ON SUPEREXCHANGE IN MAGNETIC INSULATORS. II. SYMMETRY REQUIREMENTS AND KINETIC APPROXIMATION

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The general multielectron theory of superexchange interaction formulated earlier is applied to construct the effective spin-orbital Hamiltonian within the ground crystal states. The symmetry considerations allow one to reduce a great number of dependent exchange parameters to only a few independent ones without any simplifications of the theory. Kinetic approximation reduces it to only two for arbitrary d^n-d^n pair of ions.

1. Introduction

The multielectron theory of exchange interaction in cubic crystals between transition metal ions in orbitally degenerate states resulting from different configurations has been formulated in the previous communication (Part I).

It has been shown that using many-electron states of the whole crystal, constructed from the one-electron orthogonalized molecular orbitals, up to the second order perturbation theory, one may write the exchange Hamiltonian in the form

$$H_{\mathrm{ex}}^{ij}=\sum_{\substack{\lambda\lambda'\\ qq'}}(\tilde{I}_{qq'}^{\lambda\lambda'}(i,j)+I_{qq'}^{\lambda\lambda'}(i,j)\boldsymbol{S}_i\boldsymbol{S}_j)V_{iq}^{\lambda}(\Gamma)V_{jq'}^{\lambda'}(\Gamma). \tag{1}$$

Generally, coefficients $I_{qq'}^{\lambda\lambda'}(i,j)$ have very complicated form (see Eq. (28)–(31) in Part I) with a great number of parameters (see Eq. (12) in Part I). It has been also shown that in the case of quenched orbital motion exchange parameter can be decomposed into the sum of simple channels $\gamma\nu \rightleftarrows \gamma'\nu'$ — pairs of interacting half-filled orbitals (see (35) in Part I). When the orbital degeneracy do exist the simple channels picture is not valid but we can decompose the exchange parameter into a sum of so called collective channels $\gamma_1^{k1} \rightleftarrows \gamma_2^{k2}$ — pairs of interacting subconfigurations (see (36) in Part I). Another kind of collective channels appears if we take into account the configurational mixing, i.e. $\gamma_1^{k1} \rightleftarrows (\gamma_2^{k2} \overset{e^-}{\rightarrow} \gamma_3^{k3})$ — interactions between subconfiguration and configu-

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rational changing on one ion and $(\gamma_1^{k_1} \overset{e^-}{\rightarrow} \gamma_2^{k_2}) \rightleftarrows (\gamma_3^{k_3} \overset{e^-}{\rightarrow} \gamma_4^{k_4})$ — interaction between configurations with configurational changing on both ions (see (37) Part I).

The theory presented in Part I is general and quite formal. It contains hundreds parameters, so it is very difficult to apply it in this form to real systems with any detail considerations. Thus, the next step is indispensable and our main aim is to construct the effective spin-orbital Hamiltonian which will depend on a few parameters only. So, the question is what kind of contributions from $J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_3\nu_3\gamma_4\nu_4)$ (see (12) in Part I) are significant for each channel. This problem will be examined in Section 2. In Section 3 the effective Hamiltonian in the case of ground orbital doublet and triplet will be constructed in so called kinetic approximation when we omit all contributions except of kinetic ones.

2. *Symmetry requirements*

Symmetry approach has one unquestionable advantage consisting in reduction of a number of dependent parameters to only a few independent ones without any simplifications of the theory.

As an example let us consider 180°-exchange between a pair of octahedrally coordinated cations placed in a crystal of rock salt structure. To compute contributions from the kinetic transfers, we need to determine matrix elements of one-electron scalar operator between the states from neighbouring ions $h(i\gamma\nu, j\gamma'\nu') \equiv \langle i\gamma\nu|\hat{h}|j\gamma'\nu'\rangle$. Due to Wigner–Eckart theorem, these elements do not vanish if the states $|i\gamma\nu\rangle$ and $|j\gamma'\nu'\rangle$ are the components of the same basic vector of the same irreducible representation of the group D_{4h} being the symmetry group of the discussed pair. In cubic symmetry the various one-electron states of i-th and j-th ions are as follows

$$\begin{array}{rlrl}
 & |\theta_i\rangle \equiv |(3z^2-r^2)_i\rangle & & |\theta_j\rangle \equiv |(3z^2-r^2)_j\rangle \\
e_g(i): & |\varepsilon_i\rangle \equiv |(x^2-y^2)_i\rangle & e_g(j): & |\varepsilon_j\rangle \equiv |(x^2-y^2)_j\rangle \\
 & |\zeta_i\rangle \equiv |(xy)_i\rangle & & |\zeta_j\rangle \equiv |(xy)_j\rangle \\
t_{2g}(i): & |\xi_i\rangle \equiv |(yz)_i\rangle & t_{2g}(j): & |\xi_j\rangle \equiv |(yz)_j\rangle \\
 & |\eta_i\rangle \equiv |(xz)_i\rangle & & |\eta_j\rangle \equiv |(xz)_j\rangle
\end{array} \tag{2}$$

when a four-fold axis joining these ions is used as an axis of quantization. Next, using the standard group theory methods, we construct from the set (2) the basic states of irreducible representations of the group D_{4h}

$$\begin{array}{rl}
a_{1g}^{\pm}(i,j): & |\theta_i\rangle \pm |\theta_j\rangle, \\
b_{1g}^{\pm}(i,j): & |\varepsilon_i\rangle \pm |\varepsilon_j\rangle, \\
b_{2g}^{\pm}(i,j): & |\zeta_i\rangle \pm |\zeta_j\rangle, \\
 & |\xi_i\rangle \pm |\xi_j\rangle, \\
e_g^{\pm}(i,j): & |\eta_i\rangle \pm |\eta_j\rangle.
\end{array} \tag{3}$$

