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# Magnetic exchange interaction in clusters of orbitally degenerate ions. I. Effective Hamiltonian

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## Abstract

A new effective Hamiltonian is reported for the kinetic exchange between two arbitrary terms  $^{2S_A+1}\Lambda_A$  and  $^{2S_B+1}\Lambda_B$  that can be ground or excited in octahedrally coordinated transition metal ions. This Hamiltonian is applicable to both homo- and heterometallic clusters. For the homonuclear cluster the resonance part of the effective Hamiltonian is also presented for the case when one of the ions is excited. The operator part of the exchange Hamiltonian contains symmetry adapted products of the cubic irreducible tensors acting in orbital spaces  $\Lambda_A$  and  $\Lambda_B$  and scalar product of site spin operators. The parameters of the Hamiltonian are defined by the relevant intercenter transfer integrals and the fundamental intracenter interactions, namely, crystal field and Racah parameters for the constituent metal ions in their ground, oxidized and reduced electronic configurations. These parameters contain also the reduced matrix elements of the creation (annihilation) operators linking the ground state of the many-electron ions with their reduced and oxidized states (fractional parentage coefficients),  $W$ -symbols and  $6j$ -symbols. The approach is discussed in context of the existing exchange models. © 2001 Published by Elsevier Science B.V.

## 1. Introduction

The magnetic exchange between transition metal ions with orbitally non-degenerate ground states can be described by the isotropic Heisenberg–Dirac–Van Vleck (HDVV) Hamiltonian expressed in terms of spin operators only:

$$\mathbf{H}_{\text{ex}} = -2JS_A\mathbf{S}_B,$$

where  $J$  is the multielectron parameter of the magnetic exchange between the ions  $A$  and  $B$ .

When one or both interacting ions exhibit orbital degeneracy, the HDVV Hamiltonian is invalid even as a zeroth order approximation and a more general consideration of the exchange problem is required. In

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fact, this general consideration is to be applied to a large variety of real systems. This is because, even if the local crystal fields acting on the metal sites contain relatively weak low-symmetry components, the angular orbital momenta of the constituent ions are not completely quenched. In these cases a simple HDDV model is often a poor approximation.

Many efforts were made in order to derive the effective exchange Hamiltonian for the orbitally degenerate ions [1–12]. The first ideas were proposed by Van Vleck [1] and the theory of potential exchange was worked out by Levy [2,3] and then in Refs. [4,5]. For the first time Khomskii and Kugel derived and considered the kinetic exchange Hamiltonians with the allowance of orbital degeneracy and created a new trend in solid state physics related to the problem of orbital ordering in solids (see their review paper [6] and references therein). The theory of the kinetic exchange was substantially developed by Drillon and Georges [7,8] and also by Leuenberger and Güdel [9] and Ceulemans et al. [11] and applied to  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  crystals. In the concluding part of this paper we will give a discussion of the existing models of the kinetic exchange in view of the results obtained in the present paper. Now we only note that the underlying ideas reported in Refs. [7,8] were of primary importance for the field. However, because of the lack in the use of symmetry arguments only relatively simple electronic configurations and topologies of pairs could be really tractable. Moreover, the models so far considered involve some simplifying assumptions that restrict their applicability to the discussion of real systems. In fact, these models do not take into account the complex energy spectrum of charge transfer states described by Tanabe–Sugano diagrams.

In a recent paper we proposed a new approach to the problem of the kinetic exchange between orbitally degenerate ions [13]. As distinguished from the previous considerations, we used the strong crystal field scheme for the transition metal ions taking into account all relevant charge transfer terms. The developed approach was applied to three important high-symmetric topologies: edge-shared ( $D_{2h}$ ), corner-shared ( $D_{4h}$ ) and face-shared ( $D_{3h}$ ) bioctahedral clusters [14]. The analysis of the energy patterns for these three cases elucidated the crucial importance of the topology of the system in the problem of kinetic exchange between orbitally degenerate ions.

The objective of the present paper is the further development of the theory of the kinetic exchange between orbitally degenerate ions. Using the tensorial properties of the fermionic creation and annihilation operators and Wigner–Racah algebra we express the effective Hamiltonian in terms of the cubic irreducible tensors, spin operators and restricted set of parameters depending on the fundamental quantities of the constituent moieties (namely, crystal field and Racah parameters) and the set of relevant electron transfer integrals. Reduced matrix elements of the creation and annihilation operators are presented in terms of the coefficients of fractional parentage.

We will also demonstrate how the well developed and extremely powerful technique of irreducible tensor operators of  $R_3$  group can be applied to the orbitally dependent effective Hamiltonian for the system with a given point symmetry. This forms a background for the pseudoangular momentum approach that is very useful as a computational tool and gives clear insight on the origin of the magnetic anisotropy in orbitally degenerate systems.

The theory is developed in a most general way, so the results are applicable to any homo and heteronuclear pairs with the terms  $^{2S_A+1}\Lambda_A$  and  $^{2S_B+1}\Lambda_B$  of the constituent ions. Keeping in mind not only magnetochemical but also spectroscopic applications we consider also the excited states. If one of the ions is excited the effective Hamiltonian contains the resonance part. The resonance blocks of the effective Hamiltonian are constructed for a homonuclear system.

This contribution consists of two parts. In part I (this paper) we present the effective Hamiltonian in its general form. In part II we apply the technique of the irreducible tensor operators in  $R_3$  group to the effective Hamiltonian deduced in this paper. We will show that in this way we are able to extend the theory and consider polynuclear systems and also to consider the related interactions (crystal fields, spin–orbit coupling, etc.).

## 2. The effective exchange Hamiltonian for a pair $A$ – $B$ of transition metal ions possessing $^{2S_A+1}\Lambda_A$ and $^{2S_B+1}\Lambda_B$ terms

In this section we will deduce the effective kinetic exchange Hamiltonian for a pair of transition metal ions in local cubic surroundings. It is supposed that ions  $A$  and  $B$  are in the  $^{2S_A+1}\Lambda_A$  and  $^{2S_B+1}\Lambda_B$  states, where  $\Lambda_A$  and  $\Lambda_B$  are the irreducible representations associated to the orbital part of the states. According to the Anderson's concept [15], kinetic exchange appears in the second order perturbation approximation with the unperturbed Hamiltonian,  $\mathbf{H}_0$ , including strong cubic crystal field and intracenter interelectronic interactions, and with the intercenter one-electron transfer operator,  $\mathbf{V}$ , playing the role of perturbation. In part II of the paper the relatively small non-cubic crystal fields and spin–orbit coupling will be considered as the perturbations operating within the manifold  $^{2S_A+1}\Lambda_A \otimes ^{2S_B+1}\Lambda_B$  along with the second order electron transfer processes.

The operator  $\mathbf{V}$  can be expressed as

$$\mathbf{V} = \sum_{\Gamma_A \gamma_A} \sum_{\Gamma_B \gamma_B} t(\Gamma_B \gamma_B, \Gamma_A \gamma_A) \sum_{\sigma} C_{\Gamma_A \gamma_A \sigma}^+ C_{\Gamma_B \gamma_B \sigma} + \text{h.c.}, \quad (1)$$

where the operator  $C_{\Gamma_A \gamma_A \sigma}^+$  ( $C_{\Gamma_A \gamma_A \sigma}$ ) creates (annihilates) electron on the orbital  $\phi_{\Gamma_A \gamma_A}$  of the center  $A$  with the spin projection  $\sigma$  ( $\sigma = \uparrow$  or  $\downarrow$ ), the quantization axis being taken general for both centers);  $t(\Gamma_B \gamma_B, \Gamma_A \gamma_A)$  is the transfer integral corresponding to the jump of the electron from the orbital  $\phi_{\Gamma_A \gamma_A}$  to the orbital  $\phi_{\Gamma_B \gamma_B}$ . Hereunder we will use the strong crystal field scheme for d-ions and hence  $\Gamma_A, \Gamma_B = t_2, e$ . We will use real one-electron cubic basis related to the tetragonal (with  $X, Y, Z$  along  $C_4$  axes) local coordinates, namely,  $t_2$ -basis:  $\xi \propto yz$ ,  $\eta \propto xz$ ,  $\zeta \propto xy$  and  $e$ -basis:  $u \propto 3z^2 - r^2$ ,  $v \propto \sqrt{3}(x^2 - y^2)$ . In Eq. (1) all transfer pathways  $\Gamma_A \gamma_A \leftrightarrow \Gamma_B \gamma_B$  are taken into account so the further consideration is not restricted to a particular topology of the whole system.

