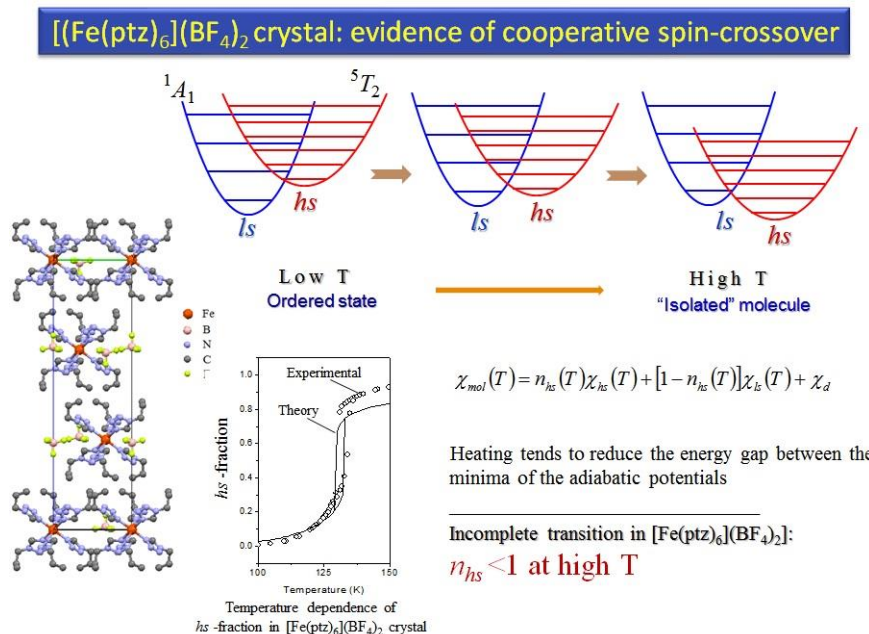
3. Cooperative and photochromic phenomena in molecule based systems

Mixed MV crystals: charge and structural ordering, thermodynamic properties, optical charge transfer bands, Mössbauer spectra in localized/delocalized states. A new model for the photochromic effect in sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ based on the concept of the pseudo-Jahn-Teller effect is proposed. The model takes into account the electron transfer from the Fe^{2+} ion to the π^* orbitals of the NO-ligand as well as the vibronic mixing of three electronic states of the Fe-NO fragment through the non-symmetric and full symmetric modes.



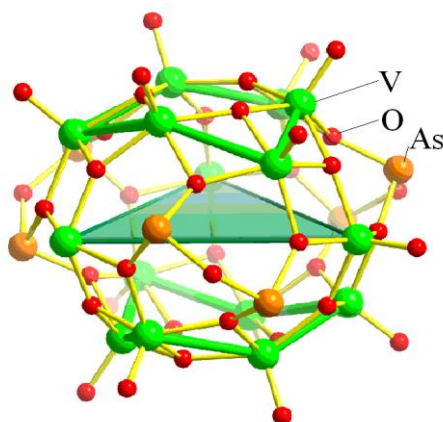
Under certain conditions the lower sheet of the adiabatic potential is shown to possess three minima with the increasing energies that correspond to the N-bound, sideways bound and O-bound NO group. The excited minima are attributed to the MS2 and MS1 metastable states observed experimentally.

