Magnetic Exchange between Orbitally Degenerate Ions: A New Development for the Effective Hamiltonian

J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado,* A. V. Palii,[†],* and B. S. Tsukerblat[†]

Departamento Quimica Inorganica, Universidad de Valencia, C/ Dr. Moliner 50, E-46100, Burjassot, Spain

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A new approach to the problem of the kinetic exchange for orbitally degenerate ions is developed. The constituent multielectron metal ions are assumed to be octahedrally coordinated, and strong crystal field scheme is employed, making it possible to take full advantage from the symmetry properties of the fermionic operators and collective electronic states. In the framework of the microscopic approach, the highly anisotropic effective Hamiltonian of the kinetic exchange is constructed in terms of spin operators and standard orbital operators (matrices of the unit cubic irreducible tensors). As distinguished from previous considerations, the effective Hamiltonian is derived for a most general case of the multielectron transition metal ions possessing orbitally degenerate ground states and for arbitrary topology of the system. The overall symmetry of the system is introduced through the restricted set of the one-electron transfer integrals implied by the symmetry conditions. All parameters of the effective Hamiltonian are expressed in terms of the relevant transfer integrals and fundamental parameters of the two moieties, namely crystal field and Racah parameters for the metal ions in their normal, reduced, and oxidized states. The developed approach is applied to two kinds of systems: edge-shared (D_{2h}) and corner-shared (D_{4h}) bioctahedral clusters. In the particular case of d^1 ions ($^2T_2-^2T_2$ problem) the energy pattern in both cases consists of several multiplets splitted by the isotropic part of exchange. In both cases we have found a weak ferromagnetic splitting for several multiplets of the system. This splitting is due to the competition of ferro- and antiferromagnetic contributions arising from the high- and low-spin reduced states in line with Anderson's considerations, Goodenough−Kanamori rules, and McConnell mechanism of ferromagnetic interaction. On the contrary, these weak ferromagnetic interaction are found to coexist with strong ferro- and antiferromagnetic contributions in which only high-spin and low-spin excited states are respectively involved. In addition to these unexpected results in both topologies the ferro- and antiferromagnenic contributions vanish separately for one of the level, the last being thus paramagnetic. These results are in a strike contradiction with the generally accepted point of view on the ferromagnetic role of orbital degeneracy in the magnetic exchange. They also show that the simple qualitative models have a restricted area of applications and that the peculiarities of the exchange problem in the case of orbital degeneracy are much more complicated. The energy pattern of the exchange levels is closely related to the topology of the system and to the network of the one-electron transfer intercenter connections forming effective parameters of the kinetic exchange in the case of orbital degeneracy.

I. Introduction

Heisenberg,[1] Dirac,[2] and Van Vleck (HDVV)[3] showed that the exchange can be described by the effective Hamiltonian

$$\mathbf{H}_{ex} = 2J\,\mathbf{S}_1\mathbf{S}_2$$

expressed in terms of the ionic full spin operators $\mathbf{S}_i$ and multielectron exchange parameter J. The last involves both potential and kinetic exchange contributions in Anderson's terminology.[4] This Hamiltonian is valid for magnetic systems consisting of orbitally nondegenerate ions. A vast variety of polynuclear compounds (exchange clusters), low dimensional systems and extended magnetic materials have been studied in the framework of the HDVV model.[5−11] In this case the isotropic term dominates and the anisotropic contributions (like dipolar and quadrupolar anisotropy, antisymmetric exchange) and also higher order isotropic terms (biquadratic exchange) are relatively small.[10,11] The situation is quite different when the orbital moments of the constituent ions are not strongly quenched by the low-symmetry crystal fields so that the orbital degeneracy remains in a high-symmetric ligand surrounding. This situation is expected to occur in many extended lattices and magnetic molecular systems. As examples we can mention the Ru^{4+} ions in $BaRuO_3$[12] and $(V_2O_{10})^{14-}$.[13] The problem of orbital degeneracy appears also in the compounds where two Ti^{3+} ions are linked by three bridging ligands. One can mention $(Et_2NH_2)_3Ti_2Cl_9$,[14,15] $Cs_3Ti_2Cl_9$,[16,17] and $Cs_3Ti_2Br_9$[18] systems whose magnetic properties have not been interpreted consistently till now. Finally, the dimeric oxo-bridged system $[L_5M-O-ML_5]^{n+}$ (M is the d^2 metal ion), considered recently in ref 19, can be exemplified.

In the case of orbital degeneracy the isotropic spin Hamiltonian (being complemented also by small anisotropic contribu-

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[†] On leave from the Quantum Chemistry Dept., Institute of Chemistry, Academy of Sciences of Moldova, MD-2028 Kishinev, Moldova.

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tions) proves to be invalid even as a zeroth order approximation. The orbital degeneracy creates highly anisotropic interactions and the effective exchange Hamiltonian cannot be expressed in terms of spin operators only and contains orbital operators as well.

Two main trends in derivation of these kinds of Hamiltonians may be noticed, namely, semiempiric and microscopic. In the semiempirical theory the general form of the Hamiltonian may be found applying only point symmetry and time reversal arguments in constructing a general invariant operator involving also interaction of the system with the external (magnetic and electric) fields.[20−22] This semiempirical approach deals with large numbers of independent (from the symmetry point of view) parameters so that the application of the theory to a real material cannot be always meaningful.

The microscopic theory of the exchange interaction between orbitally degenerate ions has been developed by several authors.[22−32] The idea that different orbital states have different exchange parameters was proposed by Van Vleck,[23] and the theory of the potential exchange was worked out by Levy.[25] Effective potential exchange Hamiltonian for orbitally degenerate ions in a strong cubic crystal field scheme is given in refs 31 and 32.

In most cases the kinetic exchange arising from the partial electron delocalization into the excited charge transfer (CT) states is the dominant contribution to the overall exchange parameter. According to the Anderson's concept[4] and Goodenough−Kanamori rules,[33] three different cases should be distinguished: (1) intercenter electron transfer between the half-occupied orbitals giving rise to the antiferromagnetic exchange, (2) transfer from the half-occupied orbital to the empty orbital, and (3) transfer from the double occupied orbitals to the half-filled orbital. In the last two cases, delocalization results in a relatively weak ferromagnetic interaction arising from the competition of ferro- and antiferromagnetic contributions to the overall exchange. The order of the resulting kinetic exchange parameter can be estimated as

$$\frac{t^2}{U-J_0}-\frac{t^2}{U+J_0}\approx\frac{2t^2}{U}\frac{t}{J_0}$$

where t is the intercenter transfer integral, U is the intracenter Coulomb repulsion energy, and J_0 is the intracenter exchange of the mobile electron with the spin core; consequently, $U - J_0$ and $U + J_0$ are the energies of the high-spin and low-spin CT terms. Similar ideas were proposed by McConnell[34] and later by Breslow et al.[35,36] (for review and discussion see refs 9 and 37).

The above conclusions were drawn out in the framework of one-electron (orbital) model. For orbitally degenerate systems the three mentioned cases should be adapted to account for the multielectronic terms of the interacting ions. In fact, only if all orbitals are half-filled (case 1) we deal with orbital singlets and then the HDVV Hamiltonian is applicable. In the other two cases we have empty (or double-occupied) orbitals possessing the same energy as that of other half-filled orbitals. Under this condition the HDVV spin Hamiltonian requires essential modifications.

The complete Hamiltonian for the kinetic exchange between two orbitally degenerate ions was proposed by Drillon and Georges.[29,30] These authors assumed a weak crystal field scheme expressing the generalized Hamiltonian in terms of orbital angular momentum and spin operators. However, this computational procedure proved to be cumbersome so that only relatively simple electronic configurations and topologies can be really considered. In the framework of the used model all reduced (oxidized) ionic spin levels possessing the same site spin were assumed to have equal energies. Therefore, this simplified model did not take into account the complex energy spectrum of transition metal ions described by the Tanabe and Sugano diagrams.[38] A formally similar model with a different mathematical procedure has been developed in ref 39.

The present paper is an attempt to develop a new efficient approach to the problem of kinetic exchange between orbitally degenerate multielectron ions. We will use the important idea of ref 29 of factorization of the full secondary quantized Hamiltonian. However, as distinguished from ref 29, we start with the strong crystal field scheme (with the subsequent allowance of mixing of all configurations). This makes possible the use of symmetry properties of the fermionic operators ref 40 and collective electronic states to the full extent. We will show that taking full advantage of the symmetry one can construct the effective Hamiltonian involving spin operators and standard orbital operators (matrices of the unit cubic irreducible tensors). At the same time, the developed approach allows us to take into account carefully all important CT states using the fundamental parameters of the constituent moieties, namely, the set of relevant crystal field and Racah parameters. In this sense the developed approach is expected to provide the possibility to rationalize the properties of real systems in terms of relevant crystal field parameters determined independently for the constituent magnetic sites (for example, from spectroscopic data). The second important advantage of the developed approach is that the effective Hamiltonian retains its general form for a definite ground term of each individual site, independently of both the overall symmetry of the cluster and the internal structure of the ground states. The overall symmetry requirements are introduced through the set of relevant electron transfer pathways; meanwhile, the internal structure of the multielectron states of d^n ions and CT states determines the effective parameters of the general Hamiltonian. From this point of view it can be said that the suggested effective Hamiltonian provides the same level of generality in the problem of exchange interactions between orbitally degenerate ions as the conventional HDVV Hamiltonian for the nondegenerate spin systems.

The results obtained for two symmetries D_{2h} (edge-shared octahedra) and D_{4h} (corner-shared octahedra) shows that the energy pattern is much more complicated than that obtained in the previous simple models. Finally, in view of the results obtained in the framework of developed multielectron approach, we discuss the applicability of the qualitative results of Anderson's model and Goodenough−Kanamori rules.

II. Derivation of Effective Hamiltonian for Kinetic Exchange

Let us consider a polynuclear system containing identical paramagnetic ions. The ground states of all constituent ions are assumed to be orbitally degenerate and we denote them as $|S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}\rangle$, where S_{igr} is the ground state spin of ith ion and M_{igr} is the spin projection, Γ_{igr} stands for the irreducible representation of the O_h-group, and γ_{igr} enumerates its basis functions.

We are dealing with the transition metal ions in the cubic environments, thus the one-electron basis states in the strong crystal field will be t_2 and e, the corresponding orbitals we denote as $\varphi_{\Gamma_i\gamma_i}$ ($\Gamma_i = t_2$, e, and γ_i enumerate the basis functions).

Kinetic exchange appears in the second order of perturbation procedure with the unperturbed Hamiltonian $\mathbf{H}_0$ including all intracenter interactions and the intercenter one-electron transfer operator **V** playing the role of perturbation. This operator can be represented as a sum of the following two-center contributions:

$$\mathbf{V}(i,j) = \sum_{\Gamma_i\gamma_i}\sum_{\Gamma_j\gamma_j}(\mathbf{V}_{\Gamma_i\gamma_i,\Gamma_j\gamma_j} + \mathbf{V}_{\Gamma_j\gamma_j,\Gamma_i\gamma_i}) \tag{1}$$

Here $\mathbf{V}_{\Gamma_i\gamma_i,\Gamma_j\gamma_j}$ describes the transfer of the electron from the orbital $\varphi_{\Gamma_j\gamma_j}$ of the *j*th center to the orbital $\varphi_{\Gamma_i\gamma_i}$ of the *i*th center:

$$\mathbf{V}_{\Gamma_i\gamma_i,\Gamma_j\gamma_j} = t(\Gamma_i\gamma_i,\Gamma_j\gamma_j)\sum_{\sigma}\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}\mathbf{C}_{\Gamma_j\gamma_j\sigma} \tag{2}$$

where $\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}(\mathbf{C}_{\Gamma_i\gamma_i\sigma})$ creates (annihilates) the electron at the orbital $\varphi_{\Gamma_i\gamma_i}$ with spin projection σ ($\sigma = \uparrow$ or $\downarrow$); $t(\Gamma_j\gamma_j,\Gamma_i\gamma_i)$ is the associated transfer integral. The operator $\mathbf{V}_{\Gamma_j\gamma_j,\Gamma_i\gamma_i}$ describes the inverse transfer process.

Operator $\mathbf{V}(i,j)$ mixes the ground electronic configuration of the pair of ions $\mathrm{d}_i^n - \mathrm{d}_j^n$ with the excited charge transfer configurations $\mathrm{d}_i^{n-1} - \mathrm{d}_j^{n+1}$ and $\mathrm{d}_i^{n+1} - \mathrm{d}_j^{n-1}$. Let $|i, \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle$ be the oxidized states of ion *i* corresponding to the d_i^{n-1} configuration and $|i, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle$ are the reduced states (d_i^{n+1} configuration). Symbols ν and μ are used to enumerate the repeating ${}^{2\bar{S}+1}\bar{\Gamma}$ and ${}^{2\tilde{S}+1}\tilde{\Gamma}$ terms, respectively. The excited CT states can be taken as the products of the states of individual ions, namely, $|i, \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle|j, \tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle$ for $\mathrm{d}_i^{n-1} - \mathrm{d}_j^{n+1}$ configuration and $|i, \nu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle|j,\nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle$ for $\mathrm{d}_i^{n+1} - \mathrm{d}_j^{n-1}$ configuration. These states can be regarded as the excited eigenstates of unperturbed Hamiltonian $\mathbf{H}_0$ (the eigenstates of $\mathbf{H}_0$ belonging to the ground manifold are $|S_{i\mathrm{gr}}\Gamma_{i\mathrm{gr}}M_{i\mathrm{gr}}\gamma_{i\mathrm{gr}}\rangle|S_{j\mathrm{gr}}\Gamma_{j\mathrm{gr}}M_{j\mathrm{gr}}\gamma_{j\mathrm{gr}}\rangle$). Using these notations we can introduce the following effective second-order Hamiltonian for the *ij*-pair which is operative within the ground manifold:

$$\begin{aligned}\mathbf{H}_{\mathrm{ex}}(i,j) = -\sum_{\Gamma_i\Gamma_j\Gamma_i'\Gamma_j'}\sum_{\gamma_i\gamma_j\gamma_i'\gamma_j'}\sum_{\bar{S}\bar{\Gamma}}\sum_{\tilde{S}\tilde{\Gamma}}\sum_{\nu\mu}[\epsilon_\nu(\bar{S}\bar{\Gamma}) +{}\\ \epsilon_\mu(\tilde{S}\tilde{\Gamma})]^{-1}\sum_{\bar{M}\bar{\gamma}}\sum_{\tilde{M}\tilde{\gamma}}[\mathrm{V}_{\Gamma_j\gamma_j,\Gamma_i\gamma_i}|i, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle|j,\\ \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle\,\langle i, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|\langle j, \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}|\mathbf{V}_{\Gamma_i'\gamma_i',\Gamma_j'\gamma_j'} +{}\\ \mathbf{V}_{\Gamma_i\gamma_i,\Gamma_j\gamma_j}|i, \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle|j, \mu\,\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle \times{}\\ \langle i, \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}|\langle j, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|\mathbf{V}_{\Gamma_j'\gamma_j',\Gamma_i'\gamma_i'}]\end{aligned} \tag{3}$$

where $\epsilon_\nu(\bar{S}\bar{\Gamma})$ is the energy of νth ${}^{2\bar{S}+1}\Gamma$-term of the d^{n-1}-ion and $\epsilon_\mu(\tilde{S}\tilde{\Gamma})$ is the energy of μth ${}^{2\bar{S}+1}\Gamma$-term for d^{n+1}-ion. The energy of the ground term of the d^n-ion has been set as the origin of energy. Since *i*th and *j*th ions are assumed to be identical, these energies do not depend on the numbers *i* and *j*.