The effective second order Hamiltonian operating within the ground manifold of the  $d_A^n - d_B^n$  dimer can be presented as follows:

$$\begin{aligned} \mathbf{H}^{(2)} = & - \sum_{\Gamma_A \Gamma_B \Gamma'_A \Gamma'_B} \sum_{\gamma_A \gamma_B \gamma'_A \gamma'_B} t(\Gamma_A \gamma_A, \Gamma_B \gamma_B) t(\Gamma'_B \gamma'_B, \Gamma'_A \gamma'_A) \\ & \times \sum_{\sigma \sigma'} \left[ \sum_{\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A} \sum_{\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B} \frac{C_{\Gamma_A \gamma_A \sigma}^+ G(\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A) C_{\Gamma'_A \gamma'_A \sigma'} C_{\Gamma_B \gamma_B \sigma} G(\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B) C_{\Gamma'_B \gamma'_B \sigma'}^+}{\varepsilon(\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A) + \varepsilon(\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B)} \right. \\ & \left. + \sum_{\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B} \sum_{\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A} \frac{C_{\Gamma'_B \gamma'_B \sigma'}^+ G(\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B) C_{\Gamma_B \gamma_B \sigma} C_{\Gamma'_A \gamma'_A \sigma'} G(\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A) C_{\Gamma_A \gamma_A \sigma}^+}{\varepsilon(\bar{\nu}_B \bar{S}_B \bar{\Gamma}_B) + \varepsilon(\bar{\nu}_A \bar{S}_A \bar{\Gamma}_A)} \right]. \quad (2) \end{aligned}$$

Here  $G(\bar{\nu}_i \bar{S}_i \bar{\Gamma}_i)$  and  $G(\tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i)$  ( $i = A, B$ ) are the partial projection operators defined as:

$$\begin{aligned} G(\bar{\nu}_i \bar{S}_i \bar{\Gamma}_i) &= \sum_{\bar{M}_i \bar{\gamma}_i} |\bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle \langle \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i|, \\ G(\tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i) &= \sum_{\bar{M}_i \tilde{\gamma}_i} |\tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i \bar{M}_i \tilde{\gamma}_i\rangle \langle \tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i \bar{M}_i \tilde{\gamma}_i|. \end{aligned} \quad (3)$$

While deriving the perturbational Hamiltonian (2) we have used the idea of Drillon and Georges [7,8] of factorization of the second order Hamiltonian in order to express it in terms of the products of one-site operators. In Eq. (2) each one-site operator related to the  $i$ th ion (let say,  $C_{\Gamma_i \gamma_i \sigma}^+ G(\bar{\nu}_i \bar{S}_i \bar{\Gamma}_i) C_{\Gamma'_i \gamma'_i \sigma'}$ ) acts within the  $S_i \Lambda_i$ -manifold. In Eq. (2) the excited charge transfer states of the pair are taken as the products of the wave functions for the reduced and oxidized configurations of the constituent ions. So

$|\bar{v}_A \bar{S}_A \bar{\Gamma}_A \bar{M}_A \bar{\gamma}_A\rangle |\tilde{v}_B \tilde{S}_B \tilde{\Gamma}_B \tilde{M}_B \tilde{\gamma}_B\rangle$  correspond to the  $d_A^{n-1} - d_B^{n+1}$  charge transfer configuration meanwhile  $|\bar{v}_A \bar{S}_A \bar{\Gamma}_A \bar{M}_A \bar{\gamma}_A\rangle |\bar{v}_B \bar{S}_B \bar{\Gamma}_B \bar{M}_B \bar{\gamma}_B\rangle$  relate to the  $d_A^{n+1} - d_B^{n-1}$  configuration. Symbol  $\bar{v}_i$  is used to distinguish different cubic crystal field  $\bar{S}_i \bar{\Gamma}_i$  terms (oxidized states) of the same symmetry,  $\tilde{v}_i$  has the same meaning for the repeated  $\tilde{S}_i \tilde{\Gamma}_i$  terms (reduced states). The corresponding energies are denoted as  $\varepsilon(\bar{v}_i \bar{S}_i \bar{\Gamma}_i)$  and  $\varepsilon(\tilde{v}_i \tilde{S}_i \tilde{\Gamma}_i)$ . One should notice that the symbols  $\bar{v}_i$  and  $\tilde{v}_i$  enumerate the exact energy levels in a cubic crystal field with the allowance of the configuration mixing of all  $\bar{S}_i \bar{\Gamma}_i$  and  $\tilde{S}_i \tilde{\Gamma}_i$  states respectively. The wave functions of the crystal field states are represented by the following linear combinations:

$$\begin{aligned} |\bar{v}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle &= \sum_{\bar{k}_i} \langle \bar{k}_i | \bar{v}_i \rangle |d^{n-1}, \bar{k}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle, \\ |\tilde{v}_i \tilde{S}_i \tilde{\Gamma}_i \tilde{M}_i \tilde{\gamma}_i\rangle &= \sum_{\tilde{k}_i} \langle \tilde{k}_i | \tilde{v}_i \rangle |d^{n+1}, \tilde{k}_i \tilde{S}_i \tilde{\Gamma}_i \tilde{M}_i \tilde{\gamma}_i\rangle, \end{aligned} \quad (4)$$

where  $|d^{n-1}, \bar{k}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle$  and  $|d^{n+1}, \tilde{k}_i \tilde{S}_i \tilde{\Gamma}_i \tilde{M}_i \tilde{\gamma}_i\rangle$  are the wave functions for the oxidized and reduced states without taking into account the interelectronic interaction. Symbol  $\bar{k}_i$  stands for different electronic configurations  $t_2^m e^{n-1-m} (d_i^{n-1})$  and includes also additional quantum numbers  $\bar{S}_i' \bar{\Gamma}_i' \bar{S}_i'' \bar{\Gamma}_i''$  giving rise to  $\bar{S}_i \bar{\Gamma}_i$  term,  $|k_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle \equiv |t_2^m (\bar{S}_i' \bar{\Gamma}_i'), e^{n-1-m} (\bar{S}_i'' \bar{\Gamma}_i'') \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i\rangle$ . Symbol  $\tilde{k}_i$  plays the same role for  $d_i^{n+1}$  ion.

In the same way, we can present the wave functions for  $S_i \Lambda_i(d^n)$  term as

$$|v_i S_i \Lambda_i M_i \lambda_i\rangle = \sum_{k_i} \langle k_i | v_i \rangle |d^n, k_i S_i \Lambda_i M_i \lambda_i\rangle, \quad (5)$$

where symbol  $k_i$  plays the same role for  $S_i \Lambda_i(d^n)$  term as the symbols  $\bar{k}_i$  and  $\tilde{k}_i$  do for  $\bar{S}_i \bar{\Gamma}_i(d^{n-1})$  and  $\tilde{S}_i \tilde{\Gamma}_i(d^{n+1})$  terms. The coefficients  $\langle \dots | \dots \rangle$  in Eqs. (4) and (5) form the eigenvectors of the matrices of the intracenter Coulomb interaction. These matrices in terms of Racah parameters are given in Ref. [16] for all  $d^n$  ions in the crystal field of cubic symmetry.

Since all configuration interactions in the ground and excited crystal field states are taken into account the theory of the kinetic exchange presented here is essentially many electron. This calls one comment concerning the transfer integrals involved in the second order Hamiltonian (2). One can see that this Hamiltonian contains the product of two transfer integrals  $t(\Gamma_A \gamma_A, \Gamma_B \gamma_B) t(\Gamma_B' \gamma_B', \Gamma_A' \gamma_A')$ . Since in the one-electron approximation each  $S_i \Lambda_i(d^n)$  term involves the only  $t_2^m e^{n-m}$  configuration, the one-site operator  $C_{\Gamma_i \gamma_i \sigma}^+ G(\bar{v}_i \bar{S}_i \bar{\Gamma}_i) C_{\Gamma_i' \gamma_i' \sigma'}$  should not change the numbers of electrons occupying  $t_2$  and  $e$  orbitals. This requirement can be satisfied only providing  $\Gamma_i = \Gamma_i'$ . So if the configuration interactions are neglected the Hamiltonian (2) will contain only the products of the transfer integrals of the same type, namely,  $t(t_2, t_2) t(t_2, t_2); t(e, e) t(e, e)$  and  $t(t_2, e) t(t_2, e)$ . However it is not true in the framework of the many-electron approach dealing with the configuration interactions. In fact in this case one-site operator have non-vanishing matrix elements in  $S_i \Lambda_i(d^n)$  basis not only for  $\Gamma_i = \Gamma_i'$  but also for  $\Gamma_i \neq \Gamma_i'$ . This is due to the fact that the  $S_i \Lambda_i(d^n)$  crystal field term now is a mixture of different electronic configurations, and one-site operator with  $\Gamma_i \neq \Gamma_i'$  links some of them (e.g.,  $t_2^m e^{n-m}$  with  $t_2^{m\pm 1} e^{n-m\mp 1}$ ). This means that along with the products of transfer integrals of the same kind, the products of different transfer integrals like  $t(t_2, t_2) t(e, e)$  will also contribute to the second order Hamiltonian.