Vibronic approach to the spin-crossover phenomenon

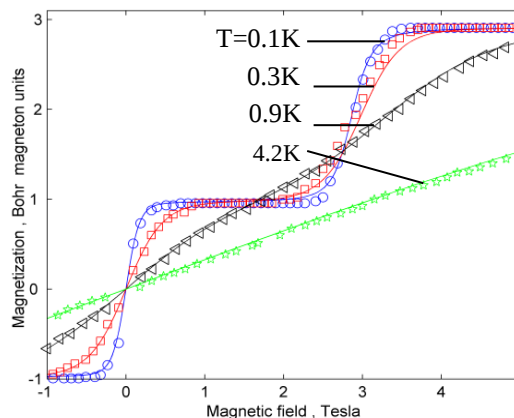


4. Magnetic anisotropy of spin-frustrated systems, Rabi oscillations

The study is mainly focused on the famous nanoscopic V_{15} cluster (Fig.3) and on the general analysis of the concept of spin frustration in high-nuclearity magnetic clusters. The ground state of this system was proved to be orbitally degenerate and therefore the spin-orbital interaction acts as a first order perturbation. The antisymmetric (AS) exchange gives rise to a strong magnetic anisotropy and acts as a source for the zero-field splitting.

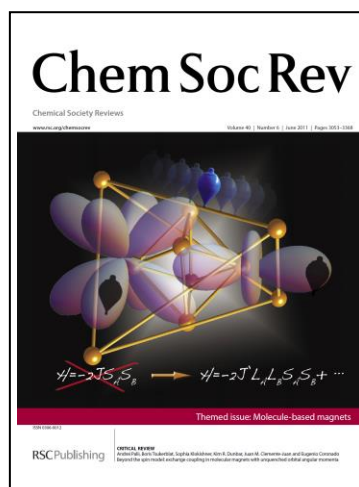
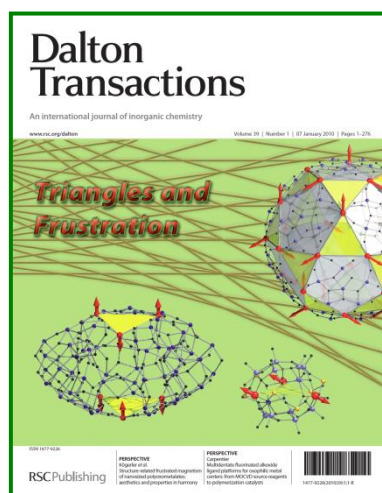


Structure of V_{15} cluster



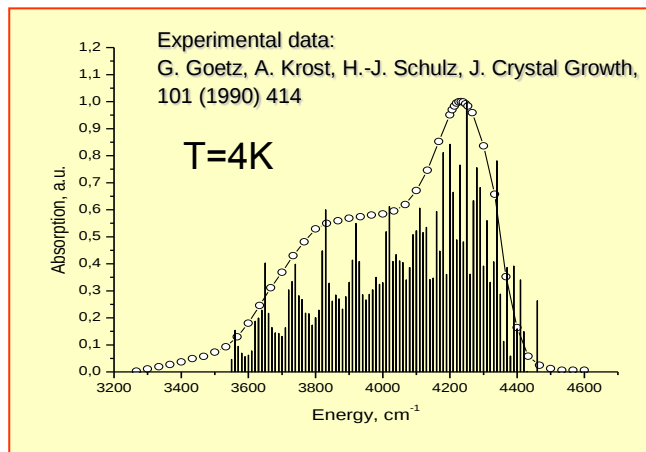
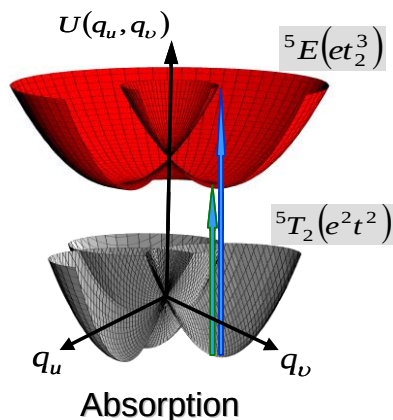
Static stepwise magnetization of V_{15}
(theory vs experiment)

The shapes of the steps in magnetization reflect the magnetic anisotropy caused by the AS exchange. Spin-frustration inherently related to the orbital degeneracy creates a structural instability that is shown to be antagonistic to the AS exchange. The pseudo Jahn-Teller is shown to reduce AS exchange giving rise to the restoration of magnetic anisotropy quenched by AS exchange.