Following the idea of ref 29 one can represent the two-site operator 3 in terms of the products of one-site operators:

$$\begin{aligned}\mathbf{H}_{\mathrm{ex}}(i,j) = -\sum_{\Gamma_i\Gamma_j}\sum_{\gamma_i\gamma_j\gamma_i'\gamma_j'}\sum_{\bar{S}\bar{\Gamma}}\sum_{\tilde{S}\tilde{\Gamma}}\sum_{\nu\mu}[\epsilon_\nu(\bar{S}\bar{\Gamma}) +{}\\ \epsilon_\mu(\tilde{S}\tilde{\Gamma})]^{-1}t(\Gamma_i\gamma_i,\Gamma_j\gamma_j)t(\Gamma_j\gamma_j,\Gamma_i\gamma_i')\sum_{\bar{M}\bar{\gamma}}\sum_{\tilde{M}\tilde{\gamma}}\sum_{\sigma\sigma'} \times{}\\ [\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}|i, \nu\,\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle\,\langle i, \nu\,\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}|\mathbf{C}_{\Gamma_i\gamma_i'\sigma'}\mathbf{C}_{\Gamma_j\gamma_j\sigma}|j, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle \times{}\\ \langle j, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|\mathbf{C}^{+}_{\Gamma_j\gamma_j'\sigma'} + \mathbf{C}^{+}_{\Gamma_j\gamma_j'\sigma'}|j, \nu\,\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle \times{}\\ \langle j, \nu\,\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}|\mathbf{C}_{\Gamma_j\gamma_j\sigma}\mathbf{C}_{\Gamma_i\gamma_i'\sigma'}|i, \mu\,\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle\,\langle i, \mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}]\end{aligned} \tag{4}$$

In eq 4 we have taken into account that $\Gamma_i = \Gamma_i'$ (both are t_2 or e) and $\Gamma_j = \Gamma_j'$. Due to this condition, the system is apparently returned to the ground manifold after the two transfer processes involved in the second order perturbation procedure.

This Hamiltonian is quite similar to that proposed by Georges and Drillon.[11] The main advantage of such-type Hamiltonian is that it is expressed in terms of one-site operators. Now we can pass from the second quantization representation of the exchange Hamiltonian to the effective Hamiltonian involving standard orbital operators and spin operators. The most efficient way of doing that is to take into account symmetry arguments. First, the creation and annihilation operators behave as an irreducible tensor operator of the rotation group of the rank $^1/_2$ acting in the spin space. Second, the fermionic $\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}$ and $\mathbf{C}_{\Gamma_i\gamma_i\sigma}$ and the corresponding operators[41] $\mathbf{T}^{1/2,\sigma}_{\Gamma_i\gamma_i}$ and $\mathbf{T}^{1/2,-\sigma}_{\Gamma_i\gamma_i}$ are transformed in the space of electronic coordinates like the irreducible tensors of the type of $\Gamma_i\gamma_i$ under the action of point symmetry operations.

Applying this two important points and the Wigner−Eckart theorem[24] we can obtain a general expression for the effective Hamiltonian in function of unit operator I_i, ionic spin operators $\mathbf{S}_i^{1,\mathrm{q}}$, and orbital irreducible tensors $\mathbf{O}^i_{\Gamma\gamma}$. The details of the derivation is given in Appendix I. This Hamiltonian is of the form

$$\begin{aligned}\mathbf{H}_{\mathrm{ex}} = \sum_{i<j}\mathbf{H}_{\mathrm{ex}}(i,j) = -2\sum_{i<j}\sum_{\Gamma_i\Gamma_j}\sum_{\gamma_i\gamma_j\gamma_i'\gamma_j'}\sum_{\Gamma\gamma}\sum_{\Gamma'\gamma'}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma_i'\rangle \times{}\\ \langle\Gamma'\gamma'|\,\Gamma_j\gamma_j\Gamma_j\gamma_j'\rangle\,\mathbf{O}^i_{\Gamma\gamma}\,\mathbf{O}^j_{\Gamma'\gamma'}[U_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j')\,\boldsymbol{I}_i\,\boldsymbol{I}_j +{}\\ J_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j')\,\boldsymbol{S}_i\boldsymbol{S}_j]\end{aligned} \tag{5}$$

where $J_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j')$ is an exchange parameter between the four orbitals involved in the electron transfers (one electron is transferred from $\Gamma_i\gamma_i$ to $\Gamma_j\gamma_j$, and the other from $\Gamma_j\gamma_j'$ to $\Gamma_i\gamma_i'$) and Γ and Γ' denote the irreducible representations coming from the direct products $\Gamma_i \times \Gamma_i = \sum\Gamma$, $\Gamma_j \times \Gamma_j = \sum\Gamma$. $U_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j')$ is an additional spin-independent parameter that accompany the exchange parameter. This parameter is also present in the HDVV Hamiltonian but is omitted because only shifts all energies in a constant. These effective parameters are defined as follows:

$$\begin{aligned}U_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j') = t(\Gamma_i\gamma_i,\Gamma_j\gamma_j)\,t(\Gamma_j\gamma_j',\Gamma_i\gamma_i') \times{}\\ \sum_{\bar{S}\bar{\Gamma}}\sum_{\tilde{S}\tilde{\Gamma}}\sum_{\nu\mu}[\epsilon_\nu(\bar{S}\bar{\Gamma}) + \epsilon_\mu(\tilde{S}\tilde{\Gamma})]^{-1}[a_1^{\Gamma}(\Gamma_i, \nu\bar{S}\bar{\Gamma})b_1^{\Gamma'}(\Gamma_j, \mu\,\tilde{S}\tilde{\Gamma}) +{}\\ a_1^{\Gamma'}(\Gamma_j, \nu\bar{S}\bar{\Gamma})b_1^{\Gamma}(\Gamma_i, \mu\,\tilde{S}\tilde{\Gamma})]\end{aligned}$$

$$\begin{aligned}J_{\Gamma,\Gamma'}(\Gamma_i\gamma_i,\Gamma_j\gamma_j,\Gamma_i\gamma_i',\Gamma_j\gamma_j') ={}\\ -t(\Gamma_i\gamma_i,\Gamma_j\gamma_j)\,t(\Gamma_j\gamma_j',\Gamma_i\gamma_i')\sum_{\bar{S}\bar{\Gamma}}\sum_{\tilde{S}\tilde{\Gamma}}\sum_{\nu\mu}[\epsilon_\nu(\bar{S}\bar{\Gamma}) +{}\\ \epsilon_\mu(\tilde{S}\tilde{\Gamma})]^{-1}[a_2^{\Gamma}(\Gamma_i, \nu\bar{S}\bar{\Gamma})b_2^{\Gamma'}(\Gamma_j, \mu\,\tilde{S}\tilde{\Gamma}) +{}\\ a_2^{\Gamma'}(\Gamma_j, \nu\bar{S}\bar{\Gamma})b_2^{\Gamma}(\Gamma_i, \mu\,\tilde{S}\tilde{\Gamma})]\end{aligned} \tag{6}$$

where the *a*- and *b*-parameters are defined in Appendix I (eq AI.8) and evaluated in Appendix II. The parameters of eqs 6 are expressed in terms of transfer parameters and energies of the different electronic terms involved in the transfers. The *a*- and *b*-parameters, as it is possible to see in Appendix II, depend on the mixing between the different terms, so depend on the single-ion crystal field and the Racah parameters of the individual ions.

The Hamiltonian in eq 5 does not contain any restrictions on the symmetry of the whole system while the constituent moieties are supposed to have a high symmetry (octahedral). The symmetry of the binuclear unit may be introduced implying specific conditions for the transfer parameters *t*'s connecting magnetic orbitals of the interacting ions. This Hamiltonian

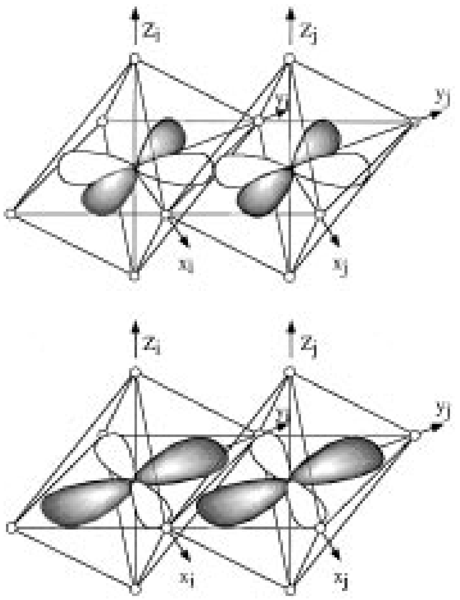

Figure 1. Two main kinds of d−d overlap in the edge-shared bioctahedral cluster: (a) $\zeta-\zeta$ overlap, (b) v−v overlap.

involves two different parts: one spin independent part as direct product of orbital matrices and unit matrices $\mathbf{O}^i_{\Gamma\gamma}\,\mathbf{O}^j_{\Gamma'\gamma'}$, $\mathbf{I}_i\mathbf{I}_j$, and a second spin dependent part as a product of these orbital matrices and the spin matrices $\mathbf{O}^i_{\Gamma\gamma}\,\mathbf{O}^j_{\Gamma'\gamma'}$ $\mathbf{S}_i\mathbf{S}_j$. When $\Gamma,\Gamma' = A_1$ the direct product $\mathbf{O}^i_{\Gamma\gamma}\,\mathbf{O}^j_{\Gamma'\gamma'}$, represents the unit matrix and this Hamiltonian becomes the well-known HDVV Hamiltonian. Only when $\Gamma,\Gamma' \neq A_1$ we obtain highly anisotropic contributions which is inherent to the exchange problem of the orbital degeneracy. The relative importance of the different contributions governing the magnetic properties may be derived for each particular case of $S_{igr}\Gamma_{igr}$, $S_{jgr}\Gamma_{jgr}$ terms and the overall symmetry of the binuclear system. Selected examples will be considered in the following Sections.

III. Kinetic Exchange in Edge-Shared Bioctahedral (D_{2h}) Dimer

In this Section we illustrate the developed formalism considering the particular case of edge-shared bioctahedral cluster of D_{2h} symmetry (Figure 1). We will use the conventional strong crystal field basis for one-electron orbitals

$$\xi \approx yz, \quad \eta \approx y \times z, \quad \zeta \approx xy \qquad (t_2)$$

$$u \approx 3z^2 - r^2, v \approx \sqrt{3}(x^2 - y^2) \qquad (e)$$

In order to adapt the general Hamiltonian of eq 5 to this topology, we should imply the D_{2h} symmetry conditions on the set of transfer integrals. As one can see only two kinds of orbitals overlap in an effective manner, namely, ζ orbitals (Figure 1a) and v-orbitals (Figure 1b). The corresponding transfer integrals will be denoted as $\langle\zeta_j|\mathbf{h}|\zeta_i\rangle \equiv t$, $\langle v_j|\mathbf{h}|\, v_i\rangle \equiv t'$. The $\zeta_i \leftrightarrow \zeta_j$ transfer can be considered as the direct process, meanwhile the transfer involving e-orbitals ($v_i \leftrightarrow v_j$) occurs through the ligands. For the sake of simplicity we will take into consideration only these two sigma pathways neglecting much less efficient allowed pathways, involving ξ, η, and u orbitals.

Under these conditions only the terms with $\Gamma_i\gamma_i = \Gamma_i\gamma_i' = t_2\zeta$, $\Gamma_j\gamma_j = \Gamma_j\gamma_j' = t_2\zeta$ and $\Gamma_i\gamma_i = \Gamma_i\gamma_i' = ev$, $\Gamma_j\gamma_j = \Gamma_j\gamma_j' = ev$ prove to be nonvanishing in the Hamiltonian of eq 5. For the nonzero Clebsch−Gordan coefficients in eq 5, $\Gamma\gamma$, $\Gamma\gamma'$ are A_1, Eu, and Ev,[38] and hence the Hamiltonian can be expressed in terms of the direct products of the orbital operators $\mathbf{O}^i_{A_1}$, $\mathbf{O}^i_{Eu}$, $\mathbf{O}^i_{Ev}$, and scalar product of spin operators. After simple calculations, we arrive at the following Hamiltonian:

$$\begin{aligned}\mathbf{H}_{ex}(i,j) = -\Big[&({}^4/_3U_{EE}(\zeta) + U_{EE}(v))\mathbf{O}^i_{Eu}\,\mathbf{O}^j_{Eu} + \\ &\left(\frac{2\sqrt{2}}{3}U_{A_1E}(\zeta) + U_{A_1E}(v)\right)(\mathbf{O}^i_{A_1}\,\mathbf{O}^j_{Eu} + \mathbf{O}^i_{Eu}\,\mathbf{O}^j_{A_1})\Big]\mathbf{I}_i\mathbf{I}_j - \\ \Big[&({}^2/_3J_{A_1A_1}(\zeta) + J_{A_1A_1}(v))\mathbf{O}^i_{A_1}\mathbf{O}^j_{A_1} + \\ &\left(\frac{4}{3}J_{EE}(\zeta) + J_{EE}(v)\right)\mathbf{O}^i_{Eu}\,\mathbf{O}^j_{Eu} + \\ &\left(\frac{2\sqrt{2}}{3}J_{A_1E}(\zeta) + J_{A_1E}(v)\right)(\mathbf{O}^i_{A_1}\,\mathbf{O}^j_{Eu} + \mathbf{O}^i_{Eu}\,\mathbf{O}^j_{A_1})\Big]\mathbf{S}_i\mathbf{S}_j \qquad (7)\end{aligned}$$

In eqs 7 the short notations $U_{EE}[(t_2\zeta)_i(t_2\zeta)_j(t_2\zeta)_i(t_2\zeta)_j] \equiv U_{EE}(\zeta)$, etc., are used.

The Hamiltonian of eq 7 is apparently invariant under symmetry transformations of D_{2h} point group as well as with respect to the time reversal operation. From this point of view this Hamiltonian is formally similar to the effective Hamiltonian that can be derived on the basis of symmetry arguments only. This last is overparametrized since it contains additional invariant products of $\mathbf{O}_{\Gamma\gamma}$ operators, for example $\mathbf{O}_{T_1\gamma}\mathbf{O}_{T_1\gamma}$ which are odd under time reversions. Each one of these invariant forms is related to an independent (semiempiric) parameter. For D_{2h} symmetry, the number of additional parameters of this kind is equal to 19.