One of the key points in our consideration is the use of the tensorial properties of the fermionic creation and annihilation operators [17] that allows us to take full advantage from the Racah algebra for point groups. In fact, the creation operator can be regarded as the double tensor operator acting as a spherical irreducible tensor of the rank 1/2 in the spin subspace and as an irreducible tensor of  $\Gamma_i$ -type ( $i = A, B$ ) in the space of the electronic coordinates. Thus in the conventional tensorial notations we can write for the creation operator  $C_{\Gamma_i \gamma_i \sigma}^+ = \mathbf{T}_{\Gamma_i \gamma_i (1/2) \sigma}$  with two spin projections  $\sigma = \pm 1/2$  being the components of spin tensor and  $\gamma_i$  enumerating the components of the cubic tensor of  $\Gamma_i$ -type. We will follow the conventionally accepted rule for the choice of phases of the irreducible tensors of  $R_3$  (see Ref. [18, p. 62]). Then, for the

annihilation operator we have the relation  $C_{\Gamma_i\gamma_i\sigma} = (-1)^{(1/2)-\sigma} \mathbf{T}_{\Gamma_i\gamma_i(1/2)-\sigma}$  that is implied by the requirement of the Hermitian conjugation of the creation and annihilation operators. We have also taken into account that one-electron cubic basis related to the tetragonal axes of the sites is real. Since the partial projection operators  $G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i)$  and  $G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i)$  are apparently scalars in both coordinate and spin subspaces, the one-site operators  $C_{\Gamma_i\gamma_i\sigma}^+ G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma_i'\gamma_i'\sigma'}$  and  $C_{\Gamma_i\gamma_i\sigma} G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma_i'\gamma_i'\sigma'}^+$  represent the double tensor operators being transformed as the direct product  $\Gamma_i \otimes \Gamma_i' = \sum \Gamma$  in the coordinate space and  $D^{(1/2)} \otimes D^{(1/2)} = \sum_{k=0,1} D^{(k)}$  in the spin space. In general, they are reducible and can be expanded in the series of irreducible tensors  $\mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i)$  and  $\mathbf{Z}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i)$  by means of the following unitary transformations:

$$\begin{aligned} C_{\Gamma_i\gamma_i\sigma}^+ G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma_i'\gamma_i'\sigma'} &= (-1)^{(1/2)-\sigma'} \mathbf{T}_{\Gamma_i\gamma_i\frac{1}{2}\sigma} G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) \mathbf{T}_{\Gamma_i'\gamma_i'\frac{1}{2}-\sigma'} \\ &= (-1)^{(1/2)-\sigma'} \sum_{kq} \langle kq | \frac{1}{2}\frac{1}{2} - \sigma' \rangle \sum_{\Gamma\gamma} \langle \Gamma\gamma | \Gamma_i\gamma_i\Gamma_i'\gamma_i' \rangle \mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) \end{aligned} \quad (6)$$

and

$$\begin{aligned} C_{\Gamma_i\gamma_i\sigma} G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma_i'\gamma_i'\sigma'}^+ &= (-1)^{(1/2)-\sigma} \mathbf{T}_{\Gamma_i\gamma_i\frac{1}{2}-\sigma} G(\tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) \mathbf{T}_{\Gamma_i'\gamma_i'\frac{1}{2}\sigma'} \\ &= (-1)^{(1/2)-\sigma} \sum_{kq} \langle kq | \frac{1}{2} - \sigma \frac{1}{2}\sigma' \rangle \sum_{\Gamma\gamma} \langle \Gamma\gamma | \Gamma_i\gamma_i\Gamma_i'\gamma_i' \rangle \mathbf{Z}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i). \end{aligned} \quad (7)$$

In Eqs. (6) and (7)  $\langle kq | (1/2)\sigma(1/2) - \sigma' \rangle \equiv C_{(1/2)\sigma(1/2)-\sigma'}^{kq}$  etc. are the Clebsch–Gordan coefficients for rotation group (Wigner coefficients) and  $\langle \Gamma\gamma | \Gamma_i\gamma_i\Gamma_i'\gamma_i' \rangle$  etc. are the Clebsch–Gordan coefficients for the point group  $\mathbf{O}$ .

In order to calculate the matrices of the operators  $\mathbf{X}_{\Gamma\gamma kq}$  and  $\mathbf{Z}_{\Gamma\gamma kq}$  within the basis of  $^{2S_i+1}\Lambda_i$  of one can apply the Wigner–Eckart theorem [16]:

$$\begin{aligned} \langle v_i S_i \Lambda_i M_i \lambda_i | \mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) | v_i S_i \Lambda_i M_i' \lambda_i' \rangle \\ = [(2S_i + 1)(\Lambda_i)]^{-1/2} \langle v_i S_i \Lambda_i | \mathbf{X}_{\Gamma k}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) | v_i S_i \Lambda_i \rangle \langle S_i M_i | S_i M_i' kq \rangle \langle \Lambda_i \lambda_i | \Lambda_i \lambda_i' \Gamma\gamma \rangle, \end{aligned} \quad (8)$$

where  $(\Lambda_i)$  is the dimension of the irreducible representation  $\Lambda_i$ , and similar relation is to be used for the matrix element of the operator  $\mathbf{Z}_{\Gamma\gamma kq}$ . In Eq. (8) we have used the conventional notation  $\langle \dots || \dots || \dots \rangle$  for the reduced matrix element. Eq. (8) allows us to express the operators  $\mathbf{X}_{\Gamma\gamma kq}$  and  $\mathbf{Z}_{\Gamma\gamma kq}$  in terms of orbital operators  $\mathbf{O}_{\Gamma\gamma}^i$  and spin operators  $\mathbf{S}_{kq}^i$  as follows:

$$\begin{aligned} \mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) &= \frac{\langle v_i S_i \Lambda_i | \mathbf{X}_{\Gamma k}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) | v_i S_i \Lambda_i \rangle}{\langle S_i || S_k^i || S_i \rangle \langle \Lambda_i || \mathbf{O}_{\Gamma}^i || \Lambda_i \rangle} \mathbf{O}_{\Gamma\gamma}^i \mathbf{S}_{kq}^i, \\ \mathbf{Z}_{\Gamma\gamma kq}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) &= \frac{\langle v_i S_i \Lambda_i | \mathbf{Z}_{\Gamma k}(\Gamma_i\Gamma_i', \tilde{v}_i\tilde{S}_i\tilde{\Gamma}_i) | v_i S_i \Lambda_i \rangle}{\langle S_i || S_k^i || S_i \rangle \langle \Lambda_i || \mathbf{O}_{\Gamma}^i || \Lambda_i \rangle} \mathbf{O}_{\Gamma\gamma}^i \mathbf{S}_{kq}^i. \end{aligned} \quad (9)$$

Here  $\mathbf{O}_{\Gamma\gamma}^i$  is the irreducible tensor operator acting in the orbital  $\Lambda_i \lambda_i$ -manifold of the center  $i$ . This operator is defined in such a way that its reduced matrix element is  $\langle \Lambda_i || \mathbf{O}_{\Gamma}^i || \Lambda_i \rangle = (\Lambda_i)^{1/2}$ , so that the matrix elements of these operators coincide with the Clebsch–Gordan coefficients of the  $\mathbf{O}$  group in Eq. (8):  $\langle \Lambda_i \lambda_i | \mathbf{O}_{\Gamma\gamma}^i | \Lambda_i \lambda_i' \rangle = \langle \Lambda_i \lambda_i | \Lambda_i \lambda_i' \Gamma\gamma \rangle$ .

The  $\mathbf{O}_{\Gamma\gamma}^i$  matrices for the orbital triplet  $\Lambda_i = T_2$  are given in the appendix. The operators  $\mathbf{S}_{kq}^i$  ( $k = 0, 1$ ) act in the spin subspace  $S_i M_i$ . Their reduced matrix elements are the following:

$$\begin{aligned} \langle S_i || \mathbf{S}_0^i || S_i \rangle &= (2S_i + 1)^{1/2}, \\ \langle S_i || \mathbf{S}_1^i || S_i \rangle &= [S_i(S_i + 1)(2S_i + 1)]^{1/2}. \end{aligned} \quad (10)$$

Therefore, the operators  $\mathbf{S}_{00}^i$  and  $\mathbf{S}_{1q}^i$  ( $q = 0, \pm 1$ ) prove to be the unit operator and the cyclic components of the spin operator correspondingly, so that their matrix elements are the Wigner coefficients:  $\langle S_i M_i | \mathbf{S}_{1q}^i | S_i M_i' \rangle = \langle S_i M_i | S_i M_i' k q \rangle$ .

Now we are in the position to pass from the original perturbational Hamiltonian (2) expressed in terms of the creation and annihilation operators to the new representation of this Hamiltonian involving the standard orbital operators  $\mathbf{O}_{\Gamma\gamma}^i$  and one-site spin operators. As distinguished from the perturbational Hamiltonian, this Hamiltonian can be referred to as effective one. Inserting Eqs. (6), (7) and (9) into Eq. (2), we arrive to the following formula for the effective exchange Hamiltonian:

$$\begin{aligned} \mathbf{H}_{\text{ex}} = & -2 \sum_{\Gamma_A \Gamma_B \Gamma'_A \Gamma'_B} \sum_{\gamma_A \gamma_B \gamma'_A \gamma'_B} \sum_{\Gamma\gamma} \sum_{\Gamma'\gamma'} \langle \Gamma\gamma | \Gamma_A \gamma_A \Gamma'_A \gamma'_A \rangle \langle \Gamma'\gamma' | \Gamma_B \gamma_B \Gamma'_B \gamma'_B \rangle \mathbf{O}_{\Gamma\gamma}^A \mathbf{O}_{\Gamma'\gamma'}^B \\ & \times \left[ J_{\Gamma\Gamma'}^{(0)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) + J_{\Gamma\Gamma'}^{(1)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) \mathbf{S}_A \mathbf{S}_B \right]. \end{aligned} \quad (11)$$