II. Vibronic interactions and Jahn-Teller effect in molecules and crystals. Spectroscopy of transition metal complexes and impurity centers in doped crystals

1. **A model of the Jahn-Teller impurity** ion in crystal is suggested. The theory of polarization dichroism spectra based on the new approach to the moments method was developed. Linear stress and magnetic circular dichroism spectra are considered in detail for F-centers and transition metal ions in crystals.



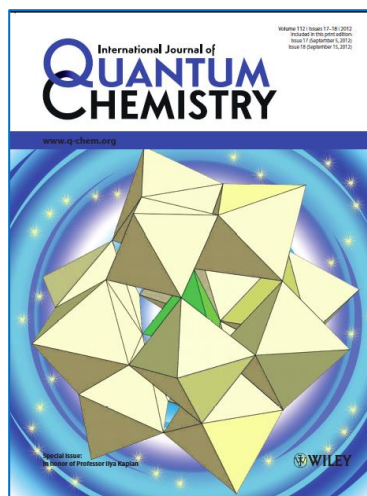
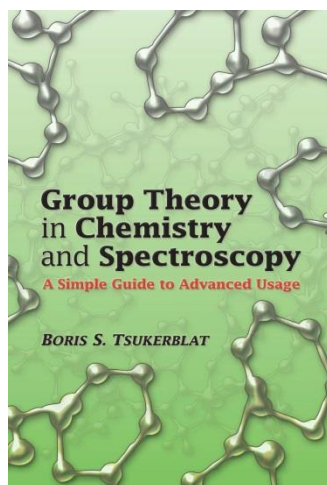
Jahn-Teller effect in a Cr(II) impurity of the tetrahedral symmetry, calculated phonon-assisted optical absorption band in CdSe-Cr(II) crystals (fine structure of the vibronic levels and the enveloping curve) and experimental data.

This approach is shown to provide an efficient tool for the study of the Jahn-Teller effect by means of spectroscopic methods. A new approach (independent ordering approximation) for the calculation of the optical bands shape in the Jahn-Teller centers was developed. Optical bands of Jahn-Teller ions and small radius excitons are investigated. Specific case of quadratic (Renner-type) vibronic interaction is considered. The theory of multiphonon non-radiative transitions and energy transfer processes in Jahn-Teller systems is formulated. Theory was applied to the first laser material, chromium ion in ruby (multiphonon bands, zero-phonon lines, non-radiative transitions) and rare-earth ions in crystals. A pseudo-Jahn-Teller dynamic vibronic model dealing with the hybrid electron-vibrational states is proposed for the excited states of CdIn₂S₄-Cr(III) and CdSe-Cr(II) crystals widely used as the infrared tunable lasers. The model provides a good explanation of the absorption and luminescence band shapes and anomalous decay life-times that is crucially important for the rational design of the new infrared media.

III. Group theory with application to molecular magnetism and Jahn-Teller effect, computational approaches

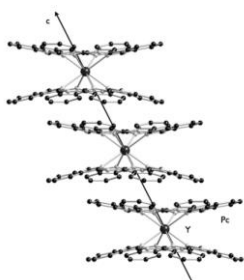
1. **A general group-theoretical approach was developed for the analysis of spin-orbital multiplets of polynuclear multielectron exchange clusters.** On the base of the group-theoretical method (B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy*, Dover Pub., Mineola-NY, 2006) "accidental" degeneracies of spin states in the Heisenberg-Dirac-Van Vleck model are

investigated and the theory of non-Heisenberg exchange interactions was developed on the basis of the irreducible tensor operators (ITO) approach. A MAGPACK software, A Package to Calculate the Energy Levels, Bulk Magnetic Properties, and Inelastic Neutron Scattering Spectra of High