As distinguished from the effective Hamiltonian, derived in the semiempiric way, the Hamiltonian of eq 7 is based on the microscopic theory of kinetic exchange, and therefore it is obtained from the first principles. The main advantage of the microscopic consideration is that it leads to the relationships between the parameters involved in the effective Hamiltonian and reduces considerably the number of the independent parameters. In fact, the $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ parameters are not independent (they only depend on two transfer integrals t and t'). Moreover, under some realistic physical assumptions about the transfer integrals some parameters (along with the allowed operator invariants) do not appear in the Hamiltonian.

The Hamiltonian of eq 7 is valid for all kinds of ground $S_{igr}\Gamma_{igr}$ terms of the constituent ions but the dependence of $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ parameters on the transfer integrals is specific for each ground ionic state. We will focus on the orbital triplets $\Gamma_{igr} = T_2$ or T_1. In this case the operators $\mathbf{O}^i_{\Gamma\gamma}$ are represented by the matrices given in Appendix III.

The Hamiltonian of eq 7 contains only diagonal orbital matrices and hence it can be diagonalized in the spin coupled representation:

$$|S_{igr}\Gamma_{igr}\gamma_{igr}, S_{jgr}\Gamma_{jgr}\gamma_{jgr}, SM\rangle = \sum_{M_{igr}M_{jgr}} \mathbf{C}^{SM}_{S_{igr}M_{igr}S_{jgr}M_{jgr}}|S_{igr}M_{igr}, S_{jgr}M_{jgr}\rangle \qquad (8)$$

Now one can easily obtain the eigenfunctions of the Hamiltonian of eq 7. The energy pattern consists of two groups of accidentally four-fold degenerate levels and one nondegenerate level. The energies of the ${}^{2S+1}\Gamma_d$ terms of the dimer are summarized in Table 1. The parameters U_k and J_k (k = 1, 2, and 3) as a function of $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ parameters are summarized in Table 2.

TABLE 1: Energies of the $^{2S+1}\Gamma_d$ Terms of an Edge-Shared Dimer with Symmetry D_{2h}[a]

terms	energy
$^{2S+1}A_g, {}^{2S+1}B_{3g}, {}^{2S+1}B_{2u}$	$U_1 - J_1[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}A_u, {}^{2S+1}B_{3u}, {}^{2S+1}B_{1g}, {}^{2S+1}B_{2g}$	$U_2 - J_2[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}A_g$	$U_3 - J_3[S(S+1) - 2S_{gr}(S_{gr}+1)]$

[a] S is the total spin of dimer. Γ_d stands for the irreducible representations of D_{2h} group. For two identical ions $S_{igr} = S_{igr} = S_{gr}$ and $S = 0, 1, ..., 2S_{gr}$.

TABLE 2: U_k and J_k Parameters for the Edge-Shared Dimer with Symmetry D_{2h}

parameter	
U_1	$-{}^1/_3U_{EE}(\zeta) + \frac{2\sqrt{2}}{3}U_{A_1E}(\zeta) - {}^1/_4U_{EE}(v) + U_{A_1E}(v)$
U_2	${}^2/_3U_{EE}(\zeta) - \frac{\sqrt{2}}{3}U_{A_1E}(\zeta) + {}^1/_2U_{EE}(v) - {}^1/_2U_{A_1E}(v)$
U_3	$-{}^4/_3U_{EE}(\zeta) - \frac{4\sqrt{2}}{3}U_{A_1E}(\zeta) - U_{EE}(v) - 2U_{A_1E}(v)$
J_1	${}^1/_3J_{A_1A_1}(\zeta) + {}^1/_6J_{EE}(\zeta) - \frac{\sqrt{2}}{3}J_{A_1E}(\zeta) + {}^1/_2J_{A_1A_1}(v) + {}^1/_8J_{EE}(v) - {}^1/_2J_{A_1E}(v)$
J_2	${}^1/_3J_{A_1A_1}(\zeta) - {}^1/_3J_{EE}(\zeta) + \frac{1}{3\sqrt{2}}J_{A_1E}(\zeta) + {}^1/_2J_{A_1A_1}(v) - {}^1/_4J_{EE}(v) + {}^1/_4J_{A_1E}(v)$
J_3	${}^1/_3J_{A_1A_1}(\zeta) + {}^2/_3J_{EE}(\zeta) + \frac{2\sqrt{2}}{3}J_{A_1E}(\zeta) + {}^1/_2J_{A_1A_1}(v) + {}^1/_2J_{EE}(v) + J_{A_1E}(v)$

Inspection of Table 1 shows that the energy spectrum for D_{2h} pair of $S_{igr}\Gamma_{igr}$ ions is formed by two accidentally degenerate electronic levels comprising four terms each and one nondegenerate level. The levels are splitted by the isotropic exchange interactions according to the Lande's rule. This result is general for a D_{2h} pair of transition metal ions possessing orbital ground state triplets and arbitrary S_{gr}. The parameters U_k and J_k can be expressed in terms of the relevant crystal field parameters Dq and Racah parameters A, B, and C defining the energy spectrum of the constituent moieties in their ground, oxidized, and reduced configurations. This task can be solved for each particular ionic $d^nS_{igr}\Gamma_{igr}$ state.

We will illustrate the developed approach taking as an example a simple case of $d_i^1(^2T_2) - d_j^1(^2T_2)$ pair for which all $d^2{-}d^0$ CT states can be found analytically. These charge transfer states represent the products of the oxidized vacuum state (d^0 configuration) denoted by $|0\rangle \equiv |^1A_1\rangle$ and reduced states involving all crystal field $\tilde{S}\tilde{\Gamma}$ states of d^2 configuration ($^3T_1(t_2^2,t_2e)$, $^1E(t_2^2,e^2)$, $^1A_1(t_2^2,e^2)$ and $^1T_2(t_2^2,t_2e)$). The wave functions for the repeating $\tilde{S}\tilde{\Gamma}$ states are given in Appendix IV.

Due to the fact that in the ground state only t_2 shell is populated v ↔ v transfer process is not relevant and the corresponding parameters $U_{EE}(v)$, $U_{A_1E}(v)$, $J_{A_1A_1}(v)$, $J_{EE}(v)$, and $J_{A_1E}(v)$ vanish. The remaining parameters $U_{EE}(\zeta)$, $U_{A_1E}(\zeta)$, $J_{A_1A_1}(\zeta)$, $J_{EE}(\zeta)$, and $J_{A_1E}(\zeta)$ can be found by means of the calculation of the sets of a- and b-parameters with the use of the procedure described in Appendix II. The application of this procedure requires the knowledge of the reduced matrix elements of the fermionic operators involved in eqs AII.5 and AII.6 which can be easily obtained using eqs AII.3 and AII.4 and explicit expressions for the wave functions. Considering, for example, the oxidized (vacuum) state and taking into account eq AII.3 and relation

$$\mathbf{C}^+_{\zeta\uparrow}|0\rangle \equiv \mathbf{C}^+_{\zeta\uparrow}|^1A_1\rangle = |^2T_2, M_{gr} = \frac{1}{2}, \zeta\rangle$$

one finds that

$$\langle^2T_2||\mathbf{T}^{1/2}_{T_2}||^1A_1\rangle = \langle^2T_2, M_{gr} = {}^1/_2, \zeta|\mathbf{C}^+_{\zeta\uparrow}|^1A_1\rangle = 1$$

Substituting this reduced matrix element into eq AII.5 we can calculate any matrix element of one-site operator corresponding to the vacuum state. Particularly, we get

$$\langle^2T_2, M_{gr} = {}^1/_2, \zeta|\mathbf{C}^+_{\zeta\uparrow}\bar{G}(^1A_1)\mathbf{C}_{\zeta\uparrow}|^2T_2, M_{gr} = {}^1/_2, \zeta\rangle = 1 \tag{9}$$

On the other hand, upon applying eq AII.1 the same matrix element can be represented as

$$\frac{1}{\sqrt{3}}a_1^{A_1}(t_2, {}^1A_1) + \frac{1}{2\sqrt{3}}a_2^{A_1}(t_2, {}^1A_1) + \frac{2}{\sqrt{6}}a_1^{E}(t_2, {}^1A_1) + \frac{1}{\sqrt{6}}a_2^{E}(t_2, {}^1A_1) \tag{10}$$

Combining eqs 9 and 10 we obtain one equation containing four unknown a-parameters. The remaining three equations can be obtained in a similar way from other matrix elements. Solving this system of equations we find the four a parameters. They are given in Appendix V (eq AV.1).

In order to find the b-parameters the matrix elements of the one-site operator related to the reduced $\mu\tilde{S}\tilde{\Gamma}$ states (d^2 configuration) should be considered (eqs AII.2 and AII.6). Let us focus, for instance, on the spin-triplet reduced state $|1, {}^3T_1\rangle$. The last includes the contribution of t_2^2 configuration which is represented by the only Slater determinant:[38]

$$|(t_2^2)^3T_1, \tilde{M} = 1, \beta\rangle = -|\xi\zeta| \tag{11}$$

where ξ are ζ are t_2 spin orbitals with spin projections $\sigma = \uparrow$. The creation operator acting on the ground state gives:

$$\mathbf{C}^+_{\zeta\uparrow}|^2T_2, M_{gr} = \frac{1}{2}, \xi\rangle = -|\xi\zeta| \tag{12}$$

Combining eqs 11 and 12 and Appendix II, we get

$$\langle 1, {}^3T_1, \tilde{M} = 1, \beta|\mathbf{C}^+_{\zeta\uparrow}|^2T_2, M_{gr} = \frac{1}{2}, \xi\rangle = \cos\theta \tag{13}$$

Substituting the result into eq A2.4 we obtain for the reduced matrix element

$$\langle 1, {}^3T_1||\mathbf{T}^{1/2}_{T_2}||^2T_2\rangle = -3\sqrt{2}\cos\theta \tag{14}$$

For the second reduced $^3T_1$ state the analogous calculation leads to the following result:

$$\langle 2, {}^3T_1||\mathbf{T}^{1/2}_{T_2}||^2T_2\rangle = -3\sqrt{2}\sin\theta \tag{15}$$

Substituting the reduced matrix element of eq 14 into eq AII.6 one can find all matrix elements of the one-site operator $\mathbf{C}_{\zeta\uparrow}\,\tilde{G}(1, {}^3T_1)\,\mathbf{C}^+_{\zeta\uparrow}$. For example, we have

$$\begin{aligned}
&\langle {}^2\mathrm{T}_2, M_{\mathrm{gr}} = \tfrac{1}{2}, \xi | \mathbf{C}_{\zeta\uparrow}\, \tilde{G}(1, {}^3\mathrm{T}_1)\, \mathbf{C}^{+}_{\zeta\uparrow} | {}^2\mathrm{T}_2, M_{\mathrm{gr}} = \tfrac{1}{2}, \xi \rangle = \cos^2\theta \\
&\langle {}^2\mathrm{T}_2, M_{\mathrm{gr}} = -\tfrac{1}{2}, \xi | \mathbf{C}_{\zeta\uparrow}\, \tilde{G}(1, {}^3\mathrm{T}_1)\, \mathbf{C}^{+}_{\zeta\uparrow} | {}^2\mathrm{T}_2, M_{\mathrm{gr}} = -\tfrac{1}{2}, \xi \rangle = \tfrac{1}{2}\cos^2\theta \\
&\langle {}^2\mathrm{T}_2, M_{\mathrm{gr}} = \tfrac{1}{2}, \zeta | \mathbf{C}_{\zeta\uparrow}\, \tilde{G}(1, {}^3\mathrm{T}_1)\, \mathbf{C}^{+}_{\zeta\uparrow} | {}^2\mathrm{T}_2, M_{\mathrm{gr}} = \tfrac{1}{2}, \zeta \rangle = 0 \\
&\langle {}^2\mathrm{T}_2, M_{\mathrm{gr}} = -\tfrac{1}{2}, \zeta | \mathbf{C}_{\zeta\uparrow}\, \tilde{G}(1, {}^3\mathrm{T}_1)\, \mathbf{C}^{+}_{\zeta\uparrow} | {}^2\mathrm{T}_2, M_{\mathrm{gr}} = -\tfrac{1}{2}, \zeta \rangle = 0
\end{aligned} \tag{16}$$

The matrix elements of the operator $\mathbf{C}_{\zeta\uparrow}\, \tilde{G}(2, {}^3\mathrm{T}_1)\, \mathbf{C}^{+}_{\zeta\uparrow}$ related to the second reduced state of ${}^3\mathrm{T}_1$ type are obtained from the corresponding matrix elements of eq 16 by means of the change $\cos^2\theta \rightarrow \sin^2\theta$. Expressing the same matrix elements through the parameters $b_1^{\Gamma}(\mathrm{t}_2, \mu\ {}^3\mathrm{T}_1)$ and $b_2^{\Gamma}(\mathrm{t}_2, \mu\ {}^3\mathrm{T}_1)$ ($\mu = 1$ and 2) according to eq AII.2 and solving the systems of linear equations obtained in this way one gets the *b*-parameters associated to the ${}^3\mathrm{T}_1$ state (see Appendix V eq AV.2). The *b*-parameters associated to the reduced states ${}^1\mathrm{A}_1$, ${}^1\mathrm{E}$, ${}^1\mathrm{T}_2$ can be calculated in a similar way. They are given by eqs AV.3–AV.5.

Substituting *a*- and *b*-parameters into the definitions of eqs 6 we find the $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ parameters of the effective Hamiltonian expressed in terms of the transfer integral *t*, Dq parameter and Racah parameters of d^2-ion. These are summarized in Table 3.

For the sake of simplicity, the difference between the orbital t_2 energies in d^1 and d^2-ions is neglected. That is why the excitation energies in Table 3 are roughly associated with the energies of $\mu\tilde{S}\tilde{\Gamma}$ terms of d^2-ion in cubic crystal field. It should be stressed that all these energies must be supplemented by an additive contribution equal to the Racah parameter *A* (analog to the Coulomb energy *U* in Anderson's theory).

Finally, introducing the $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ parameters (Table 3) into the formulas of Table 2 we arrive at the final expressions for U_k and J_k (Table 4) defining the energies for the ${}^2\mathrm{T}_2 - {}^2\mathrm{T}_2$ edge-shared pair.

In Figure 2, we have plotted the energy pattern for this kind of exchange-coupled systems. As parameters we have used the Racah parameters calculated for free Ti^{2+} ion in ref 42: $A = 141\,000$ cm^{-1}, $B = 900$ cm^{-1}, $C = 3300$ cm^{-1} (these values are close to those found in octahedral crystal field[38]). The cubic field splitting parameter Dq is taken to be Dq = 1000 cm^{-1} that is typical for divalent metal ions.[38] The transfer parameter is taken to be $t = 4000$ cm^{-1} (this is within the Anderson's estimation[4]). The spin-independent part of the effective Hamiltonian splits the nine orbital states of the pair in three sets of levels. The accidentally degenerate group of levels I comprising the orbital states $\mathrm{A_u}$, $\mathrm{B_{3u}}$, $\mathrm{B_{1g}}$, and $\mathrm{B_{2g}}$ proves to be the ground one. The first excited level II is the nondegenerate $\mathrm{A_g}$. The highest excited group of levels III comprises the orbital states $2\mathrm{A_g}$, $\mathrm{B_{3g}}$, and $\mathrm{B_{2u}}$.