The parameters  $J_{\Gamma\Gamma'}^{(0)}(\dots)$  and  $J_{\Gamma\Gamma'}^{(1)}(\dots)$  involved in the Hamiltonian are defined as follows:

$$\begin{aligned} J_{\Gamma\Gamma'}^{(k)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) \\ = & (-1)^{k+1} \frac{t(\Gamma_A \gamma_A, \Gamma_B \gamma_B) t(\Gamma'_B \gamma'_B, \Gamma'_A \gamma'_A)}{2 \langle S_A | \mathbf{S}_k^A | S_A \rangle \langle S_B | \mathbf{S}_k^B | S_B \rangle \sqrt{(\Lambda_A)(\Lambda_B)}} \\ & \times \left[ \sum_{\tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A} \sum_{\tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B} \frac{\langle \nu_A S_A \Lambda_A | \mathbf{X}_{\Gamma k}(\Gamma_A \Gamma'_A, \tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A) | \nu_A S_A \Lambda_A \rangle \langle \nu_B S_B \Lambda_B | \mathbf{Z}_{\Gamma' k}(\Gamma_B \Gamma'_B, \tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B) | \nu_B S_B \Lambda_B \rangle}{\varepsilon(\tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A) + \varepsilon(\tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B)} \right. \\ & \left. + \sum_{\tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B} \sum_{\tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A} \frac{\langle \nu_B S_B \Lambda_B | \mathbf{X}_{\Gamma' k}(\Gamma_B \Gamma'_B, \tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B) | \nu_B S_B \Lambda_B \rangle \langle \nu_A S_A \Lambda_A | \mathbf{Z}_{\Gamma k}(\Gamma_A \Gamma'_A, \tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A) | \nu_A S_A \Lambda_A \rangle}{\varepsilon(\tilde{\nu}_B \tilde{S}_B \tilde{\Gamma}_B) + \varepsilon(\tilde{\nu}_A \tilde{S}_A \tilde{\Gamma}_A)} \right]. \end{aligned} \quad (12)$$

The parameters  $J_{\Gamma\Gamma'}^{(k)}$  are expressed through the reduced matrix elements of  $\mathbf{X}$  and  $\mathbf{Z}$ ; they should be calculated. As distinguished from the conventionally accepted HDVV Hamiltonian expressed in terms of spin operators only, the effective Hamiltonian (11) operates in both spin and orbital spaces of the interacting orbitally degenerate ions. In fact, this Hamiltonian contains the orbital part (spin-independent), and mixed part containing both orbital and spin operators. The last part contains also the orbitally independent term  $\propto \mathbf{S}_A \mathbf{S}_B$  as a particular contribution. It should be noticed that the orbital operators  $\mathbf{O}_{\Gamma\gamma}^A$  and  $\mathbf{O}_{\Gamma\gamma}^B$  are defined in their local coordinate systems ( $x_A, y_A, z_A$  and  $x_B, y_B, z_B$ ) whereas the spin operators  $\mathbf{S}_A$  and  $\mathbf{S}_B$  are defined in a common (molecular) coordinate system. It should be noted that the Hamiltonian (11) operates within the space of the direct product of orbital and spin functions  $|\Lambda_A \lambda_A\rangle |\Lambda_B \lambda_B\rangle |S_A M_A\rangle |S_B M_B\rangle$  (but not in the basis formed by the symmetry adapted combinations of Slater determinants). Therefore the eigenvectors of this Hamiltonian cannot be directly put in the correspondence to the true wave functions of the cluster  $|\Lambda \lambda S M\rangle$  that are the solutions of the Schrödinger equation. The group-theoretical classification has to be done separately. In the part II of this paper we will introduce pseudoangular momentum labeling for the full states of the systems. It might be noted that the second order Hamiltonian, Eq. (11), contains only bilinear spin and orbital contributions like  $\mathbf{S}_A \mathbf{S}_B$  and  $\mathbf{O}_{\Gamma\gamma}^A \mathbf{O}_{\Gamma'\gamma'}^B$ . The higher order perturbation theory is expected to provide the terms like  $(\mathbf{S}_A \mathbf{S}_B)^2$  (biquadratic exchange) and higher order orbital–orbital and spin–orbital forms. Although these contributions are normally small they can be important in the cases of accidentally degenerate levels.

### 3. Parameters of the effective Hamiltonian

Here we describe the decoupling procedure that allows us to calculate the reduced matrix elements of the double tensor operators  $\mathbf{X}_{\Gamma\gamma kq}$  and  $\mathbf{Z}_{\Gamma\gamma kq}$  incorporated in the parameters of the effective Hamiltonian. First let us apply the inverse transformation to Eqs. (6), (7) expressing thus  $\mathbf{X}_{\Gamma\gamma kq}$  and  $\mathbf{Z}_{\Gamma\gamma kq}$  in terms of the following bilinear forms of the creation and annihilation operators:

$$\begin{aligned}\mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma'_i, \bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) &= (k + \tfrac{1}{2})^{1/2} \sum_{\sigma\sigma'} \sum_{\gamma_i\gamma'_i} \langle \tfrac{1}{2}\sigma'kq | \tfrac{1}{2}\sigma \rangle \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i | \Gamma\gamma \rangle C_{\Gamma_i\gamma_i\sigma}^+ G(\bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}, \\ \mathbf{Z}_{\Gamma\gamma kq}(\Gamma_i\Gamma'_i, \tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) &= (-1)^{k+1} (k + \tfrac{1}{2})^{1/2} \sum_{\sigma\sigma'} \sum_{\gamma_i\gamma'_i} \langle \tfrac{1}{2}\sigma kq | \tfrac{1}{2}\sigma' \rangle \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i | \Gamma\gamma \rangle C_{\Gamma_i\gamma_i\sigma} G(\tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}^+.\end{aligned}\quad (13)$$

In accordance with the definition of partial projection operators the matrix elements of one-site operators  $C_{\Gamma_i\gamma_i\sigma}^+ G(\bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}$  and  $C_{\Gamma_i\gamma_i\sigma} G(\tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}^+$  represent the sum of products of the matrix elements of the creation and annihilation operators. The further factorization can be reached applying the Wigner–Eckart theorem to the fermionic operators. We get:

$$\langle \nu_i S_i \Lambda_i M_i \lambda_i | C_{\Gamma_i\gamma_i\sigma}^+ | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \bar{M}_i \bar{\gamma}_i \rangle = [(2S_i + 1)(\Lambda_i)]^{-1/2} \langle \nu_i S_i \Lambda_i | \mathbf{T}_{\Gamma_i 1/2} | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \rangle \langle S_i M_i | \bar{S}_i \bar{M}_i \tfrac{1}{2}\sigma \rangle \langle \Lambda_i \lambda_i | \bar{\Gamma}_i \bar{\gamma}_i \Gamma_i \gamma_i \rangle. \quad (14)$$

Then the matrix of the operator  $C_{\Gamma_i\gamma_i\sigma}^+ G(\bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}$  can be expressed through the only reduced matrix element of the creation operator:

$$\begin{aligned}\langle \nu_i S_i \Lambda_i M_i \lambda_i | C_{\Gamma_i\gamma_i\sigma}^+ G(\bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'} | \nu_i S_i \Lambda_i M'_i \lambda'_i \rangle \\ = \langle \nu_i S_i \Lambda_i | \mathbf{T}_{\Gamma_i 1/2} | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \rangle \langle \nu_i S_i \Lambda_i | \mathbf{T}_{\Gamma'_i 1/2} | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \rangle [(2S_i + 1)(\Lambda_i)]^{-1} \\ \times \sum_{\bar{\gamma}_i} \langle \Lambda_i \lambda_i | \bar{\Gamma}_i \bar{\gamma}_i \Gamma_i \gamma_i \rangle \langle \Lambda_i \lambda'_i | \bar{\Gamma}_i \bar{\gamma}_i \Gamma'_i \gamma'_i \rangle \sum_{\bar{M}_i} \langle S_i M_i | \bar{S}_i \bar{M}_i \tfrac{1}{2}\sigma \rangle \langle S_i M'_i | \bar{S}_i \bar{M}_i \tfrac{1}{2}\sigma' \rangle.\end{aligned}\quad (15)$$

In the same way for the matrix elements of the operator  $C_{\Gamma_i\gamma_i\sigma} G(\tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}^+$  one can find:

$$\begin{aligned}\langle \nu_i S_i \Lambda_i M_i \lambda_i | C_{\Gamma_i\gamma_i\sigma} G(\tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) C_{\Gamma'_i\gamma'_i\sigma'}^+ | \nu_i S_i \Lambda_i M'_i \lambda'_i \rangle \\ = \langle \tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i | \mathbf{T}_{\Gamma_i 1/2} | \nu_i S_i \Lambda_i \rangle \langle \tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i | \mathbf{T}_{\Gamma'_i 1/2} | \nu_i S_i \Lambda_i \rangle [(2\tilde{S}_i + 1)(\tilde{\Gamma}_i)]^{-1} \\ \times \sum_{\tilde{\gamma}_i} \langle \tilde{\Gamma}_i \tilde{\gamma}_i | \Lambda_i \lambda_i \Gamma_i \gamma_i \rangle \langle \tilde{\Gamma}_i \tilde{\gamma}_i | \Lambda_i \lambda'_i \Gamma'_i \gamma'_i \rangle \sum_{\tilde{M}_i} \langle \tilde{S}_i \tilde{M}_i | S_i M_i \tfrac{1}{2}\sigma \rangle \langle \tilde{S}_i \tilde{M}_i | S_i M'_i \tfrac{1}{2}\sigma' \rangle.\end{aligned}\quad (16)$$