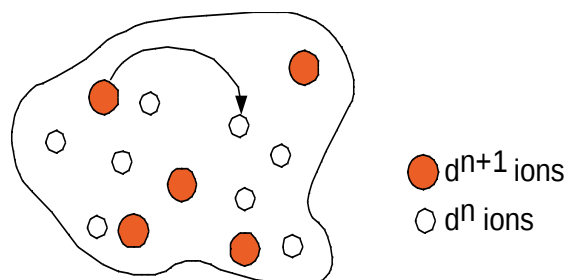


Nuclearity Spin Clusters based on the use of the ITO technique is designed and distributed (on request) in the molecular magnetism society. MAGPACK is an efficient tool to evaluate magnetic properties and inelastic neutron scattering cross-section in the exchange magnetic cluster with the due account for all kinds of isotropic and anisotropic exchange interactions.

2. **A general approach to the problem of electron delocalization in the high-nuclearity (nanosize) mixed-valence clusters** containing an arbitrary number of localized spins and itinerant electrons is developed. Along with the double exchange, we consider the isotropic magnetic exchange between the localized electrons as well as the Coulomb intercenter repulsion. Taking full advantage of the powerful angular momentum technique, we were have derived closed form analytical expressions for the matrix elements of the full Hamiltonian. These expressions provide an efficient tool for treating complex mixed-valence systems, because they contain only products of $6j$ -symbols and $9j$ -symbols and do not contain high-order recoupling coefficients and $3j$ -symbols that essentially constrained all previous theories of mixed valency. The approach developed here is accompanied by an efficient computational procedure that allows us to calculate the bulk thermodynamic properties (magnetic susceptibility, magnetization, and magnetic specific heat) of high-nuclearity MV clusters.



Stacking of diphthalocyanine units in $[Y\text{Pc}_2] \cdot \text{CH}_2\text{Cl}_2$ compound localized



Scheme of MV system containing arbitrary numbers of the spins and itinerant electrons

Finally, this approach has been used to discuss the magnetic properties of the octanuclear MV cluster $[\text{Fe}_8(\mu_4\text{-O})_4(4\text{-Cl-pz})_{12}\text{Cl}_4]^-$ and the diphthalocyanine chains $[\text{YPc}_2] \cdot \text{CH}_2\text{Cl}_2$ and $[\text{ScPc}_2] \cdot \text{CH}_2\text{Cl}_2$ composed of MV dimers interacting through the magnetic exchange and Coulomb repulsion.

3. A symmetry adapted approach to the dynamic Jahn-Teller problem aimed to the accurate solution of the dynamic vibronic problem in large scale Jahn-Teller systems was developed. The algorithm for the solution of the eigen-problem takes full advantage of the point symmetry arguments. The system under consideration is supposed to consist of a set of electronic levels mixed by the active Jahn-Teller and pseudo Jahn-Teller vibrational modes. Applying the successive coupling of the bosonic creation operators, we introduce the irreducible tensors that are called multivibronic operators. Action of the irreducible multivibronic operators on the vacuum state creates the vibrational symmetry adapted basis that is subjected to the Gram-Schmidt orthogonalization at each step of evaluation. Finally, the generated vibrational basis is coupled to

Simplification of the vibronic matrices for a double reduced Keggin anion

Dimension of the basis:

$$N = 12 \rightarrow G = 37128$$

Dimensions of the reduced matrices

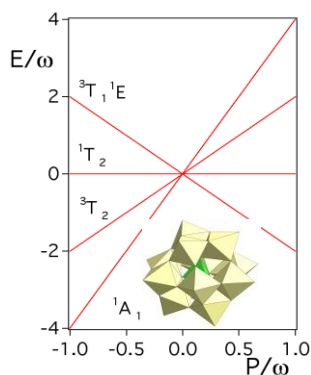
$$({}^1T_2 + {}^1E + {}^1A_1) \otimes (e + t_2)$$