Let us focus now on the effect of the spin-dependent part of the Hamiltonian. Table 4 allows to make an important conclusion concerning the general feature of the exchange splittings in the system under consideration. The degenerate levels in group I splits under the influence of a weak ferromagnetic contribution ($J_2 > 0$) coming from the mixture of these dimer terms with the excited spin singlet $2{}^1\mathrm{T}_2$ and the spin triplet $2{}^3\mathrm{T}_1$ terms of the d^2 configuration. For group II we observe a strong antiferromagnetic splitting ($J_3 \sim -210$ cm^{-1}) since only spin singlet states contribute to this parameter ($2{}^1\mathrm{A}_1$, $2{}^1\mathrm{E}$). As a result, the singlet level of this group is strongly stabilized and becomes the ground state of the system. Finally, for group III we observe no exchange splitting ($J_1 = 0$), so this group represent a paramagnetic mixture of singlet and triplet states. It should be stressed that the ferromagnetic effect in group I arising from two competing interactions is much weaker than the antiferromagnetic interaction in the group II where only spin singlets contribute and therefore the ground state of the system is antiferromagnetic. In spite of the fact that the exchange splitting in each group of levels can be described by the Lande's rule, the general pattern is much more complicated comparatively to the simple Heisenberg scheme due to the interpenetration of several groups of levels.

IV. Kinetic Exchange in Corner-Shared Bioctahedral (D_{4h}) Cluster

Now we will consider briefly the corner-shared bioctahedral system of D_{4h} symmetry. In this case it is reasonable to neglect all transfer integrals with the exception of $\langle \xi_j | \mathbf{h} | \xi_i \rangle = \langle \eta_j | \mathbf{h} | \eta_i \rangle \equiv t$ and $\langle \mathrm{u}_j | \mathbf{h} | \mathrm{u}_i \rangle \equiv t'$ that involves efficiently overlapping orbitals (Figure 3a,b). Implying these conditions on the Hamiltonian of eq 5 we obtain after some rearrangements:

$$\begin{aligned}
\mathbf{H}_{\mathrm{ex}}(i,j) = \Bigg[&-\left(\frac{1}{3}[U_{\mathrm{EE}}(\xi) + U_{\mathrm{EE}}(\eta)] + U_{\mathrm{EE}}(\mathrm{u})\right)\mathbf{O}^{i}_{\mathrm{Eu}}\, \mathbf{O}^{j}_{\mathrm{Eu}} - \\
&[U_{\mathrm{EE}}(\xi) + U_{\mathrm{EE}}(\eta)]\mathbf{O}^{i}_{\mathrm{Ev}}\, \mathbf{O}^{j}_{\mathrm{Ev}} + \left(\frac{\sqrt{2}}{3}[U_{\mathrm{A_1E}}(\xi) + U_{\mathrm{A_1E}}(\eta)] + \right. \\
&\left. U_{\mathrm{A_1E}}(\mathrm{u})\right)(\mathbf{O}^{i}_{\mathrm{A_1}}\, \mathbf{O}^{j}_{\mathrm{Eu}} + \mathbf{O}^{i}_{\mathrm{Eu}}\, \mathbf{O}^{j}_{\mathrm{A_1}}) - 2U_{\mathrm{T_1T_1}}(\xi\eta)\mathbf{O}^{i}_{\mathrm{T_1}\gamma}\, \mathbf{O}^{j}_{\mathrm{T_1}\gamma} - \\
&2U_{\mathrm{T_2T_2}}(\xi\eta)\mathbf{O}^{i}_{\mathrm{T_2}\zeta}\, \mathbf{O}^{j}_{\mathrm{T_2}\zeta}\Bigg]\mathbf{I}_i\mathbf{I}_j + \Bigg[-\left(\frac{2}{3}[J_{\mathrm{A_1A_1}}(\xi) + J_{\mathrm{A_1A_1}}(\eta)] + \right. \\
&\left. J_{\mathrm{A_1A_1}}(\mathrm{u})\right)\mathbf{O}^{i}_{\mathrm{A_1}}\, \mathbf{O}^{j}_{\mathrm{A_1}} - \left(\frac{1}{3}[J_{\mathrm{EE}}(\xi) + J_{\mathrm{EE}}(\eta)] + \right. \\
&\left. J_{\mathrm{EE}}(\mathrm{u})\right)\mathbf{O}^{i}_{\mathrm{Eu}}\, \mathbf{O}^{j}_{\mathrm{Eu}} - [J_{\mathrm{EE}}(\xi) + J_{\mathrm{EE}}(\eta)]\mathbf{O}^{i}_{\mathrm{Ev}}\, \mathbf{O}^{j}_{\mathrm{Ev}} + \\
&\left(\frac{\sqrt{2}}{3}[\mathrm{J}_{\mathrm{A_1E}}(\xi) + J_{\mathrm{A_1E}}(\eta)] + J_{\mathrm{A_1E}}\,(\mathrm{u})\right)(\mathbf{O}^{i}_{\mathrm{A_1}}\, \mathbf{O}^{j}_{\mathrm{Eu}} + \\
&\mathbf{O}^{i}_{\mathrm{Eu}}\, \mathbf{O}^{j}_{\mathrm{A_1}})2J_{\mathrm{T_1T_1}}(\xi\eta)\mathbf{O}^{i}_{\mathrm{T_1}\gamma}\, \mathbf{O}^{j}_{\mathrm{T_1}\gamma} - 2J_{\mathrm{T_2T_2}}(\xi\eta)\mathbf{O}^{i}_{\mathrm{T_2}\zeta}\, \mathbf{O}^{j}_{\mathrm{T_2}\zeta}\Bigg]\mathbf{S}_i\mathbf{S}_j
\end{aligned} \tag{17}$$

where the short notations $U_{\Gamma\Gamma'}[(\mathrm{t}_2\xi)_i(\mathrm{t}_2\xi)_j(\mathrm{t}_2\eta)_i(\mathrm{t}_2\eta)_j] = U_{\Gamma\Gamma'}[(\mathrm{t}_2\eta)_i(\mathrm{t}_2\eta)_j(\mathrm{t}_2\xi)_i(\mathrm{t}_2\xi)_j] \equiv U_{\Gamma\Gamma'}(\xi\eta)$, etc., are used.

As distinguished from the Hamiltonian of eq 7 related to the bioctahedral edge-shared cluster the Hamiltonian of eq 17 proves to be nondiagonal in the basis (eq 8) due to the terms containing bilinear operator forms $\mathbf{O}^{i}_{\mathrm{T_1}\gamma}\mathbf{O}^{j}_{\mathrm{T_1}\gamma}$ and $\mathbf{O}^{i}_{\mathrm{T_2}\zeta}\mathbf{O}^{j}_{\mathrm{T_2}\zeta}$. The diagonalization can be easily performed using symmetry adapted basis, the results are summarized in Table 5 in function of the U_k and J_k parameters given in Table 6. While deriving Table 6 we took into account that $U_{\Gamma\Gamma'}(\eta) = U_{\Gamma\Gamma'}(\xi)$ and $J_{\Gamma\Gamma'}(\eta) = J_{\Gamma\Gamma'}(\xi)$ due to the equivalence of two kinds of electron transfer $\xi \leftrightarrow \xi$ and $\eta \leftrightarrow \eta$.

Table 5 shows that the energy pattern of bioctahedral D_{4h} cluster with the ground orbital triplets of constituent ions includes six levels split by the isotropic exchange. Five of them represent the orbital singlets and one is accidentally degenerate comprising two orbital doublets ($\mathrm{E_g}$ and $\mathrm{E_u}$).

Now we will consider again the particular case of ${}^2\mathrm{T}_2$–${}^2\mathrm{T}_2$ pair. In this case the u $\leftrightarrow$ u transfer does not participate in the second order process and hence the parameters $U_{\mathrm{EE}}(\mathrm{u})$, $U_{\mathrm{A_1E}}(\mathrm{u})$, $J_{\mathrm{A_1A_1}}(\mathrm{u})$, $J_{\mathrm{EE}}(\mathrm{u})$, and $J_{\mathrm{A_1E}}(\mathrm{u})$ should be omitted in Table 6.

TABLE 3: $U_{\Gamma\Gamma'}$ and $J_{\Gamma\Gamma'}$ Parameters for $^2T_2-^2T_2$ Edge-Shared Dimer[a]

$U_{EE}(\zeta)$	$t^2\left[-\frac{\cos^2\theta}{2\epsilon_1(^3T_1)}-\frac{\sin^2\theta}{2\epsilon_2(^3T_1)}+\frac{\cos^2\alpha}{9\epsilon_1(^1A_1)}+\frac{\sin^2\alpha}{9\epsilon_2(^1A_1)}+\frac{2\cos^2\beta}{9\epsilon_1(^1E)}+\frac{2\sin^2\beta}{9\epsilon_2(^1E)}-\frac{\cos^2\delta}{6\epsilon_1(^1T_2)}-\frac{\sin^2\delta}{6\epsilon_2(^1T_2)}\right]$
$U_{A_1E}(\zeta)$	$t^2\left[\frac{\cos^2\theta}{4\sqrt{2}\epsilon_1(^3T_1)}+\frac{\sin^2\theta}{4\sqrt{2}\epsilon_2(^3T_1)}+\frac{\cos^2\alpha}{9\sqrt{2}\epsilon_1(^1A_1)}+\frac{\sin^2\alpha}{9\sqrt{2}\epsilon_2(^1A_1)}+\frac{2\cos^2\beta}{9\sqrt{2}\epsilon_1(^1E)}+\frac{2\sin^2\beta}{9\sqrt{2}\epsilon_2(^1E)}+\frac{\cos^2\delta}{12\sqrt{2}\epsilon_1(^1T_2)}+\frac{\sin^2\delta}{12\sqrt{2}\epsilon_2(^1T_2)}\right]$
$J_{A_1A_1}(\zeta)$	$-t^2\left[-\frac{2\cos^2\theta}{3\epsilon_1(^3T_1)}-\frac{2\sin^2\theta}{3\epsilon_2(^3T_1)}+\frac{2\cos^2\alpha}{9\epsilon_1(^1A_1)}+\frac{2\sin^2\alpha}{9\epsilon_2(^1A_1)}+\frac{4\cos^2\beta}{9\epsilon_1(^1E)}+\frac{4\sin^2\beta}{9\epsilon_2(^1E)}+\frac{2\cos^2\delta}{3\epsilon_1(^1T_2)}+\frac{2\sin^2\delta}{3\epsilon_2(^1T_2)}\right]$
$J_{EE}(\zeta)$	$-t^2\left[\frac{2\cos^2\theta}{3\epsilon_1(^3T_1)}+\frac{2\sin^2\theta}{3\epsilon_2(^3T_1)}+\frac{4\cos^2\alpha}{9\epsilon_1(^1A_1)}+\frac{4\sin^2\alpha}{9\epsilon_2(^1A_1)}+\frac{8\cos^2\beta}{9\epsilon_1(^1E)}+\frac{8\sin^2\beta}{9\epsilon_2(^1E)}-\frac{2\cos^2\delta}{3\epsilon_1(^1T_2)}-\frac{2\sin^2\delta}{3\epsilon_2(^1T_2)}\right]$
$J_{A_1E}(\zeta)$	$-t^2\left[-\frac{\cos^2\theta}{3\sqrt{2}\epsilon_1(^3T_1)}-\frac{\sin^2\theta}{3\sqrt{2}\epsilon_2(^3T_1)}+\frac{4\cos^2\alpha}{9\sqrt{2}\epsilon_1(^1A_1)}+\frac{4\sin^2\alpha}{9\sqrt{2}\epsilon_2(^1A_1)}+\frac{8\cos^2\beta}{9\sqrt{2}\epsilon_1(^1E)}+\frac{8\sin^2\beta}{9\sqrt{2}\epsilon_2(^1E)}+\frac{\cos^2\delta}{3\sqrt{2}\epsilon_1(^1T_2)}+\frac{\sin^2\delta}{3\sqrt{2}\epsilon_2(^1T_2)}\right]$

[a] The energies (without A) can be taken directly from the Tanabe–Sugano diagrams (the matrices for the repeated terms are given in ref 38, p 294). The mixing coefficients (defined by α, β, θ, and δ angles) are given in Appendix II.

TABLE 4: U_k and J_k Parameters for $^2T_2-^2T_2$ Edge-Shared Dimer Expressed in Function of Transfer Parameter and Energies

U_1	$t^2\left[\frac{\cos^2\theta}{3\epsilon_1(^3T_1)}+\frac{\sin^2\theta}{3\epsilon_2(^3T_1)}+\frac{\cos^2\alpha}{27\epsilon_1(^1A_1)}+\frac{\sin^2\alpha}{27\epsilon_2(^1A_1)}+\frac{2\cos^2\beta}{27\epsilon_1(^1E)}+\frac{2\sin^2\beta}{27\epsilon_2(^1E)}+\frac{\cos^2\delta}{9\epsilon_1(^1T_2)}+\frac{\sin^2\delta}{9\epsilon_2(^1T_2)}\right]$
U_2	$t^2\left[-\frac{5\cos^2\theta}{12\epsilon_1(^3T_1)}-\frac{5\sin^2\theta}{12\epsilon_2(^3T_1)}+\frac{\cos^2\alpha}{27\epsilon_1(^1A_1)}+\frac{\sin^2\alpha}{27\epsilon_2(^1A_1)}+\frac{2\cos^2\beta}{27\epsilon_1(^1E)}+\frac{2\sin^2\beta}{27\epsilon_2(^1E)}-\frac{5\cos^2\delta}{36\epsilon_1(^1T_2)}-\frac{5\sin^2\delta}{36\epsilon_2(^1T_2)}\right]$
U_3	$t^2\left[\frac{\cos^2\theta}{3\epsilon_1(^3T_1)}+\frac{\sin^2\theta}{3\epsilon_2(^3T_1)}-\frac{8\cos^2\alpha}{27\epsilon_1(^1A_1)}-\frac{8\sin^2\alpha}{27\epsilon_2(^1A_1)}-\frac{16\cos^2\beta}{27\epsilon_1(^1E)}-\frac{16\sin^2\beta}{27\epsilon_2(^1E)}+\frac{\cos^2\delta}{9\epsilon_1(^1T_2)}+\frac{\sin^2\delta}{9\epsilon_2(^1T_2)}\right]$
J_1	0
J_2	$\frac{t^2}{2}\left[\frac{\cos^2\theta}{\epsilon_1(^3T_1)}+\frac{\sin^2\theta}{\epsilon_2(^3T_1)}-\frac{\cos^2\delta}{\epsilon_1(^1T_2)}-\frac{\sin^2\delta}{\epsilon_2(^1T_2)}\right]$
J_3	$-\frac{2t^2}{3}\left[\frac{\cos^2\alpha}{\epsilon_1(^1A_1)}+\frac{\sin^2\alpha}{\epsilon_2(^1A_1)}+\frac{2\cos^2\beta}{\epsilon_1(^1E)}+\frac{2\sin^2\beta}{\epsilon_2(^1E)}\right]$

In addition to the a-, and b-parameters already calculated (eqs AV.1–AV.5) some new kinds of these parameters appear for the D_{4h} topology. The results for them are given in the Appendix V (eqs AV.6–AV.10). Substituting a- and b-parameters into Table 6 we express U_k and J_k parameters through the transfer integral t and the set of the ionic energy spectrum parameters. The results are in Table 7.