Combining Eqs. (13), (15) and (16) we arrive at the following expressions:

$$\begin{aligned}\langle \nu_i S_i \Lambda_i M_i \lambda_i | \mathbf{X}_{\Gamma\gamma kq}(\Gamma_i\Gamma'_i, \bar{\nu}_i\bar{S}_i\bar{\Gamma}_i) | \nu_i S_i \Lambda_i M'_i \lambda'_i \rangle \\ = (k + \tfrac{1}{2})^{1/2} [(2S_i + 1)(\Lambda_i)]^{-1} \langle \nu_i S_i \Lambda_i | \mathbf{T}_{\Gamma_i 1/2} | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \rangle \langle \nu_i S_i \Lambda_i | \mathbf{T}_{\Gamma'_i 1/2} | \bar{\nu}_i \bar{S}_i \bar{\Gamma}_i \rangle \\ \times \sum_{\gamma_i\gamma'_i\bar{\gamma}_i} \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i | \Gamma\gamma \rangle \langle \Lambda_i \lambda_i | \bar{\Gamma}_i \bar{\gamma}_i \Gamma_i \gamma_i \rangle \langle \Lambda_i \lambda'_i | \bar{\Gamma}_i \bar{\gamma}_i \Gamma'_i \gamma'_i \rangle \sum_{\sigma\sigma'\bar{M}_i} \langle \tfrac{1}{2}\sigma'kq | \tfrac{1}{2}\sigma \rangle \langle S_i M_i | \bar{S}_i \bar{M}_i \tfrac{1}{2}\sigma \rangle \langle S_i M'_i | \bar{S}_i \bar{M}_i \tfrac{1}{2}\sigma' \rangle,\end{aligned}\quad (17)$$

$$\begin{aligned}\langle \nu_i S_i \Lambda_i M_i \lambda_i | \mathbf{Z}_{\Gamma\gamma kq}(\Gamma_i\Gamma'_i, \tilde{\nu}_i\tilde{S}_i\tilde{\Gamma}_i) | \nu_i S_i \Lambda_i M'_i \lambda'_i \rangle \\ = (-1)^{k+1} (k + \tfrac{1}{2})^{1/2} [(2\tilde{S}_i + 1)(\tilde{\Gamma}_i)]^{-1} \langle \tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i | \mathbf{T}_{\Gamma_i 1/2} | \nu_i S_i \Lambda_i \rangle \langle \tilde{\nu}_i \tilde{S}_i \tilde{\Gamma}_i | \mathbf{T}_{\Gamma'_i 1/2} | \nu_i S_i \Lambda_i \rangle \\ \times \sum_{\gamma_i\gamma'_i\tilde{\gamma}_i} \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i | \Gamma\gamma \rangle \langle \tilde{\Gamma}_i \tilde{\gamma}_i | \Lambda_i \lambda_i \Gamma_i \gamma_i \rangle \langle \tilde{\Gamma}_i \tilde{\gamma}_i | \Lambda_i \lambda'_i \Gamma'_i \gamma'_i \rangle \sum_{\sigma\sigma'\tilde{M}_i} \langle \tfrac{1}{2}\sigma kq | \tfrac{1}{2}\sigma' \rangle \langle \tilde{S}_i \tilde{M}_i | S_i M_i \tfrac{1}{2}\sigma \rangle \langle \tilde{S}_i \tilde{M}_i | S_i M'_i \tfrac{1}{2}\sigma' \rangle.\end{aligned}\quad (18)$$



The sums involving the products of three Wigner coefficients in Eqs. (17) and (18) can be calculated using the following expressions [18]:

$$\sum_{\sigma\sigma'\tilde{M}_i} \langle \tfrac{1}{2}\sigma'kq|\tfrac{1}{2}\sigma\rangle \langle S_iM_i|\tilde{S}_i\tilde{M}_i\tfrac{1}{2}\sigma\rangle \langle S_iM'_i|\tilde{S}_i\tilde{M}_i\tfrac{1}{2}\sigma'\rangle = (-1)^{k-(1/2)-\tilde{S}_i-S_i} [2(2S_i+1)]^{1/2} \left\{ \begin{matrix} S_i & S_i & k \\ \frac{1}{2} & \frac{1}{2} & \tilde{S}_i \end{matrix} \right\} \langle S_iM_i|S_iM'_ikq\rangle, \quad (19)$$

$$\begin{aligned} & \sum_{\sigma\sigma'\tilde{M}_i} \langle \tfrac{1}{2}\sigma'kq|\tfrac{1}{2}\sigma'\rangle \langle \tilde{S}_i\tilde{M}_i|S_iM_i\tfrac{1}{2}\sigma\rangle \langle \tilde{S}_i\tilde{M}_i|S_iM'_i\tfrac{1}{2}\sigma'\rangle \\ & = (-1)^{-(1/2)-\tilde{S}_i-S_i} (2\tilde{S}_i+1)(S_i+\tfrac{1}{2})^{-1/2} \left\{ \begin{matrix} S_i & S_i & k \\ \frac{1}{2} & \frac{1}{2} & \tilde{S}_i \end{matrix} \right\} \langle S_iM_i|S_iM'_ikq\rangle. \end{aligned} \quad (20)$$

In order to perform the summations over the triads  $\gamma_i\gamma'_i\tilde{\gamma}_i$  and  $\gamma_i\gamma'_i\tilde{\gamma}_i$  in Eqs. (17) and (18) we will use, instead of the Clebsch–Gordan coefficients, the  $V$ -symbols defined according to Griffith [19]. The  $V$ -symbols are related to the Clebsch–Gordan coefficients as

$$\langle a\alpha b\beta|c\gamma\rangle = (-1)^{f(a,b,c)} (c)^{1/2} V \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}. \quad (21)$$

Here the Greek letters  $\alpha$ ,  $\beta$  and  $\gamma$  are used to enumerate the basis of the irreducible representations  $a$ ,  $b$  and  $c$ ; the phase factor  $(-1)^{f(a,b,c)}$  is introduced to take into account the difference in phases between the Sugano–Tanabe’s definition of Clebsch–Gordan coefficients [16] we use throughout this paper and their definition given in the book of Griffith (see in Ref. [19, p. 104]). The  $V$ -symbol in Eq. (21) satisfy a symmetry property, namely, it is multiplied by  $(-1)^{a+b+c}$  when its columns undergo any odd permutation. For the cubic group this symbolic notation means that  $(-1)^{A_1} = (-1)^E = (-1)^{T_2} = +1$  and  $(-1)^{A_2} = (-1)^{T_1} = -1$ .

In addition to this rule one should take into account the following formula for the sum involving the products of three  $V$ -symbols [19]:

$$\sum_{\delta\epsilon\varphi} V \begin{pmatrix} a & e & f \\ \alpha & \epsilon & \varphi \end{pmatrix} V \begin{pmatrix} b & f & d \\ \beta & \varphi & \delta \end{pmatrix} V \begin{pmatrix} c & d & e \\ \gamma & \delta & \epsilon \end{pmatrix} = W \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix} V \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}, \quad (22)$$

where  $W \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$  is the  $W$ -symbol [19].

Making use of this formula, the permutation rules and the definition (21) one can find:

$$\sum_{\gamma_i\gamma'_i\tilde{\gamma}_i} \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i|\Gamma\gamma\rangle \langle \Lambda_i\lambda_i|\bar{\Gamma}_i\tilde{\gamma}_i\Gamma_i\gamma_i\rangle \langle \Lambda_i\lambda'_i|\bar{\Gamma}_i\tilde{\gamma}_i\Gamma'_i\gamma'_i\rangle = (-1)^{\bar{f}} [(\Lambda_i)(\Gamma)]^{1/2} W \begin{pmatrix} \Lambda_i & \Lambda_i & \Gamma \\ \Gamma_i & \Gamma'_i & \bar{\Gamma}_i \end{pmatrix} \langle \Lambda_i\lambda_i|\Lambda_i\lambda'_i\Gamma\gamma\rangle, \quad (23)$$

$$\sum_{\gamma_i\gamma'_i\tilde{\gamma}_i} \langle \Gamma_i\gamma_i\Gamma'_i\gamma'_i|\Gamma\gamma\rangle \langle \tilde{\Gamma}_i\tilde{\gamma}_i|\Lambda_i\lambda_i\Gamma_i\gamma_i\rangle \langle \tilde{\Gamma}_i\tilde{\gamma}_i|\Lambda_i\lambda'_i\Gamma'_i\gamma'_i\rangle = (-1)^{\tilde{f}} (\tilde{\Gamma}_i)[(\Gamma)/(\Lambda_i)]^{1/2} W \begin{pmatrix} \Lambda_i & \Lambda_i & \Gamma \\ \Gamma_i & \Gamma'_i & \tilde{\Gamma}_i \end{pmatrix} \langle \Lambda_i\lambda_i|\Lambda_i\lambda'_i\Gamma\gamma\rangle. \quad (24)$$

In Eqs. (23) and (24)  $\bar{f}$  and  $\tilde{f}$  are the phase factors defined by the following symbolic equations:

$$\begin{aligned} \bar{f} &= f(\Gamma_i, \Gamma'_i, \Gamma) + f(\Lambda_i, \Gamma, \Lambda_i) + f(\bar{\Gamma}_i, \Gamma_i, \Lambda_i) + f(\bar{\Gamma}_i, \Gamma'_i, \Lambda_i) + \Lambda_i + \Gamma_i + \bar{\Gamma}_i + \Gamma, \\ \tilde{f} &= f(\Gamma_i, \Gamma'_i, \Gamma) + f(\Lambda_i, \Gamma, \Lambda_i) + f(\Lambda_i, \Gamma_i, \tilde{\Gamma}_i) + f(\Lambda_i, \Gamma'_i, \tilde{\Gamma}_i) + \Lambda_i + \Gamma_i + \tilde{\Gamma}_i + \Gamma. \end{aligned} \quad (25)$$