$$({}^3T_1 + {}^3T_2) \otimes (e + t_2)$$

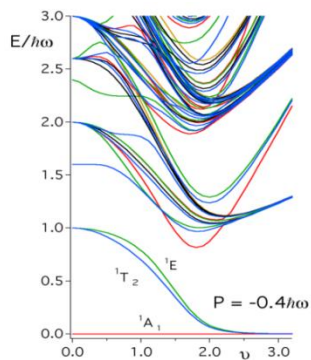
N	Spin singlets					Spin triplets				
	A ₁	A ₂	E	T ₁	T ₂	A ₁	A ₂	E	T ₁	T ₂
12	1652	1512	3164	4536	4676	1512	1512	3024	4676	4676

the electronic one to get the symmetry adapted electron-vibrational (vibronic) basis within which the full matrix of the Jahn-Teller Hamiltonian is blocked according to the irreducible representations (irreps) of the point group. The proposed approach is a part of our study of the nanosized mixed valence (MV) clusters with large number of delocalized electrons that are at the border line between quantum and classical objects.

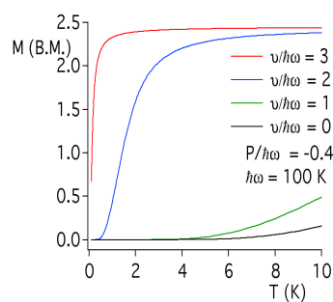
We illustrate in detail the developed technique by the application to the 2e-reduced MV dodecanuclear Keggin anion in which the electronic pair is delocalized over twelve sites (overall symmetry T_d) giving rise to the $({}^1T_2 + {}^1E + {}^1A_1) \otimes (e + t_2)$ $({}^3T_1 + {}^3T_2) \otimes (e + t_2)$ combined Jahn-Teller /pseudo Jahn-Teller problems for the spin-singlet and spin-triplet states. The symmetry based approach allows to essentially reduce the Hilbert space and to make the tractable the problem of the evaluation of the energy levels and intervalence optical bands.



Electronic energy levels of the 2e-reduced Keggin polyanion



Electron-vibrational energy levels of the 2e-reduced Keggin polyanion



Magnetic moments, effect of the vibronic localization

Nanosized metal clusters: the theoretical tools in hands

MAGPACK, spin levels, localized electrons/spins

- J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, B. Tsukerblat, **High-Nuclearity Magnetic Clusters: Generalized Spin Hamiltonian and Its Use for the Calculation of the Energy Levels, Bulk Magnetic Properties, and Inelastic Neutron Scattering Spectra**, *Inorg. Chemistry*, 38 (1999) 6081.
- J.M. Clemente-Juan, J.J. Borrás-Almenar, E. Coronado, A. Pali, B. Tsukerblat, **MAGPACK: a package to calculate the energy levels, bulk magnetic properties and INS spectra of high nuclearity spin clusters**, *J. Comput. Chemistry*, 22 (2001) 985.

MVPACK, mixed valence systems- electronic levels

- J. M. Clemente-Juan, J. J. Borrás-Almenar, E. Coronado, A. V. Pali, B.S. Tsukerblat, **High-Nuclearity Mixed Valence Clusters and Mixed Valence Chains: General Approach to the Calculation of the Energy Levels and Bulk Magnetic Properties**, *Inorg. Chemistry*, 48 (2009) 4557.
- J.M. Clemente-Juan, J.J. Borrás-Almenar, E. Coronado, A. Pali, B. Tsukerblat, **MVPACK: a package to calculate energy levels and magnetic properties of high nuclearity mixed valence clusters**, *J. Comput. Chemistry*, 31 (2010) 1321.

MV-VIB, mixed valence systems-vibronic levels

- B. Tsukerblat, A. Pali, J.M. Clemente-Juan, A. Gaita-Ariño, E. Coronado, **A Symmetry Adapted Approach to the Dynamic Jahn-Teller Problem: Application to Mixed-Valence Polyoxometalate Clusters with Keggin Structure**, *Int. J. Quantum Chemistry*, 112 (2012) 2957.