The energy pattern for $^2T_2-^2T_2$ corner-shared pair (D_{4h} topology) calculated for the same set of parameters as in the edge-shared dimer (D_{2h} topology) is shown in Figure 4. In this case the spin-independent part of the Hamiltonian leads to a splitting of the dimer terms in six levels. These are further splitted under the action of spin-dependent part of the Hamiltonian in such a way that several terms ($^{1,3}B_{2u}$, $^{1,3}B_{1g}$, $^{1,3}A_{1g}$) split in a antiferromagnetic fashion (J_1, J_2, J_4 < 0), others ($^{1,3}E_u$, $^{1,3}E_g$, $^{1,3}A_{1u}$) in a ferromagnetic one (J_3, J_5 > 0), and the term $^{1,3}A_{1g}$ do not split ($J_6 = 0$). The ferromagnetic parameter J_3 is the largest one ($J_3 \approx 235$ cm^{-1}) due to the fact that J_3 does not contain competitive antiferromagnetic terms (Table 7). Thus, the term $^3A_{1u}$ proves to be the ground one and the dimer is expected to be ferromagnetic. The next excited level $^{1,3}E_u$, $^{1,3}E_g$ (accidentally degenerate) exhibits a weak ferromagnetic splitting ($J_5 \approx 5$ cm^{-1}) due to the competition of ferromagnetic (coming from 2^3T_1 terms in CT spectrum) and antiferromagnetic (coming from 2^1T_2 terms) contributions. The next terms $^{1,3}B_{2u}$, $^{1,3}B_{1g}$, $^{1,3}A_{1g}$ are very close in energy and the corresponding exchange interactions are strongly antiferromagnetic ($J_1 \approx J_2 \approx J_4 \approx -216$ cm^{-1}) due to the contribution of different low-spin excited states. It is remarkable that all spin triplets arising from antiferromagnetically split levels coincide with the nonsplitted $^{1,3}A_{1g}$ level.

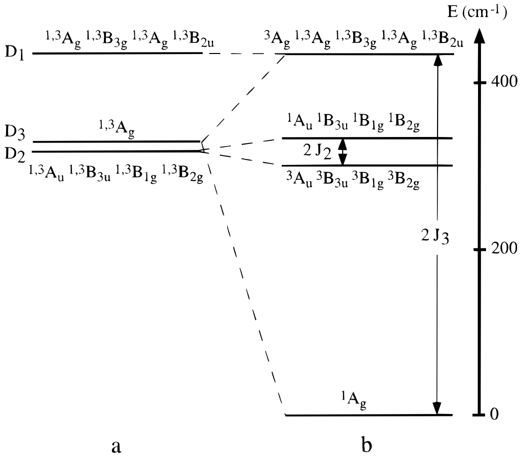

Figure 2. Energy pattern of the edge-shared bioctahedral (D_{2h}) cluster consisting of one-electron ions: (a) spin-independent splitting, (b) spin-dependent splitting.

V. Concluding Remarks

In this paper we have presented a new approach to the problem of kinetic exchange for orbitally degenerate ions. The constituent metal ions are supposed to be octahedrally coordinated (although the general expressions do not restrict in this point), and strong crystal field scheme is employed. The highly

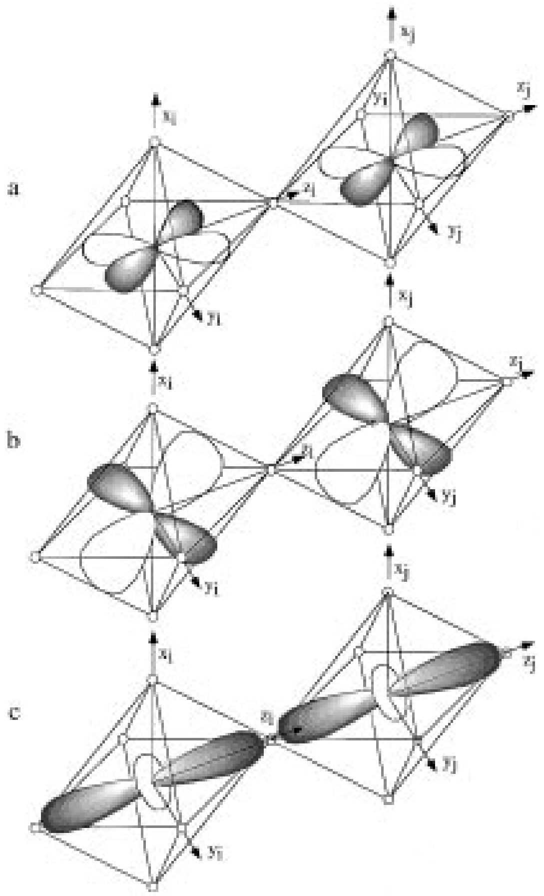

Figure 3. Three main kinds of d−d overlap in the corner-shared bioctahedral cluster: (a) $\xi-\xi$ overlap, (b) $\eta-\eta$ overlap, (c) u−u overlap.

TABLE 5: Energies of the $^{2S+1}\Gamma_d$ Terms of an Corner-Shared Dimer with Symmetry D_{4h}[a]

terms	energy
$^{2S+1}A_{1g}$	$U_1 - J_1[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}B_{1g}$	$U_2 - J_2[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}A_{1u}$	$U_3 - J_3[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}B_{2u}$	$U_4 - J_4[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}E_u, {}^{2S+1}E_g$	$U_5 - J_5[S(S+1) - 2S_{gr}(S_{gr}+1)]$
$^{2S+1}A_{1g}$	$U_6 - J_6[S(S+1) - 2S_{gr}(S_{gr}+1)]$

[a] S is the total spin of dimer; Γ_d stands for the irreducible representations of D_{4h} group. For two identical ions $S_{igr} = S_{igr} = S_{gr}$ and S = 0, 1, ..., $2S_{gr}$.

anisotropic effective Hamiltonian of the kinetic exchange is expressed in terms of standard matrices of the unit irreducible cubic tensors acting in the space of orbital functions and spin operators. Starting from the definite ground terms $S_{gr}\Gamma_{gr}$ of building blocks (octahedral subunits), we construct the most general form of the effective Hamiltonian containing orbital operators $\mathbf{O}_{\Gamma\gamma}$ (with $\Gamma \in \Gamma_{gr} \times \Gamma_{gr}$) and spin operators.

The parameters of the exchange Hamiltonian are expressed in terms of the fundamental parameters of the monomeric subunits and a set of one-electron transfer parameters. The problem of eigenstates and spin vectors for each octahedral site is supposed to be solved with due accuracy. In the framework of crystal field theory we are dealing with the cubic field splitting and Racah parameters that can be determined independently, for instance, from spectroscopic data. The effects of covalency can be also included in the evaluation of the effective Hamiltonian parameters if the corresponding data about the internal structure of monomeric subunits are available.

The overall symmetry of the system is implied by the restricted set of the transfer parameters. The suggested approach can be applied not only to the ground states of interacting ions but also to their excited states. This could be useful, for example, in the problem of optical spectroscopy of this type of exchange dimer.

In order to illustrate the mathematical procedure and some consequences of the exchange in the case of orbital degeneracy we have considered two cases: edge-shared (D_{2h}) and corner-shared (D_{4h}) octahedral dimers. For both cases the effective Hamiltonian was derived for arbitrary $S_{gr}\Gamma_{gr}$ terms. As distinguished from the general (semiempirical) Hamiltonian, based on the point symmetry and time reversal arguments, the Hamiltonian derived in the framework of microscopic approach proves to be much more simple. In fact, the number of parameters entering in the last Hamiltonian is much less, moreover all these parameters are not independent and are expressed in terms of two transfer integrals.

In particular case of d^1-ions ($^2T_2$ ground terms) we have found unexpected features of the exchange splitting contradicting the conventional points of view on the role of degeneracy. In both cases (D_{2h} and D_{4h}) we found a weak ferromagnetic splitting for several multiplets of the system. The exchange parameter for these multiplets is formed by competitive ferro- and antiferromagnetic contributions arising from high- and low-spin reduced states. This result is in compliance with Anderson's definition of third-order effect ($J_{ferro} \approx (t^2/U)(t/J_0)$) and Goodenough−Kanamori rules. At the same time, in the edge-shared system strong antiferromagnetic interaction (coming from low-spin excited terms, only) was found for a group of multiplets giving rise to an antiferromagnetic ground state for the dimer. In the corner-shared system we have found one strong ferromagnetic interaction (coming from high-spin states only and giving rise to a ferromagnetic ground state of the dimer), and two strong antiferromagnetic interaction (arising from low-spin excited states). These conclusions show that McConell mechanism of ferromagnetic interaction for orbitally degenerate subunits can be invalid under some conditions. The results show also that the simple qualitative models have a restricted area of application for the high-symmetric exchange system possessing orbital degeneracy.

In this article we have not considered the third actual topology of the dimer, namely, face-shared dimer. We are aimed to consider this problem elsewere with particular emphasis on the magnetic data concerning $[Ti_2Cl_9]^{3-}$ dimers and the contradictory theoretical conclusions of refs 30 and 39. The other problem we are going to address to is the exchange interaction between orbitally degenerate ions Fe^{2+} and Co^{2+}. Many clusters of this kind are known that requires the development of a rigorous exchange model taking into account the orbital momentum contributions. Notice in particular the series of high-symmetrical M_4 clusters embedded in polyoxometalate frameworks of the type $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ recently characterized by us from magnetic susceptibility and inelastic neutron scattering spectroscopy (see review article ref 43 and references therein). Finally, it should be noted that in our consideration we were intended mainly to derive the effective Hamiltonian for the kinetic exchange and to illustrate the mathematical procedure. For this reason we have neglected spin−orbital interaction that can be important for orbital triplets and should be taken into account in discussion of experimental data along with low symmetry crystal fields. From the computational point of view these problems dealing with one-center interactions do not present difficulties and will be considered in the next future.

TABLE 6: U_k and J_k Parameters for the Corner-Shared Dimer with Symmetry D_{4h}

U_1	$-{}^{5}/_{3}U_{\mathrm{EE}}(\xi) - \frac{4}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) + U_{\mathrm{T_1T_1}}(\xi\eta) + U_{\mathrm{T_2T_2}}(\xi\eta) - {}^{1}/_{4}U_{\mathrm{EE}}(\mathrm{u}) - U_{\mathrm{A_1E}}(\mathrm{u})$
U_2	$-{}^{5}/_{3}U_{\mathrm{EE}}(\xi) - \frac{4}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) - U_{\mathrm{T_1T_1}}(\xi\eta) - U_{\mathrm{T_2T_2}}(\xi\eta) - {}^{1}/_{4}U_{\mathrm{EE}}(\mathrm{u}) - U_{\mathrm{A_1E}}(\mathrm{u})$
U_3	${}^{4}/_{3}U_{\mathrm{EE}}(\xi) - \frac{4}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) - U_{\mathrm{T_1T_1}}(\xi\eta) + U_{\mathrm{T_2T_2}}(\xi\eta) - {}^{1}/_{4}U_{\mathrm{EE}}(\mathrm{u}) - U_{\mathrm{A_1E}}(\mathrm{u})$
U_4	${}^{4}/_{3}U_{\mathrm{EE}}(\xi) - \frac{4}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) + U_{\mathrm{T_1T_1}}(\xi\eta) - U_{\mathrm{T_2T_2}}(\xi\eta) - {}^{1}/_{4}U_{\mathrm{EE}}(\mathrm{u}) - U_{\mathrm{A_1E}}(\mathrm{u})$
U_5	${}^{1}/_{3}U_{\mathrm{EE}}(\xi) + \frac{2}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) + {}^{1}/_{2}U_{\mathrm{EE}}(\mathrm{u}) + {}^{1}/_{2}U_{\mathrm{A_1E}}(\mathrm{u})$
U_6	$-{}^{2}/_{3}U_{\mathrm{EE}}(\xi) + \frac{8}{3\sqrt{2}}U_{\mathrm{A_1E}}(\xi) - U_{\mathrm{EE}}(\mathrm{u}) + 2U_{\mathrm{A_1E}}(\mathrm{u})$
J_1	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) + {}^{5}/_{6}J_{\mathrm{EE}}(\xi) + \frac{2}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) - {}^{1}/_{2}U_{\mathrm{T_1T_1}}(\xi\eta) - {}^{1}/_{2}J_{\mathrm{T_2T_2}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) + {}^{1}/_{8}J_{\mathrm{EE}}(\mathrm{u}) + {}^{1}/_{2}J_{\mathrm{A_1E}}(\mathrm{u})$
J_2	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) + {}^{5}/_{6}J_{\mathrm{EE}}(\xi) + \frac{2}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) + {}^{1}/_{2}U_{\mathrm{T_1T_1}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{T_2T_2}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) + {}^{1}/_{8}J_{\mathrm{EE}}(\mathrm{u}) + {}^{1}/_{2}J_{\mathrm{A_1E}}(\mathrm{u})$
J_3	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) - {}^{2}/_{3}J_{\mathrm{EE}}(\xi) + \frac{2}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) + {}^{1}/_{2}J_{\mathrm{T_1T_1}}(\xi\eta) - {}^{1}/_{2}J_{\mathrm{T_2T_2}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) + {}^{1}/_{8}J_{\mathrm{EE}}(\mathrm{u}) + {}^{1}/_{2}J_{\mathrm{A_1E}}(\mathrm{u})$
J_4	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) - {}^{2}/_{3}J_{\mathrm{EE}}(\xi) + \frac{2}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) - {}^{1}/_{2}J_{\mathrm{T_1T_1}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{T_2T_2}}(\xi\eta) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) + {}^{1}/_{8}J_{\mathrm{EE}}(\mathrm{u}) + {}^{1}/_{2}J_{\mathrm{A_1E}}(\mathrm{u})$
J_5	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) - {}^{1}/_{6}J_{\mathrm{EE}}(\xi) - \frac{1}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) - {}^{1}/_{4}J_{\mathrm{EE}}(\mathrm{u}) - {}^{1}/_{4}J_{\mathrm{A_1E}}(\mathrm{u})$
J_6	${}^{2}/_{3}J_{\mathrm{A_1A_1}}(\xi) + {}^{1}/_{3}J_{\mathrm{EE}}(\xi) - \frac{4}{3\sqrt{2}}J_{\mathrm{A_1E}}(\xi) + {}^{1}/_{2}J_{\mathrm{A_1A_1}}(\mathrm{u}) - {}^{1}/_{2}J_{\mathrm{EE}}(\mathrm{u}) - J_{\mathrm{A_1E}}(\mathrm{u})$