Now using Eqs. (19), (20), (23) and (24) we arrive at the following results for the reduced matrix elements involved in the definition of the parameters of the Hamiltonian:

$$\begin{aligned} & \langle v_i S_i \Lambda_i \| \mathbf{X}_{\Gamma k}(\Gamma_i \Gamma'_i, \bar{v}_i \bar{S}_i \bar{\Gamma}_i) \| v_i S_i \Lambda_i \rangle \\ &= (-1)^{\bar{J}} [(2k+1)(\Gamma)]^{1/2} \left\{ \begin{matrix} S_i & S_i & k \\ \frac{1}{2} & \frac{1}{2} & \bar{S}_i \end{matrix} \right\} W \left( \begin{matrix} \Lambda_i & \Lambda_i & \Gamma \\ \Gamma_i & \Gamma'_i & \bar{\Gamma}_i \end{matrix} \right) \langle v_i S_i \Lambda_i \| \mathbf{T}_{\Gamma_i 1/2} \| \bar{v}_i \bar{S}_i \bar{\Gamma}_i \rangle \langle v_i S_i \Lambda_i \| \mathbf{T}_{\Gamma'_i 1/2} \| \bar{v}_i \bar{S}_i \bar{\Gamma}_i \rangle, \end{aligned} \quad (26)$$

$$\begin{aligned} & \langle v_i S_i \Lambda_i \| \mathbf{Z}_{\Gamma k}(\Gamma_i \Gamma'_i, \tilde{v}_i \tilde{S}_i \tilde{\Gamma}_i) \| v_i S_i \Lambda_i \rangle \\ &= (-1)^{\tilde{J}} [(2k+1)(\Gamma)]^{1/2} \left\{ \begin{matrix} S_i & S_i & k \\ \frac{1}{2} & \frac{1}{2} & \tilde{S}_i \end{matrix} \right\} W \left( \begin{matrix} \Lambda_i & \Lambda_i & \Gamma \\ \Gamma_i & \Gamma'_i & \tilde{\Gamma}_i \end{matrix} \right) \langle \tilde{v}_i \tilde{S}_i \tilde{\Lambda}_i \| \mathbf{T}_{\Gamma_i 1/2} \| v_i S_i \Lambda_i \rangle \langle \tilde{v}_i \tilde{S}_i \tilde{\Lambda}_i \| \mathbf{T}_{\Gamma'_i 1/2} \| v_i S_i \Lambda_i \rangle. \end{aligned} \quad (27)$$

Eqs. (26) and (27) allow us to express the parameters of the effective Hamiltonian through the reduced matrix elements of creation operators. Since these matrix elements are still defined in multielectron basis we should make the last step and to express them through the one-electron matrix elements. With this aim one can use the following relationships between the reduced matrix elements of the creation operator and the coefficients of fractional parentage [20]:

$$\langle d^n, k_i S_i \Lambda_i \| \mathbf{T}_{\Gamma_i(1/2)} \| d^{n-1}, \bar{k}_i \bar{S}_i \bar{\Gamma}_i \rangle = (-1)^n [n(2S_i+1)(\Lambda_i)]^{1/2} \langle (d^{n-1}) \bar{k}_i \bar{S}_i \bar{\Gamma}_i, \Gamma_i | \rangle \langle d^n k_i S_i \Lambda_i \rangle, \quad (28)$$

$$\langle d^{n+1}, \tilde{k}_i \tilde{S}_i \tilde{\Gamma}_i \| \mathbf{T}_{\Gamma_i(1/2)} \| d^n, k_i S_i \Lambda_i \rangle = (-1)^{n+1} [(n+1)(2\tilde{S}_i+1)(\tilde{\Gamma}_i)]^{1/2} \langle (d^n) k_i S_i \Lambda_i, \Gamma_i | \rangle \langle d^{n+1} \tilde{k}_i \tilde{S}_i \tilde{\Gamma}_i \rangle. \quad (29)$$

In Eqs. (28) and (29) the usually accepted notation  $\langle \dots | \rangle \dots$  is used for the coefficients of fractional parentage [21]. Using Eqs. (28), (29), (4) and (5) one finds the following expressions for the reduced matrix elements involved in Eqs. (26) and (27):

$$\langle v_i S_i \Lambda_i \| \mathbf{T}_{\Gamma_i(1/2)} \| \bar{v}_i \bar{S}_i \bar{\Gamma}_i \rangle = (-1)^n [n(2S_i+1)(\Lambda_i)]^{1/2} \sum_{k_i \bar{k}_i} \langle v_i | k_i \rangle \langle \bar{k}_i | \bar{v}_i \rangle \langle (d^{n-1}) \bar{k}_i \bar{S}_i \bar{\Gamma}_i, \Gamma_i | \rangle \langle d^n k_i S_i \Lambda_i \rangle \quad (30)$$

and

$$\langle \tilde{v}_i \tilde{S}_i \tilde{\Gamma}_i \| \mathbf{T}_{\Gamma_i(1/2)} \| v_i S_i \Lambda_i \rangle = (-1)^{n+1} [(n+1)(2\tilde{S}_i+1)(\tilde{\Gamma}_i)]^{1/2} \sum_{k_i \tilde{k}_i} \langle \tilde{v}_i | \tilde{k}_i \rangle \langle k_i | v_i \rangle \langle (d^n) k_i S_i \Lambda_i, \Gamma_i | \rangle \langle d^{n+1} \tilde{k}_i \tilde{S}_i \tilde{\Gamma}_i \rangle. \quad (31)$$

Eqs. (26) and (27) accompanied by Eqs. (30) and (31) make it possible to calculate the parameters  $J_{\Gamma\Gamma'}^{(k)}$  (Eq. (12)) entering in the effective exchange Hamiltonian (11). The values of the intracenter parameters (crystal field and Racah parameters) can be extracted from the spectroscopic data and the transfer integrals can be considered as the adjustable parameters.

#### 4. The effective Hamiltonian of resonance interaction

Let us consider a dimer containing equivalent metal ions. One of the ions is assumed to be excited, meanwhile another one is in the ground state. As before we do not imply any restrictions on the nature of the ground and excited terms denoted as  $\Lambda^g S^g$  and  $\Lambda^e S^e$ , particularly, spins  $S^g$  and  $S^e$  can be different. The excited state of the dimer is additionally double degenerate due to the existence of two possible localization

of the excitation. Two sets of basis functions belonging to the excited states with  $B$  and  $A$  localizations of the excitation can be labeled as:

$$|v_A^g S_A^g \Lambda_A^g M_A^g \lambda_A^g\rangle, |v_B^c S_B^c \Lambda_B^c M_B^c \lambda_B^c\rangle, |v_A^c S_A^c \Lambda_A^c M_A^c \lambda_A^c\rangle, |v_B^g S_B^g \Lambda_B^g M_B^g \lambda_B^g\rangle. \quad (32)$$

We will consider the second order electron transfer processes as a mechanism responsible for the migration of excitation and hence for the resonance splitting of the excited states. Then the full matrix of the second order operator  $\mathbf{H}^{(2)}$  (Eq. (2)) involves two diagonal blocks describing the kinetic exchange interaction between two ions (one of them is in the ground state and another one is excited). The off-diagonal blocks of the full Hamiltonian produce the resonance splitting of the exchange levels. The first problem (exchange) has been considered in the previous sections and now we will focus on the resonance blocks.

In order to deduce the resonance Hamiltonian corresponding to the block  $\langle A^g B^c | \mathbf{H}^{(2)} | A^c B^g \rangle$  one has to evaluate the following four one-site matrix elements:

$$\begin{aligned} \langle v_A^g S_A^g \Lambda_A^g M_A^g \lambda_A^g | \mathbf{X}_{\Gamma\gamma kq}^A | v_A^c S_A^c \Lambda_A^c M_A^c \lambda_A^c \rangle, & \quad \langle v_B^c S_B^c \Lambda_B^c M_B^c \lambda_B^c | \mathbf{Z}_{\Gamma\gamma kq}^B | v_B^g S_B^g \Lambda_B^g M_B^g \lambda_B^g \rangle, \\ \langle v_B^c S_B^c \Lambda_B^c M_B^c \lambda_B^c | \mathbf{X}_{\Gamma\gamma kq}^B | v_B^g S_B^g \Lambda_B^g M_B^g \lambda_B^g \rangle, & \quad \langle v_A^c S_A^c \Lambda_A^c M_A^c \lambda_A^c | \mathbf{Z}_{\Gamma\gamma kq}^A | v_A^g S_A^g \Lambda_A^g M_A^g \lambda_A^g \rangle, \end{aligned} \quad (33)$$

where the short notations  $\mathbf{X}_{\Gamma\gamma kq}(\Gamma_A \Gamma'_A, \bar{v}_A \bar{S}_A \bar{\Lambda}_A) \equiv \mathbf{X}_{\Gamma\gamma kq}^A$  etc. are used. Applying the Wigner–Eckart theorem to these matrix elements we can find the matrix representation of the one-site operators  $\mathbf{X}_{\Gamma\gamma kq}^i$  and  $\mathbf{Z}_{\Gamma\gamma kq}^i$ . Thus, for the operators related to the site  $A$  we get:

$$\begin{aligned} \mathbf{X}_{\Gamma\gamma kq}^A(g\ e) &= \frac{\langle v_A^g S_A^g \Lambda_A^g | \mathbf{X}_{\Gamma k}^A | v_A^c S_A^c \Lambda_A^c \rangle}{\langle S^g || \mathbf{S}_k || S^c \rangle \langle \Lambda^g || \mathbf{O}_\Gamma || \Lambda^c \rangle} \mathbf{O}_{\Gamma\gamma}^A(g\ e) \mathbf{S}_{kq}^A(g\ e), \\ \mathbf{Z}_{\Gamma\gamma kq}^A(g\ e) &= \frac{\langle v_A^g S_A^g \Lambda_A^g | \mathbf{Z}_{\Gamma k}^A | v_A^c S_A^c \Lambda_A^c \rangle}{\langle S^g || \mathbf{S}_k || S^c \rangle \langle \Lambda^g || \mathbf{O}_\Gamma || \Lambda^c \rangle} \mathbf{O}_{\Gamma\gamma}^A(g\ e) \mathbf{S}_{kq}^A(g\ e). \end{aligned} \quad (34)$$

The reduced matrix elements in the denominators in Eq. (34) are independent of the site, so symbol  $A$  is omitted. The remaining two matrices  $\mathbf{X}_{\Gamma\gamma kq}^B(g\ e)$  and  $\mathbf{Z}_{\Gamma\gamma kq}^B(g\ e)$  relating to the site  $B$  are obtained similarly. Eq. (34) contain the off-diagonal orbital and spin blocks  $\mathbf{O}_{\Gamma\gamma}^A(g\ e)$  and  $\mathbf{S}_{kq}^A(g\ e)$  linking the ground state with the excited one. The reduced matrix element of the operator  $\mathbf{O}_{\Gamma\gamma}^A(g\ e)$  is defined by

$$\langle \Lambda^g || \mathbf{O}_\Gamma || \Lambda^c \rangle = (\Lambda^g)^{1/2}. \quad (35)$$

The operators  $\mathbf{S}_{kq}^A(g\ e)$  ( $k = 0, 1$ ) are the irreducible tensor operators, so they connect spin states with  $|S^c - S^g| = 0, 1$ . The reduced matrix elements of the operators  $\mathbf{S}_{kq}^A(g\ e)$  are defined by

$$\begin{aligned} \langle S^g || \mathbf{S}_0 || S^c \rangle &= (2S^g + 1)^{1/2}, \\ \langle S^g || \mathbf{S}_1 || S^c \rangle &= [S^g(S^g + 1)(2S^g + 1)]^{1/2}. \end{aligned} \quad (36)$$

Within the definitions given by Eqs. (35) and (36), the operators  $\mathbf{O}_{\Gamma\gamma}^A(g\ e)$  and  $\mathbf{S}_{kq}^A(g\ e)$  are represented by the  $(\Lambda^g) \times (\Lambda^c)$  and  $(2S^g + 1) \times (2S^c + 1)$  rectangular matrices. Their matrix elements are given by

$$\begin{aligned} \langle \Lambda_A^g \lambda_A^g | \mathbf{O}_{\Gamma\gamma}^A(g\ e) | \Lambda_A^c \lambda_A^c \rangle &= \langle \Lambda_A^g \lambda_A^g | \Lambda_A^c \lambda_A^c \Gamma\gamma \rangle, \quad \langle S_A^g M_A^g | \mathbf{S}_{00}^A(g\ e) | S_A^c M_A^c \rangle = \delta_{S_A^g S_A^c} \delta_{M_A^g M_A^c}, \\ \langle S_A^g M_A^g | \mathbf{S}_{1q}^A(g\ e) | S_A^c M_A^c \rangle &= [S^g(S^g + 1)]^{1/2} \langle S_A^g M_A^g | S_A^c M_A^c 1q \rangle. \end{aligned} \quad (37)$$

In particular case  $S_A^g = S_A^c$  the operator  $\mathbf{S}_{00}^A(g\ e)$  represents the unit operator and  $\mathbf{S}_{1q}^A(g\ e)$  becomes the usual spin operators. Providing  $S_A^g \neq S_A^c$  the matrices  $\mathbf{X}_{\Gamma\gamma 00}^A(g\ e)$  and  $\mathbf{Z}_{\Gamma\gamma 00}^A(g\ e)$  vanish. Using Eq. (34) we arrive at the following final expression for the resonance Hamiltonian:

$$\begin{aligned}
\mathbf{H}_{\text{res}}(A^g B^c, A^c B^g) = & -2 \sum_{\Gamma_A \Gamma_B \Gamma'_A \Gamma'_B} \sum_{\gamma_A \gamma_B \gamma'_A \gamma'_B} \sum_{\Gamma_\gamma} \sum_{\Gamma'_\gamma} \langle \Gamma_\gamma | \Gamma_A \gamma_A \Gamma'_A \gamma'_A \rangle \langle \Gamma'_\gamma | \Gamma_B \gamma_B \Gamma'_B \gamma'_B \rangle \\
& \times \mathbf{O}_{\Gamma_\gamma}^A(\mathbf{g} \mathbf{e}) \mathbf{O}_{\Gamma'_\gamma}^B(\mathbf{e} \mathbf{g}) \left[ R_{\Gamma\Gamma'}^{(0)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) \mathbf{S}_{00}^A(\mathbf{g} \mathbf{e}) \mathbf{S}_{00}^B(\mathbf{e} \mathbf{g}) \right. \\
& \left. + R_{\Gamma\Gamma'}^{(1)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) \mathbf{S}_A(\mathbf{g} \mathbf{e}) \mathbf{S}_B(\mathbf{e} \mathbf{g}) \right]. \quad (38)
\end{aligned}$$

The parameter  $R_{\Gamma\Gamma'}^{(0)}(\dots)$  and  $R_{\Gamma\Gamma'}^{(1)}(\dots)$  are given by the following expression:

$$\begin{aligned}
R_{\Gamma\Gamma'}^{(k)}(\Gamma_A \gamma_A, \Gamma_B \gamma_B, \Gamma'_A \gamma'_A, \Gamma'_B \gamma'_B) \\
= & (-1)^{k+1} \frac{t(\Gamma_A \gamma_A, \Gamma_B \gamma_B) t(\Gamma'_B \gamma'_B, \Gamma'_A \gamma'_A)}{2 \langle S^g \| \mathbf{S}_k \| S^e \rangle \langle S^e \| \mathbf{S}_k \| S^g \rangle \sqrt{(\Lambda^g)(\Lambda^e)}} \\
& \times \sum_{\tilde{S}\tilde{\Gamma}} \sum_{\tilde{S}\tilde{\Gamma}} \sum_{\tilde{\nu}\tilde{\nu}'} [\varepsilon(\tilde{\nu}\tilde{S}\tilde{\Gamma}) + \varepsilon(\tilde{\nu}'\tilde{S}\tilde{\Gamma})]^{-1} [\langle \nu_A^g S_A^g \Lambda_A^g \| \mathbf{X}_{\Gamma k}(\Gamma_A \Gamma'_A, \tilde{\nu}\tilde{S}\tilde{\Gamma}) \| \nu_A^e S_A^e \Lambda_A^e \rangle \\
& \times \langle \nu_B^e S_B^e \Lambda_B^e \| \mathbf{Z}_{\Gamma' k}(\Gamma_B \Gamma'_B, \tilde{\nu}'\tilde{S}\tilde{\Gamma}) \| \nu_B^g S_B^g \Lambda_B^g \rangle + \langle \nu_A^g S_A^g \Lambda_A^g \| \mathbf{Z}_{\Gamma k}(\Gamma_A \Gamma'_A, \tilde{\nu}\tilde{S}\tilde{\Gamma}) \| \nu_A^e S_A^e \Lambda_A^e \rangle \\
& \times \langle \nu_B^e S_B^e \Lambda_B^e \| \mathbf{X}_{\Gamma' k}(\Gamma_B \Gamma'_B, \tilde{\nu}'\tilde{S}\tilde{\Gamma}) \| \nu_B^g S_B^g \Lambda_B^g \rangle]. \quad (39)
\end{aligned}$$

Since in this section we are dealing with the homonuclear system the labels  $A$  and  $B$  are omitted in the notations of the charge transfer states.

The exchange Hamilton supplemented by the resonance Hamilton deduced here is applicable in the study of the excited states by the optical spectroscopy. It provides also a theoretical background for the ERP study of the optically excited states.

## 5. Discussion

In this section we will discuss the effective Hamiltonian reported here and compare the present approach with the previous studies in the field.

Conceptually the background of our approach is close to those of Drillon and Georges [7,8] and Leuenberger and Güdel [9]. However, there are at least two significant differences. The first difference is in the mathematical procedure. In Refs. [7–9] the T–P analogy was employed and the Hamiltonian was expressed in terms of fictitious orbital angular momentum operators and spin operators. In the present approach we start with the strong crystal field scheme (with subsequent allowance of mixing of all configurations) and express the Hamiltonian through the irreducible cubic tensors  $\mathbf{O}_{\Gamma_\gamma}^{A(B)}$  and spin operators. As distinguished from these two earlier approaches our consideration is essentially based on the tensorial properties of the fermionic operators and point symmetry arguments. The use of T–P analogy in Refs. [7–9] implies two restrictions, namely, only orbital triplets ( $T_1, T_2$ ) can be considered and only transfer pathways involving the electrons from  $t_2$  shells can be taken into account. At the same time the effective Hamiltonian proposed in the present paper is much more general because it is applicable to all electronic configurations and terms.