TABLE 7: U_k and J_k Parameters for ${}^2\mathrm{T}_2-{}^2\mathrm{T}_2$ Corner-Shared Dimer Expressed in Function of Transfer Parameter and Energies

U_1	$\mathrm{t}^2\left[\frac{2\cos^2\theta}{3\epsilon_1({}^3\mathrm{T}_1)} + \frac{2\sin^2\theta}{3\epsilon_2({}^3\mathrm{T}_1)} + \frac{2\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} - \frac{23\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} - \frac{23\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} + \frac{2\cos^2\delta}{9\epsilon_1({}^1\mathrm{T}_2)} + \frac{2\sin^2\delta}{9\epsilon_2({}^1\mathrm{T}_2)}\right]$
U_2	$\mathrm{t}^2\left[\frac{2\cos^2\theta}{3\epsilon_1({}^3\mathrm{T}_1)} + \frac{2\sin^2\theta}{3\epsilon_2({}^3\mathrm{T}_1)} - \frac{16\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} - \frac{16\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} - \frac{5\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} - \frac{5\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} + \frac{2\cos^2\delta}{9\epsilon_1({}^1\mathrm{T}_2)} + \frac{2\sin^2\delta}{9\epsilon_2({}^1\mathrm{T}_2)}\right]$
U_3	$\mathrm{t}^2\left[-\frac{7\cos^2\theta}{3\epsilon_1({}^3\mathrm{T}_1)} - \frac{7\sin^2\theta}{3\epsilon_2({}^3\mathrm{T}_1)} + \frac{2\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} + \frac{4\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} + \frac{4\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} + \frac{2\cos^2\delta}{9\epsilon_1({}^1\mathrm{T}_2)} + \frac{2\sin^2\delta}{9\epsilon_2({}^1\mathrm{T}_2)}\right]$
U_4	$\mathrm{t}^2\left[\frac{2\cos^2\theta}{3\epsilon_1({}^3\mathrm{T}_1)} + \frac{2\sin^2\theta}{3\epsilon_2({}^3\mathrm{T}_1)} + \frac{2\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} + \frac{4\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} + \frac{4\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} - \frac{7\cos^2\delta}{9\epsilon_1({}^1\mathrm{T}_2)} - \frac{7\sin^2\delta}{9\epsilon_2({}^1\mathrm{T}_2)}\right]$
U_5	$\mathrm{t}^2\left[-\frac{\cos^2\theta}{12\epsilon_1({}^3\mathrm{T}_1)} - \frac{\sin^2\theta}{12\epsilon_2({}^3\mathrm{T}_1)} + \frac{2\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} + \frac{4\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} + \frac{4\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} - \frac{\cos^2\delta}{36\epsilon_1({}^1\mathrm{T}_2)} - \frac{\sin^2\delta}{36\epsilon_2({}^1\mathrm{T}_2)}\right]$
U_6	$\mathrm{t}^2\left[\frac{2\cos^2\theta}{3\epsilon_1({}^3\mathrm{T}_1)} + \frac{2\sin^2\theta}{3\epsilon_2({}^3\mathrm{T}_1)} + \frac{2\cos^2\alpha}{27\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{27\epsilon_2({}^1\mathrm{A}_1)} + \frac{4\cos^2\beta}{27\epsilon_1({}^1\mathrm{E})} + \frac{4\sin^2\beta}{27\epsilon_2({}^1\mathrm{E})} + \frac{2\cos^2\delta}{9\epsilon_1({}^1\mathrm{T}_2)} + \frac{2\sin^2\delta}{9\epsilon_2({}^1\mathrm{T}_2)}\right]$
J_1	$-2\mathrm{t}^2\left[\frac{\cos^2\beta}{\epsilon_1({}^1\mathrm{E})} + \frac{\sin^2\beta}{\epsilon_2({}^1\mathrm{E})}\right]$
J_2	$-{}^{2}/_{3}\mathrm{t}^2\left[\frac{2\cos^2\alpha}{\epsilon_1({}^1\mathrm{A}_1)} + \frac{2\sin^2\alpha}{\epsilon_2({}^1\mathrm{A}_1)} + \frac{\cos^2\beta}{\epsilon_1({}^1\mathrm{E})} + \frac{\sin^2\beta}{\epsilon_2({}^1\mathrm{E})}\right]$
J_3	$2\mathrm{t}^2\left[\frac{\cos^2\theta}{\epsilon_1({}^3\mathrm{T}_1)} + \frac{\sin^2\theta}{\epsilon_2({}^3\mathrm{T}_1)}\right]$
J_4	$-2\mathrm{t}^2\left[\frac{\cos^2\delta}{\epsilon_1({}^1\mathrm{T}_2)} + \frac{\sin^2\delta}{\epsilon_2({}^1\mathrm{T}_2)}\right]$
J_5	$\frac{\mathrm{t}^2}{2}\left[\frac{\cos^2\theta}{\epsilon_1({}^3\mathrm{T}_1)} + \frac{\sin^2\theta}{\epsilon_2({}^3\mathrm{T}_1)} - \frac{\cos^2\delta}{\epsilon_1({}^1\mathrm{T}_2)} - \frac{\sin^2\delta}{\epsilon_2({}^1\mathrm{T}_2)}\right]$
J_6	0

The problem of vibronic Jahn−Teller interaction[44] seems to be inherent for the orbitally degenerate ions. This problem deserves special consideration. The vibronic interaction can reduce some interionic interactions in clusters[45] and give rise to the correlation between local distortions in crystals (orbital and structural ordering phenomena).[46,47] Consideration of the

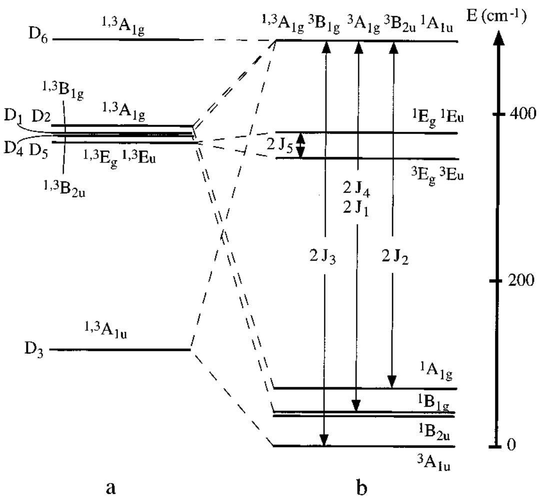

Figure 4. Energy pattern of the corner-shared bioctahedral (D_{4h}) cluster consisting of one-electron ions: (a) spin-independent splitting, (b) spin-dependent splitting.

magnetic vibronic problem in clusters and cooperative phenomena in solids consisting of degenerate metal ions require the knowledge of the explicit form of the exchange Hamiltonian. We hope that the results presented here may be helpful in this area, and in future we give a comparison between the theoretical results and experimental edge-shared and corner-shared clusters.

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Appendix I. Evaluation of the Hamiltonian

In order to consider the symmetry properties of the one-site operators entering in eq 4 we will define the "partial" projection operators:

$$\bar{G}_i(\nu\bar{S}\bar{\Gamma}) = \sum_{\bar{M}\bar{\gamma}} |i,\ \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle\langle i,\ \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}| \qquad \text{(AI.1)}$$

$$\tilde{G}_j(\mu\,\tilde{S}\tilde{\Gamma}) = \sum_{\tilde{M}\tilde{\gamma}} |j,\ \mu\,\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle\langle j,\ \mu\,\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|$$

These operators are evidently invariant under the transformations of the point symmetry group of local surrounding of metal sites as well as under the rotations in spin space. Due to the scalar properties of the operators (eq AI.1) the symmetry (in both coordinate and spin spaces) properties of the one-site operators

$$\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}\,\bar{G}_i(\nu\bar{S}\bar{\Gamma})\,\mathbf{C}_{\Gamma_i\gamma'_i\sigma'} \text{ and } \mathbf{C}_{\Gamma_j\gamma_j\sigma}\tilde{G}_j(\mu\,\tilde{S}\tilde{\Gamma})\,\mathbf{C}^{+}_{\Gamma_j\gamma'_j\sigma'}$$

are determined only by the products of creation and annihilation operators. Therefore these operators represent the double-tensor operators being transformed like the direct product $\Gamma_i{\times}\Gamma_i = \sum\Gamma$ in the coordinate space and $D^{(1/2)} \times D^{(1/2)} = \sum_{k=0,1}D^{(k)}$ in the spin space. They are in general reducible and can be represented in terms of irreducible tensors $\mathbf{X}^{kq}_{\Gamma\gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})$ and $\mathbf{Z}^{kq}_{\Gamma\gamma}(\Gamma_j,\ \mu\ \tilde{S}\tilde{\Gamma})$ by means of the following unitary transformation:

$$\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}\,\bar{G}_i(\nu\bar{S}\bar{\Gamma})\,\mathbf{C}_{\Gamma_i\gamma'_i\sigma'} = (-1)^{1/2-\sigma'}\,\mathbf{T}^{1/2,\sigma}_{\Gamma_i\gamma_i}\bar{G}_{\mathrm{i}}(\nu\bar{S}\bar{\Gamma})\,\mathbf{T}^{1/2,-\sigma'}_{\Gamma_i\gamma'_i} = (-1)^{1/2-\sigma'}\sum_{kq}\mathbf{C}^{kq}_{1/2\sigma1/2-\sigma'}\sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma'_i\rangle\,\mathbf{X}^{kq}_{\Gamma\gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) \qquad \text{(AI.2)}$$

and

$$\mathbf{C}_{\Gamma_j\gamma_j\sigma}\tilde{\mathrm{G}}_j(\mu\,\tilde{S}\tilde{\Gamma})\,\mathbf{C}^{+}_{\Gamma_j\gamma'_j\sigma'} = (-1)^{1/2-\sigma}\,\mathbf{T}^{1/2,-\sigma}_{\Gamma_j\gamma_j}\,\tilde{G}_j(\mu\,\tilde{S}\tilde{\Gamma})\,\mathbf{T}^{1/2,\sigma'}_{\Gamma_j\gamma'_j} = (-1)^{1/2-\sigma}\sum_{kq}\mathbf{C}^{k\,q}_{1/2-\sigma1/2\sigma'}\sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_j\gamma_j\Gamma_j\gamma'_j\rangle\,\mathbf{Z}^{kq}_{\Gamma\gamma}(\Gamma_j,\mu\tilde{S}\tilde{\Gamma}) \qquad \text{(AI.3)}$$

In eqs AI.2 and AI.3 $\mathbf{C}^{s\ \ m}_{s_1m_1s_2m_2}$ and $\langle\Gamma\gamma|\Gamma_1\gamma_1\Gamma_2\gamma_2\rangle$ are the Clebsch−Gordan coefficients for the rotation group and local point group respectively. Since the operators $\mathbf{X}^{kq}_{\Gamma\gamma}$ and $\mathbf{Z}^{kq}_{\Gamma\gamma}$ are the irreducible double tensors, the Wigner−Eckart theorem[38] can be applied to the calculation of the matrices of these operators in the basis of the ground states of each ion. For instance,

$$\langle S_{\mathrm{igr}}\Gamma_{\mathrm{igr}}M_{\mathrm{igr}}\gamma_{\mathrm{igr}}|\mathbf{X}^{kq}_{\Gamma\gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})|S_{\mathrm{igr}}\Gamma_{\mathrm{igr}}M'_{\mathrm{igr}}\gamma'_{\mathrm{igr}}\rangle = [(2S_{\mathrm{igr}}+1)(\Gamma_{\mathrm{igr}})]^{-1/2}\langle S_{\mathrm{igr}}\Gamma_{\mathrm{igr}}||\mathbf{X}^{k}_{\Gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})||S_{\mathrm{igr}}\Gamma_{\mathrm{igr}}\rangle \times \langle\Gamma_{\mathrm{igr}}\gamma_{\mathrm{igr}}|\Gamma_{\mathrm{igr}}\gamma'_{\mathrm{igr}}\Gamma\gamma\rangle\mathbf{C}^{S_{\mathrm{igr}}M_{\mathrm{igr}}}_{S_{\mathrm{igr}}M'_{\mathrm{igr}}kq} \qquad \text{(AI.4)}$$

where $\langle\cdots||\cdots\rangle$ is the reduced matrix element and (Γ_{igr}) is the dimension of the irreducible representation Γ_{igr}. Let us define the unit operator $\mathbf{I}_i$ acting in the spin space of ith ion in the usual manner as an irreducible tensor operator of the rank $k = 0$, possessing the reduced matrix element $\langle S_{\mathrm{igr}}||\mathbf{I}_i||S_{\mathrm{igr}}\rangle = (2S_{\mathrm{igr}} + 1)^{1/2}$. Thus, according to the Wigner−Eckart theorem, one can write: $\langle S_{\mathrm{igr}}M_{\mathrm{igr}}|\mathbf{I}_i|S_{\mathrm{igr}}M'_{\mathrm{igr}}\rangle = \delta_{M_{\mathrm{igr}}M'_{\mathrm{igr}}}$. Using further the usual definition of the ionic spin operator $\mathbf{S}_i$ as an irreducible tensor operator of the rank $k = 1$, we can write for the matrix elements of its components:

$$\langle S_{\mathrm{igr}}M_{\mathrm{igr}}|\mathbf{S}^{1,q}_i|S_{\mathrm{igr}}M'_{\mathrm{igr}}\rangle = (2S_{\mathrm{igr}}+1)^{-1/2}\langle \mathrm{S}_{\mathrm{igr}}||\mathbf{S}^1_{\mathrm{i}}||\mathrm{S}_{\mathrm{igr}}\rangle\,\mathbf{C}^{S_{\mathrm{igr}}M_{\mathrm{igr}}}_{S_{\mathrm{igr}}M'_{\mathrm{igr}}1q} \qquad \text{(AI.5)}$$

where the reduced matrix element is given by the formula,

$$\langle S_{\mathrm{igr}}||\mathbf{S}^1_i||S_{\mathrm{igr}}\rangle = [S_{\mathrm{igr}}(S_{\mathrm{igr}}+1)(2S_{\mathrm{igr}}+1)]^{1/2}$$

Finally one can introduce the one-center orbital irreducible tensor operators $\mathbf{O}^i_{\Gamma\gamma}$ acting in the orbital subspace so that their reduced matrix elements are

$$\langle\Gamma_{\mathrm{igr}}||\mathbf{O}^i_{\Gamma}||\Gamma_{\mathrm{igr}}\rangle = (\Gamma_{\mathrm{igr}})^{1/2}$$

and hence

$$\langle\Gamma_{\mathrm{igr}}\gamma_{\mathrm{igr}}|\mathbf{O}^i_{\Gamma\gamma}|\Gamma_{\mathrm{igr}}\gamma'_{\mathrm{igr}}\rangle = \langle\Gamma_{\mathrm{igr}}\gamma_{\mathrm{igr}}|\Gamma_{\mathrm{igr}}\gamma'_{\mathrm{igr}}\Gamma\gamma\rangle \qquad \text{(AI.6)}$$