The second important difference between the cited papers and our study is that we took into account the complex energy spectrum of transition metal ions exhibiting by Tanabe–Sugano diagrams, meanwhile in Ref. [9] all charge-transfer energies (denominators) are set to  $U$  and in [7,8] the difference is neglected between the energies of charge transfer states with the same spin. The discrimination between different charge-transfer states has distinctive physical consequences for the mutual disposition of spin states in the ground manifold and particularly for the spin multiplicity of the ground level. As an illustration of this one can mention the Anderson's model of Ref. [15] for a pair of interacting sites with two magnetic orbitals and one electron on each. The resulting effect is weakly ferromagnetic (third order effect in Anderson's terminology) due to competition between kinetic contributions of high spin and low spin charge-transfer

states. The delicate balance between different contributions in many-electron ions with orbitally degenerate terms crucially depends on the detail structure of crystal field states that is taken into account carefully in the approach presented here.

Finally one should mention two recent studies based on the similar ideas, namely the approach of Weihe and Güdel [10] and Ceulemans with co-workers [11]. Weihe and Güdel considered the kinetic exchange in  $\mu$ -oxo bridged dimeric complexes of  $D_{4h}$  symmetry. They performed a direct calculation of the energy levels within second order perturbation procedure without usage of the effective Hamiltonian.

Ceulemans et al. constructed a second order kinetic exchange Hamiltonian for  $[\text{Ti}_2\text{Cl}_9]^{3-}$  accompanied by the ab initio calculations. In its final form this Hamiltonian acts within the ground manifold but still contains different combinations of creation and annihilation operators. Since this Hamiltonian is expressed in terms of one-electron operators acting on the spin-orbitals it cannot be regarded as an effective Hamiltonian to the full extent. Conventionally the effective Hamiltonian acts in a restricted basis and also is expressed in terms of many-electron operators acting within the space specified by the total quantum numbers of the constituents. From this point of view the Hamiltonian deduced in the present paper does represent a genuine effective Hamiltonian because it involves many-electron orbital and spin operators of the interacting ions.

The following important advantages of this Hamiltonian can be pointed out:

(1) The operator part of the Hamiltonian is independent of the internal structure of the metal ions being common for all  $d^n(S_A\Lambda_A) - d^n(S_B\Lambda_B)$  pairs with a given symmetry of the molecule. The information about the intra and interionic interactions is incorporated in a restricted number of parameters having clear physical sense. In fact, these parameters are expressed in terms of the relevant transfer integrals (implied by the symmetry conditions) and the fundamental parameters of the constituents, namely, crystal field and Racah parameters for the normal, reduced and oxidized forms of the metal ions. The information about the intracenter parameters is accessible and they can be reliably estimated from the spectroscopic data obtained for the monomeric units. As distinguished from the perturbational Hamiltonian involving one-electron operators our effective Hamiltonian expressed in terms of many-electron operators and parameters provides an efficient way for the parametrization of the experimental data. This can be illustrated using the analogy with HDVV spin Hamiltonian and comparing two forms  $\mathbf{H} = -2 \sum_{\alpha\beta} J_{A\alpha,B\beta} \mathbf{S}_{A\alpha} \mathbf{S}_{B\beta}$  and  $\mathbf{H} = -2JS_A\mathbf{S}_B (J = (n_A n_B)^{-1} \sum_{\alpha\beta} J_{A\alpha,B\beta}; n_A \text{ and } n_B \text{ are the numbers of magnetic orbitals and } J_{A\alpha,B\beta} \text{ are pairwise exchange parameters})$ . The first one contains explicitly all exchange pathways and one-electron operators, while the second one (true effective Hamiltonian) is expressed in terms of the full spin operators  $\mathbf{S}_A$  and  $\mathbf{S}_B$  and involves the only many-electron exchange parameter  $J$ . Although these two forms of the exchange Hamiltonian are physically equivalent, only the second one can be useful for the parametrization of the experimental data and has an irrefutable advantage as a computational tool.

(2) As far as the computational procedure is concerned it should be stressed that the Hamiltonian presented here provides a good background for the use of the powerful techniques coming from the theories of the irreducible tensors and angular momentum in the  $R_3$  group [16–22]. Along with the exchange interactions the related interactions (e.g., low-symmetry crystal field terms, Coulomb interactions between unfilled electronic shells, spin-orbit coupling and Zeeman interactions) can be also taken into account within a unified computational scheme. In this way the Hamiltonian (accompanied by an efficient computational procedure) can be extended to the polynuclear systems that are inaccessible for the ab initio calculations. This is demonstrated in the part II of this paper.

## 6. Concluding remarks

In this paper we have deduced kinetic exchange Hamiltonian for a pair of octahedrally coordinated transition metal ions possessing orbitally degenerate ground or excited states. This Hamiltonian is ex-

pressed through the standard orbital and spin operators and provides an efficient tool for the parametrization of the experimental data. The parameters of the Hamiltonian are found as the functions of the key parameters of the constituent moieties (cubic crystal field and Racah parameters) and the set of transfer parameters implied by the symmetry conditions. These parameters contain also the reduced matrix elements of the creation operators linking many-electron states for normal configuration with those for reduced and oxidized ones. The matrix elements are expressed in terms of one-electron matrix elements, that are calculated with the use of the coefficients of fractional parentage. We have derived also the resonance part of the effective Hamiltonian that is relevant in the optical study of the excited states of the exchange-coupled homonuclear clusters. In the second part of this paper [23] we will demonstrate how the theory of the irreducible tensor operators in  $R_3$  can be applied to the problem of orbitally dependent exchange. In this way we are able to consider the magnetic anisotropy and extend the theory to polynuclear systems.

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### Appendix A. Orbital matrices $O_{\Gamma\gamma}$ in the tetragonal $T_2$ -basis $\xi\eta\zeta$

$$\begin{aligned}
 O_{A_1} &= \begin{pmatrix} \xi & \eta & \zeta \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & O_{E_u} &= \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} & O_{E_v} &= \begin{pmatrix} \sqrt{3}/2 & 0 & 0 \\ 0 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 O_{T_1\alpha} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} \\ 0 & -1/\sqrt{2} & 0 \end{pmatrix} & O_{T_1\beta} &= \begin{pmatrix} 0 & 0 & -1/\sqrt{2} \\ 0 & 0 & 0 \\ 1/\sqrt{2} & 0 & 0 \end{pmatrix} & O_{T_1\gamma} &= \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \\
 O_{T_2\xi} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 \end{pmatrix} & O_{T_2\eta} &= \begin{pmatrix} 0 & 0 & 1/\sqrt{2} \\ 0 & 0 & 0 \\ 1/\sqrt{2} & 0 & 0 \end{pmatrix} & O_{T_2\zeta} &= \begin{pmatrix} 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}
 \end{aligned}$$

### References

- [1] J.H. Van Vleck, *Revista de Matematica y Física Teórica*, Universidad Nacional de Tucuman 14 (1962) 189.
- [2] P.M. Levy, *Phys. Rev. A* 177 (1969) 509.
- [3] P.M. Levy, *Phys. Rev. A* 155 (1964) 135.
- [4] M.V. Eremin, V.N. Kalinenkov, Y.V. Rakitin, *Phys. Status Solidi B* 89 (1978) 503.
- [5] M.V. Eremin, V.N. Kalinenkov, Y.V. Rakitin, *Phys. Status Solidi B* 90 (1978) 123.
- [6] D.I. Khomskii, K.I. Kugel, *Sov. Phys. Usp.* 136 (1982) 231.
- [7] M. Drillon, R. Georges, *Phys. Rev. B* 24 (1981) 1278.
- [8] M. Drillon, R. Georges, *Phys. Rev. B* 26 (1982) 3882.

- [9] B. Leuenberger, H.U. Güdel, *Mol. Phys.* 51 (1984) 1.
- [10] H. Weihe, H.U. Güdel, *Chem. Phys. Lett.* 261 (1996) 123.
- [11] A. Ceulemans, G.A. Heylen, L.F. Chibotaru, L.T. Maes, K. Pierloot, C. Ribbing, L.G. Vanquickenborne, *Inorg. Chim. Acta* 251 (1996) 15.
- [12] O. Kahn, *Molecular Magnetism*, VCH Publishers, New York, 1993.
- [13] J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Pali, B.S. Tsukerblat, *J. Phys. Chem. A* 102 (1998) 200–213.
- [14] J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Pali, B.S. Tsukerblat, *J. Chem. Phys.* 114 (2001) 1148–1165.
- [15] P.W. Anderson, in: G.T. Rado, H. Suhl (Eds.), *Magnetism*, Academic Press, New York, 1963.
- [16] S. Sugano, Y. Tanabe, H. Kamimura, *Multiplets of Transition Metal Ions in Crystals*, Academic Press, London, 1970.
- [17] B.R. Judd, *Second Quantization and Atomic Spectroscopy*, The Johns Hopkins Press, Baltimore, 1967.
- [18] D.A. Varshalovich, A.N. Moskalev, V.K. Khersonskii, *Quantum Theory of Angular Momentum*, World Scientific, Singapore, 1988.
- [19] J.S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups*, Prentice-Hall, New York, 1962.
- [20] T. Damhus, *Mol. Phys.* 50 (1983) 497.
- [21] L.B. Silver, *Irreducible Tensor Methods*, Academic Press, New York, 1976.
- [22] B.S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy*, Academic Press, London, 1994.
- [23] J.J. Borrás-Almenar, J.M. Clemente-Juan, E. Coronado, A.V. Pali, B.S. Tsukerblat, *Chem. Phys.* 274 (2001) 145–163.