It is now straightforward work to express the irreducible tensor operators $\mathbf{X}^{kq}_{\Gamma\gamma}$ and $\mathbf{Z}^{kq}_{\Gamma\gamma}$, in terms of unit operators $\mathbf{I}_i$, ionic spin operators $\mathbf{S}^{1,q}_i$, and orbital irreducible tensors $\mathbf{O}^i_{\Gamma\gamma}$ as follows:

$$\mathbf{X}^{00}_{\Gamma\gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) = 2a^{\Gamma}_1(\Gamma_i,\nu\bar{S}\bar{\Gamma})\mathbf{O}^i_{\Gamma\gamma}\mathbf{I}_i$$

$$\mathbf{X}^{1q}_{\Gamma\gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) = a^{\Gamma}_2(\Gamma_i,\nu\bar{S}\bar{\Gamma})\mathbf{O}^i_{\Gamma\gamma}\,\mathbf{S}^{1,q}_i$$

$$\mathbf{Z}^{00}_{\Gamma\gamma}(\Gamma_j,\mu\tilde{S}\tilde{\Gamma}) = 2b^{\Gamma}_1(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})\mathbf{O}^j_{\Gamma\gamma}\mathbf{I}_j$$

$$\mathbf{Z}^{1q}_{\Gamma\gamma}(\Gamma_j,\ \mu\,\tilde{S}\tilde{\Gamma}) = b^{\Gamma}_2(\Gamma_j,\ \mu\,\tilde{S}\tilde{\Gamma})\mathbf{O}^j_{\Gamma\gamma}\,\mathbf{S}^{1,q}_j \qquad \text{(AI.7)}$$

The coefficients a and b are proportional to the reduced matrix elements of the operators $\mathbf{X}^{kq}_{\Gamma\gamma}$ and $\mathbf{Z}^{kq}_{\Gamma\gamma}$:

$$a^{\Gamma}_{1}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) = \frac{1}{2\sqrt{2}}[(2S_{igr}+1)(\Gamma_{igr})]^{-1/2} \times \langle S_{igr}\Gamma_{igr}||X^{0}_{\Gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})||S_{igr}\,\Gamma_{igr}\rangle$$

$$a^{\Gamma}_{2}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) = \sqrt{2}[S_{igr}(S_{igr}+1)(2S_{igr}+1)(\Gamma_{igr})]^{-1/2} \times \langle S_{igr}\Gamma_{igr}||X^{1}_{\Gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})||S_{igr}\,\Gamma_{igr}\rangle$$

$$b^{\Gamma}_{1}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma}) = -\frac{1}{2\sqrt{2}}[(2S_{jgr}+1)(\Gamma_{jgr})]^{-1/2} \times \langle S_{jgr}\Gamma_{jgr}||Z^{0}_{\Gamma}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})||S_{jgr}\,\Gamma_{jgr}\rangle$$

$$b^{\Gamma}_{2}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma}) = -\sqrt{2}[S_{jgr}(S_{jgr}+1)(2S_{jgr}+1)(\Gamma_{jgr})]^{-1/2} \times \langle S_{jgr}\Gamma_{jgr}||Z^{1}_{\Gamma}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})||S_{jgr}\,\Gamma_{jgr}\rangle \quad \text{(AI.8)}$$

Performing the summations over k and q in eqs AI.2 and AI.3 and taking into account eqs AI.7 we can represent the different one-site operators involved in the Hamiltonian (eq 4) in the following form:

$$\mathbf{C}^{+}_{\Gamma_i\gamma_i\uparrow(\downarrow)}\,\bar{G}_i(\nu\bar{S}\bar{\Gamma})\,\mathbf{C}_{\Gamma_i\gamma'_i\downarrow(\uparrow)} = \mp\sqrt{2}\sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma'_i\rangle a^{\Gamma}_{2}(\Gamma_i,\nu\bar{S}\bar{\Gamma})\mathbf{O}^{i}_{\Gamma\gamma}\,\mathbf{S}^{1,\pm1}_{i}$$

$$\mathbf{C}^{+}_{\Gamma_i\gamma_i\uparrow(\downarrow)}\,\bar{G}_i(\nu\bar{S}\bar{\Gamma})\,\mathbf{C}_{\Gamma_i\gamma'_i\uparrow(\downarrow)} = \sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma'_i\rangle\mathbf{O}^{i}_{\Gamma\gamma}[a^{\Gamma}_{1}(\Gamma_i,\nu\bar{S}\bar{\Gamma})\mathbf{I}_i \pm a^{\Gamma}_{2}(\Gamma_i,\nu\bar{S}\bar{\Gamma})\,\mathbf{S}^{1,0}_{i}]$$

$$\mathbf{C}_{\Gamma_j\gamma_j\uparrow(\downarrow)}\,\tilde{G}_j(\mu\,\tilde{S}\tilde{\Gamma})\,\mathbf{C}^{+}_{\Gamma_j\gamma'_j\downarrow(\uparrow)} = \mp\sqrt{2}\sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_j\gamma_j\Gamma_j\gamma'_j\rangle b^{\Gamma}_{2}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})\mathbf{O}^{j}_{\Gamma\gamma}\,\mathbf{S}^{1,\mp1}_{j}$$

$$\mathbf{C}_{\Gamma_j\gamma_j\uparrow(\downarrow)}\,\tilde{G}_j(\mu\tilde{S}\tilde{\Gamma})\,\mathbf{C}^{+}_{\Gamma_j\gamma'_j\uparrow(\downarrow)} = \sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_j\gamma_j\Gamma_j\gamma'_j\rangle\mathbf{O}^{j}_{\Gamma\gamma}[b^{\Gamma}_{1}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})\mathbf{I}_j \pm b^{\Gamma}_{2}(\Gamma_j,\mu\,\tilde{S}\tilde{\Gamma})\mathbf{S}^{1,0}_{j}] \quad \text{(AI.9)}$$

Now we are in the position to write the final expression for the effective kinetic exchange Hamiltonian related to the system of orbitally degenerate transition metal ions. This Hamiltonian is expressed in eq 5.

Appendix II. Evaluation of the *a*- and *b*-Parameters in the Effective Hamiltonian

Equation 6 contains as unknown parameters $a^{\Gamma}_{1}(\Gamma_i,\ \nu\bar{S}\bar{\Gamma})$, $b^{\Gamma}_{1}(\Gamma_i,\ \mu\tilde{S}\tilde{\Gamma})$, etc. Now we will describe the general way to evaluate these parameters, this procedure will be exemplified latter on. First, using eqs AI.2 and AI.7 one can express the matrix elements of one-site operators $\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}\ \bar{G}_i(\nu\bar{S}\bar{\Gamma})\ \mathbf{C}_{\Gamma_i\gamma'_i\sigma'}$ related to the d_i^{n-1} ion in terms of a-parameters. Providing $\sigma = \sigma' = \uparrow$, we get

$$\langle S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}|\mathbf{C}^{+}_{\Gamma_i\gamma_i\uparrow}\bar{G}_i(\nu\bar{S}\bar{\Gamma})\mathbf{C}_{\Gamma_i\gamma'_i\uparrow}|S_{igr}\Gamma_{igr}M'_{igr}\gamma'_{igr}\rangle = \sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma'_i\rangle\langle\Gamma_{igr}\gamma_{igr}|\Gamma_{igr}\gamma'_{igr}\Gamma\gamma\rangle[a^{\Gamma}_{1}(\Gamma_i,\nu\bar{S}\bar{\Gamma}) + a^{\Gamma}_{2}(\Gamma_i,\nu\bar{S}\bar{\Gamma})\sqrt{S_{igr}(S_{igr}+1)}\mathbf{C}^{S_{igr}M_{igr}}_{S_{igr}M_{igr}10}]\delta_{M_{igr}M'_{igr}} \quad \text{(AII.1)}$$

Similarly taking into account eqs AI.3 and AI.7, one can represent the matrix element of d_i^{n+1} site operator $\mathbf{C}_{\Gamma_i\gamma_i\sigma}\tilde{G}_i(\mu\tilde{S}\tilde{\Gamma})\mathbf{C}^{+}_{\Gamma_i\gamma'_i\sigma'}$ with $\sigma = \sigma' = \uparrow$ as the following linear combination of b-parameters:

$$\langle S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}|\mathbf{C}_{\Gamma_i\gamma_i\uparrow}\tilde{G}_i(\mu\tilde{S}\tilde{\Gamma})\mathbf{C}^{+}_{\Gamma_i\gamma'_i\uparrow}|S_{igr}\Gamma_{igr}M'_{igr}\gamma'_{igr}\rangle = \sum_{\Gamma\gamma}\langle\Gamma\gamma|\Gamma_i\gamma_i\Gamma_i\gamma'_i\rangle\langle\Gamma_{igr}\gamma_{igr}|\Gamma_{igr}\gamma'_{igr}\Gamma\gamma\rangle[b^{\Gamma}_{1}(\Gamma_i,\mu\tilde{S}\tilde{\Gamma}) - b^{\Gamma}_{2}(\Gamma_i,\mu\tilde{S}\tilde{\Gamma})\sqrt{S_{igr}(S_{igr}+1)}\mathbf{C}^{S_{igr}M_{igr}}_{S_{igr}M_{igr}10}]\delta_{M_{igr}M'_{igr}} \quad \text{(AII.2)}$$

Equations AII.1 and AII.2 express the matrix elements of one-site operators in terms of the unknown parameters a_1, a_2, b_1, and b_2 involved in the effective Hamiltonian (eq 5). In order to evaluate these parameters, some of these matrix elements have to be calculated directly, decomposing these matrix elements into products of the matrix elements of the creation and annihilation operators. This calculation can be essentially simplified using the above mentioned symmetry properties of the fermionic creation and annihilation operators. Since the creation operator represents the double irreducible tensor operator acting in both coordinate and spin subspaces, the Wigner−Eckart theorem can be applied to the calculation of its matrix element. This allows to obtain the matrix element linking the ground state of the ion with its oxidized and reduced ionic states.

For the oxidized state $\bar{S}\bar{\Gamma}$ (d_i^{n-1} configuration), we have:

$$\langle S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}|\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}|i,\ \nu\bar{S}\bar{\Gamma}\bar{M}\bar{\gamma}\rangle = [(2S_{igr}+1)(\Gamma_{igr})]^{-1/2} \times \langle S_{igr}\Gamma_{igr}||\mathbf{T}^{1/2}_{\Gamma_i}||\nu\bar{S}\bar{\Gamma}\rangle\langle\Gamma_{igr}\gamma_{igr}|\bar{\Gamma}\bar{\gamma}\Gamma_i\gamma_i\rangle\mathbf{C}^{S_{igr}M_{igr}}_{\bar{S}\bar{M}1/2\sigma} \quad \text{(AII.3)}$$

where $\langle S_{igr}\Gamma_{igr}||\mathbf{T}^{1/2}_{\Gamma_i}||\nu\bar{S}\bar{\Gamma}\rangle$ is the reduced matrix element of the operator $\mathbf{T}^{1/2\,\sigma}_{\Gamma_i\gamma_i}$.

For the reduced state $\tilde{S}\tilde{\Gamma}$ (d_i^{n-1} configuration) one can write down:

$$\langle i,\mu\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}|\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}|S_{igr}\Gamma_{igr}M'_{igr}\gamma'_{igr}\rangle = [(2\tilde{S}+1)(\tilde{\Gamma})]^{-1/2} \times \langle\mu\tilde{S}\tilde{\Gamma}||\mathbf{T}^{1/2}_{\Gamma_i}||S_{igr}\Gamma_{igr}\rangle\langle\tilde{\Gamma}\tilde{\gamma}|\Gamma_{igr}\gamma'_{igr}\Gamma_i\gamma_i\rangle\mathbf{C}^{\tilde{S}\ \tilde{M}}_{S_{igr}M'_{igr}1/2\sigma} \quad \text{(AII.4)}$$

The corresponding matrices of the annihilation operator are Hermitian conjugated to those given by eqs AII.3 and AII.4.

Using eqs AII.3 and AII.4 along with the definition of the partial projection operators (eqs AI.1), one can represent the complex matrix elements (eqs AII.1 and AII.2) in terms of reduced matrix elements of creation operator linking the ionic ground state with the oxidized and reduced states. The results are the following:

$$\langle S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}|\mathbf{C}^{+}_{\Gamma_i\gamma_i\sigma}\bar{G}_i(\nu\bar{S}\bar{\Gamma})\mathbf{C}_{\Gamma_i\gamma'_i\sigma'}\ |S_{igr}\Gamma_{igr}M'_{igr}\gamma'_{igr}\rangle = [(2S_{igr}+1)(\Gamma_{igr})]^{-1}\langle S_{igr}\Gamma_{igr}||\mathbf{T}^{1/2}_{\Gamma_i}||\nu\bar{S}\bar{\Gamma}\rangle^{2}\sum_{\bar{\gamma}}\langle\Gamma_{igr}\gamma_{igr}|\bar{\Gamma}\bar{\gamma}\Gamma_i\gamma_i\rangle \times \langle\Gamma_{igr}\gamma'_{igr}|\bar{\Gamma}\bar{\gamma}\Gamma_i\gamma'_i\rangle\sum_{\bar{M}}\mathbf{C}^{S_{igr}M_{igr}}_{\bar{S}\bar{M}1/2\sigma}\,\mathbf{C}^{S_{igr}M'_{igr}}_{\bar{S}\bar{M}1/2\sigma'} \quad \text{(AII.5)}$$

$$\langle S_{igr}\Gamma_{igr}M_{igr}\gamma_{igr}|\mathbf{C}_{\Gamma_i\gamma_i\sigma}\tilde{G}_i(\mu\tilde{S}\tilde{\Gamma})\mathbf{C}^{+}_{\Gamma_i\gamma'_i\sigma'}|S_{igr}\Gamma_{igr}M'_{igr}\gamma'_{igr}\rangle = [(2\tilde{S}+1)(\tilde{\Gamma})]^{-1}\langle\mu\tilde{S}\tilde{\Gamma}||\mathbf{T}^{1/2}_{\Gamma i}||S_{igr}\Gamma_{igr}\rangle^{2}\sum_{\tilde{\gamma}}\langle\tilde{\Gamma}\tilde{\gamma}|\Gamma_{igr}\gamma_{igr}\Gamma_i\gamma_i\rangle \times \langle\tilde{\Gamma}\tilde{\gamma}|\Gamma_{igr}\gamma_{igr}\Gamma_i\gamma'_i\rangle\sum_{\tilde{M}}\mathbf{C}^{\tilde{S}\ \tilde{M}}_{S_{igr}M_{igr}1/2\sigma}\,\mathbf{C}^{\tilde{S}\ \tilde{M}}_{S_{igr}M'_{igr}1/2\sigma'} \quad \text{(AII.6)}$$

Equations AII.5 and AII.6 make it possible to find all matrix elements of one-site operators provided that we know the involved reduced matrix elements of the fermionic operators. The last can be found for each system using the explicit expressions (in terms of Slater determinants) for the wave functions of ground, reduced, and oxidized ionic states.

Setting the write sides of eqs AII.1 and AII.2 to the corresponding values of matrix elements obtained directly (eqs AII.5 and AII.6) we arrive at systems of linear algebraic equations with respect to the quantities $a_1^{\Gamma}(\Gamma_i,\nu\bar{S}\bar{\Gamma})$, $b_1^{\Gamma}(\Gamma_i,\mu\tilde{S}\tilde{\Gamma})$, etc. Solving these systems of equations and substituting the results into the eqs 6 we can finally find the parameters $U_{\Gamma,\Gamma'}(...)$ and $J_{\Gamma,\Gamma'}(...)$ defining the effective Hamiltonian (eq 5) as the functions of relevant transfer parameters and the single-ion crystal field parameters.

Appendix III

Matrices $\mathbf{O}_{\Gamma\gamma}$ in the Hamiltonians of eqs 7 and 17:

$$\mathbf{O}_{A_1} = \begin{array}{c} \begin{array}{ccc} \xi(\alpha) & \eta(\beta) & \zeta(\gamma) \end{array} \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{array}, \quad \mathbf{O}_{Eu} = \begin{array}{c} \begin{array}{ccc} \xi(\alpha) & \eta(\beta) & \zeta(\gamma) \end{array} \\ \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \end{array} \tag{AIII.1}$$

$$\mathbf{O}_{Ev} = \begin{array}{c} \begin{array}{ccc} \xi(\alpha) & \eta(\beta) & \zeta(\gamma) \end{array} \\ \begin{bmatrix} \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{array}, \quad \mathbf{O}_{T_1\gamma} = \begin{array}{c} \begin{array}{ccc} \xi(\alpha) & \eta(\beta) & \zeta(\gamma) \end{array} \\ \begin{bmatrix} 0 & \pm\frac{1}{\sqrt{2}} & 0 \\ \mp\frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{array},$$

$$\mathbf{O}_{T_2\zeta} = \begin{array}{c} \begin{array}{ccc} \xi(\alpha) & \eta(\beta) & \zeta(\gamma) \end{array} \\ \begin{bmatrix} 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{array} \tag{AIII.2}$$

where ξ, η, and ζ stand for the basis T_2 and α, β, and γ enumerate the basis of $T_1(L_x, L_y, L_z)$, the signs ± relate to the basis $T_2(T_1)$.

Appendix IV

The wave functions for the repeating $\tilde{S}\tilde{\Gamma}$ terms of d^2-ion:

$$|1,{}^3T_1\rangle = \cos\theta|t_2^2,{}^3T_1\rangle - \sin\theta|t_2e,{}^3T_1\rangle$$

$$|2,{}^3T_1\rangle = \sin\theta|t_2^2,{}^3T_1\rangle + \cos\theta|t_2e,{}^3T_1\rangle$$

$$|1,{}^1A_1\rangle = \cos\alpha|t_2^2,{}^1A_1\rangle - \sin\alpha|e^2,{}^1A_1\rangle$$

$$|2,{}^1A_1\rangle = \sin\alpha|t_2^2,{}^1A_1\rangle + \cos\alpha|e^2,{}^1A_1\rangle$$

$$|1,{}^1E\rangle = \cos\beta|t_2^2,{}^1E\rangle - \sin\beta|e^2,{}^1E\rangle$$

$$|2,{}^1E\rangle = \sin\beta|t_2^2,{}^1E\rangle + \cos\beta|e^2,{}^1E\rangle$$

$$|1,{}^1T_2\rangle = \cos\delta|t_2^2,{}^1T_2\rangle - \sin\delta|t_2e,{}^1T_2\rangle$$

$$|2,{}^1T_2\rangle = \sin\delta|t_2^2,{}^1T_2\rangle + \cos\delta|t_2e,{}^1T_2\rangle$$

where α, β, and θ and δ can be obtained from the next expressions:

$$\tan(2\theta) = \frac{12B}{10\mathrm{Dq} + 9B}, \quad \tan(2\alpha) = \frac{2\sqrt{6}(2B + C)}{20\mathrm{Dq} - 2B - C}$$

$$\tan(2\beta) = -\frac{4\sqrt{3}B}{20\mathrm{Dq} - B}, \quad \tan(2\delta) = \frac{4\sqrt{3}B}{10\mathrm{Dq} - B}$$

The expressions of the wave functions $|t_2^2\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle$, $|t_2e\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle$, and $|e^2\tilde{S}\tilde{\Gamma}\tilde{M}\tilde{\gamma}\rangle$ in terms of Slater determinants are given in ref 38 (pp 53 and 54).

Appendix V

Parameters $a_{1,2}^{A_1}(t_2,{}^1A_1)$, $a_{1,2}^{E}(t_2,{}^1A_1)$, $b_{1,2}^{A_1}(t_2,\ \mu\ \tilde{S}\tilde{\Gamma})$, and $b_{1,2}^{E}(t_2,\ \mu\ \tilde{S}\tilde{\Gamma})$ (these parameters appear for both D_{2h} and D_{4h} topologies):

$\bar{S}\bar{\Gamma}={}^1A_1$ (vacuum state)

$$a_1^{A_1}(t_2,{}^1A_1) = \frac{1}{2\sqrt{3}}, \quad a_2^{A_1}(t_2,{}^1A_1) = \frac{1}{\sqrt{3}}$$

$$a_1^{E}(t_2,{}^1A_1) = \frac{1}{\sqrt{6}}, \quad a_2^{E}(t_2,{}^1A_1) = \frac{2}{\sqrt{6}} \tag{AV.1}$$

$\tilde{S}\tilde{\Gamma} = {}^3T_1$

$$b_1^{A_1}(t_2, 1,{}^3T_1) = \frac{3}{2\sqrt{3}}\cos^2\theta, \quad b_2^{A_1}(t_2, 1,{}^3T_1) = -\frac{1}{\sqrt{3}}\cos^2\theta$$

$$b_1^{E}(t_2, 1,{}^3T_1) = -\frac{3}{2\sqrt{6}}\cos^2\theta, \quad b_2^{E}(t_2, 1,{}^3T_1) = \frac{1}{\sqrt{6}}\cos^2\theta$$

$$b_1^{A_1}(t_2, 2,{}^3T_1) = \frac{3}{2\sqrt{3}}\sin^2\theta, \quad b_2^{A_1}(t_2, 2,{}^3T_1) = -\frac{1}{\sqrt{3}}\sin^2\theta$$

$$b_1^{E}(t_2, 2,{}^3T_1) = -\frac{3}{2\sqrt{6}}\sin^2\theta, \quad b_2^{E}(t_2, 2,{}^3T_1) = \frac{1}{\sqrt{6}}\sin^2\theta \tag{AV.2}$$

$\tilde{S}\tilde{\Gamma} = {}^1A_1$

$$b_1^{A_1}(t_2, 1,{}^1A_1) = \frac{1}{6\sqrt{3}}\cos^2\alpha, \quad b_2^{A_1}(t_2, 1,{}^1A_1) = \frac{1}{3\sqrt{3}}\cos^2\alpha$$

$$b_1^{E}(t_2, 1,{}^1A_1) = \frac{1}{3\sqrt{6}}\cos^2\alpha, \quad b_2^{E}(t_2, 1,{}^1A_1) = \frac{2}{3\sqrt{6}}\cos^2\alpha$$

$$b_1^{A_1}(t_2, 2,{}^1A_1) = \frac{1}{6\sqrt{3}}\sin^2\alpha, \quad b_2^{A_1}(t_2, 2,{}^1A_1) = \frac{1}{3\sqrt{3}}\sin^2\alpha$$

$$b_1^{E}(t_2, 2,{}^1A_1) = \frac{1}{3\sqrt{6}}\sin^2\alpha, \quad b_2^{E}(t_2, 2,{}^1A_1) = \frac{2}{3\sqrt{6}}\sin^2\alpha \tag{AV.3}$$

$\tilde{S}\tilde{\Gamma} = {}^1E$

$$b_1^{A_1}(t_2, 1,{}^1E) = \frac{1}{3\sqrt{3}}\cos^2\beta, \quad b_2^{A_1}(t_2, 1,{}^1E) = \frac{2}{3\sqrt{3}}\cos^2\beta$$

$$b_1^{E}(t_2, 1,{}^1E) = \frac{2}{3\sqrt{6}}\cos^2\beta, \quad b_2^{E}(t_2, 1,{}^1E) = \frac{4}{3\sqrt{6}}\cos^2\beta$$

$$b_1^{A_1}(t_2, 2,{}^1E) = \frac{1}{3\sqrt{3}}\sin^2\beta, \quad b_2^{A_1}(t_2, 2,{}^1E) = \frac{2}{3\sqrt{3}}\sin^2\beta$$

$$b_1^{E}(t_2, 2,{}^1E) = \frac{2}{3\sqrt{6}}\sin^2\beta, \quad b_2^{E}(t_2, 2,{}^1E) = \frac{4}{3\sqrt{6}}\sin^2\beta \tag{AV.4}$$

$\tilde{S}\tilde{\Gamma} = {}^1T_2$

$$\begin{aligned}
b_1^{A_1}(t_2, 1, {}^1T_2) &= \frac{1}{2\sqrt{3}}\cos^2\delta, \quad b_2^{A_1}(t_2, 1, {}^1T_2) = \frac{1}{\sqrt{3}}\cos^2\delta\\
b_1^{E}(t_2, 1, {}^1T_2) &= -\frac{1}{2\sqrt{6}}\cos^2\delta, \quad b_2^{E}(t_2, 1, {}^1T_2) = -\frac{1}{\sqrt{6}}\cos^2\delta\\
b_1^{A_1}(t_2, 2, {}^1T_2) &= \frac{1}{2\sqrt{3}}\sin^2\delta, \quad b_2^{A_1}(t_2, 2, {}^1T_2) = \frac{1}{\sqrt{3}}\sin^2\delta\\
b_1^{E}(t_2, 2, {}^1T_2) &= -\frac{1}{2\sqrt{6}}\sin^2\delta, \quad b_2^{E}(t_2, 2, {}^1T_2) = -\frac{1}{\sqrt{6}}\sin^2\delta
\end{aligned} \tag{AV.5}$$

Parameters $a_{1,2}^{T_1}(t_2, {}^1A_1)$, $a_{1,2}^{T_2}(t_2, {}^1A_1)$, $b_{1,2}^{T_1}(t_2, \mu\ \tilde{S}\tilde{\Gamma})$, and $b_{1,2}^{T_2}(t_2, \mu\ \tilde{S}\tilde{\Gamma})$ appearing only for D_{4h} topology:
$\tilde{S}\tilde{\Gamma} = {}^1A_1$ (vacuum state)

$$\begin{aligned}
a_1^{T_1}(t_2, {}^1A_1) &= \frac{1}{2}, \quad a_2^{T_1}(t_2, {}^1A_1) = 1\\
a_1^{T_2}(t_2, {}^1A_1) &= \frac{1}{2}, \quad a_2^{T_2}(t_2, {}^1A_1) = 1
\end{aligned} \tag{AV.6}$$

$\tilde{S}\tilde{\Gamma} = {}^3T_1$

$$\begin{aligned}
b_1^{T_1}(t_2, 1, {}^3T_1) &= \frac{3}{4}\cos^2\theta, \quad b_2^{T_1}(t_2, 1, {}^3T_1) = -{}^1/_2\cos^2\theta\\
b_1^{T_2}(t_2, 1, {}^3T_1) &= -\frac{3}{4}\cos^2\theta, \quad b_2^{T_2}(t_2, 1, {}^3T_1) = {}^1/_2\cos^2\theta\\
b_1^{T_1}(t_2, 2, {}^3T_1) &= \frac{3}{4}\sin^2\theta, \quad b_2^{T_1}(t_2, 2, {}^3T_1) = -{}^1/_2\sin^2\theta\\
b_1^{T_2}(t_2, 2, {}^3T_1) &= -\frac{3}{4}\sin^2\theta, \quad b_2^{T_2}(t_2, 2, {}^3T_1) = {}^1/_2\sin^2\theta
\end{aligned} \tag{AV.7}$$

$\tilde{S}\tilde{\Gamma} = {}^1A_1$

$$\begin{aligned}
b_1^{T_1}(t_2, 1, {}^1A_1) &= {}^1/_6\cos^2\alpha, \quad b_2^{T_1}(t_2, 1, {}^1A_1) = {}^1/_3\cos^2\alpha\\
b_1^{T_2}(t_2, 1, {}^1A_1) &= {}^1/_6\cos^2\alpha, \quad b_2^{T_2}(t_2, 1, {}^1A_1) = {}^1/_3\cos^2\alpha\\
b_1^{T_1}(t_2, 2, {}^1A_1) &= {}^1/_6\sin^2\alpha, \quad b_2^{T_1}(t_2, 2, {}^1A_1) = {}^1/_3\sin^2\alpha\\
b_1^{T_2}(t_2, 2, {}^1A_1) &= {}^1/_6\sin^2\alpha, \quad b_2^{T_2}(t_2, 2, {}^1A_1) = {}^1/_3\sin^2\alpha
\end{aligned} \tag{AV.8}$$

$\tilde{S}\tilde{\Gamma} = {}^1E$

$$\begin{aligned}
b_1^{T_1}(t_2, 1, {}^1E) &= -{}^1/_6\cos^2\beta, \quad b_2^{T_1}(t_2, 1, {}^1E) = -{}^1/_3\cos^2\beta\\
b_1^{T_2}(t_2, 1, {}^1E) &= -{}^1/_6\cos^2\beta, \quad b_2^{T_2}(t_2, 1, {}^1E) = -{}^1/_3\cos^2\beta\\
b_1^{T_1}(t_2, 2, {}^1E) &= -{}^1/_6\sin^2\beta, \quad b_2^{T_1}(t_2, 2, {}^1E) = -{}^1/_3\sin^2\beta\\
b_1^{T_2}(t_2, 2, {}^1E) &= -{}^1/_6\sin^2\beta, \quad b_2^{T_2}(t_2, 2, {}^1E) = -{}^1/_3\sin^2\beta
\end{aligned} \tag{AV.9}$$

$\tilde{S}\tilde{\Gamma} = {}^1T_2$

$$\begin{aligned}
b_1^{T_1}(t_2, 1, {}^1T_2) &= -{}^1/_4\cos^2\delta, \quad b_2^{T_1}(t_2, 1, {}^1T_2) = -{}^1/_2\cos^2\delta\\
b_1^{T_2}(t_2, 1, {}^1T_2) &= {}^1/_4\cos^2\delta, \quad b_2^{T_2}(t_2, 1, {}^1T_2) = {}^1/_2\cos^2\delta\\
b_1^{T_1}(t_2, 2, {}^1T_2) &= -{}^1/_4\sin^2\delta, \quad b_2^{T_1}(t_2, 2, {}^1T_2) = -{}^1/_2\sin^2\delta\\
b_1^{T_2}(t_2, 2, {}^1T_2) &= {}^1/_4\sin^2\delta, \quad b_2^{T_2}(t_2, 2, {}^1T_2) = {}^1/_2\sin^2\delta
\end{aligned} \tag{AV.10}$$

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