Consequently, states t_{2g} and e_g are not mixed by the transfer. Because of the dominating character of s and p states of ligands in the exchange interaction, we will consider only the contributions which contain transfer via ligand placed between interacting pair. So, the only nonzero matrix elements are these between states of $a_{1g}(i,j)$ and between states of $e_g(i,j)$ (see [1]). They can be written as $h(i\theta, j\theta)$ and $h(i\xi, j\xi) = h(i\eta, j\eta)$ (compare with [2]). So, $5^4 = 625$ kinetic contributions $\frac{1}{U} h(i,j)h(i,j)$ we reduced to $3^2 = 9$, constructed from these two parameters (nonzero matrix elements)

$$\frac{1}{U} h(j\theta, i\theta)h(i\theta, j\theta) = A,$$

$$\frac{1}{U} h(j\eta, i\eta)h(i\eta, j\eta) = \frac{1}{U} h(j\xi, i\xi)h(i\xi, j\xi) = \frac{1}{U} h(j\xi, i\xi)h(i\eta, j\eta)$$

$$= \frac{1}{U} h(j\eta, i\eta)h(i\xi, j\xi) = B,$$

$$\frac{1}{U} h(j\eta, i\eta)h(i\theta, j\theta) = \frac{1}{U} h(j\xi, i\xi)h(i\theta, j\theta) = \frac{1}{U} h(j\theta, i\theta)h(i\eta, j\eta)$$

$$= \frac{1}{U} h(j\theta, i\theta)h(i\xi, j\xi) = C = \sqrt{A \cdot B}. \tag{4}$$

We assume for simplicity, that U has approximately the same value for all transfers, because

$$U \sim 10^5 \text{ cm}^{-1} \gg \Delta U \sim 10^3 \text{ cm}^{-1}, \tag{5}$$

where ΔU is the difference between various U. Because of $B \sim 0.1\, A$ [3], we have $A > C > B$. C-parameter results from the configurational mixing and contributes to the last term of the Hamiltonian (37) in Part I. So, the configurational mixing is significant if only $\sum_{m,n} \alpha_n^2 \alpha_m^2$ and $\sum_{m,n} \alpha_n \alpha_{n+1} \alpha_m \alpha_{m+1}$ occurring in Eq. (29) and (31) (in Part I) are of the same order of magnitude. In CoO for example, if we consider $m, n = 0$ and $m, n = 1$ we have $\alpha_0 = 0.97$ and $\alpha_1 = 0.25$ [4] and this condition is fulfiled.

Applying symmetry arguments to correlation contributions we find

$$a_{1g}^{\alpha}(i,j)\colon F_\alpha(\{|\theta_m\rangle |\theta_n\rangle\}, \{|\varepsilon_m\rangle |\varepsilon_n\rangle\}, \{|\zeta_m\rangle |\zeta_n\rangle\}, \{|\eta_m\rangle |\eta_n\rangle\}, \{|\xi_m\rangle |\xi_n\rangle\}),$$
$$\alpha = 1, 2, \ldots, 16$$

$$a_{2g}^{\beta}(i,j)\colon F_\beta(\{|\varepsilon_m\rangle |\zeta_n\rangle\}, \{|\eta_m\rangle |\eta_n\rangle\}, \{|\xi_m\rangle |\xi_n\rangle\}), \quad \beta = 1, 2, \ldots, 12$$

$$b_{1g}^{\gamma}(i,j)\colon F_\gamma(\{|\theta_m\rangle |\varepsilon_n\rangle\}, \{|\eta_m\rangle |\xi_n\rangle\}), \quad \gamma = 1, 2, \ldots, 12$$

$$b_{2g}^{\delta}(i,j)\colon F_\delta(\{|\theta_m\rangle |\zeta_n\rangle\}, \{|\eta_m\rangle |\xi_n\rangle\}), \quad \delta = 1, 2, \ldots, 12$$

$$e_g^{\varrho}(i,j)\colon \begin{matrix} F_\varrho^1(\{|\theta_m\rangle |\eta_n\rangle\}, \{|\varepsilon_m\rangle |\eta_n\rangle\}, \{|\zeta_m\rangle |\xi_n\rangle\}) \\ F_\varrho^2(\{|\theta_m\rangle |\xi_n\rangle\}, \{|\varepsilon_m\rangle |\xi_n\rangle\}, \{|\zeta_m\rangle |\eta_n\rangle\}), \end{matrix} \quad \varrho = 1, 2, \ldots, 12 \tag{6}$$

where $m = i, j$ and $n = i, j$ and the notation $\{|\rangle|\rangle\}$ denotes the antisymmetrizing product of one-electron functions. Applying the Wigner–Eckart theorem we can easily obtain all nonzero correlation contributions. Considering (6) one can find that there do exist $t_{2g} \to e_g$ transfers but they result from the potential exchange and second order exchange correlations, only. Second order Coulomb correlations contribute to $t_{2g}\nu \to t_{2g}\nu$ transfers and $e_g\nu \to e_g\nu'$ transfers, so they are diagonal due to the subconfigurational interaction, and, moreover, they are also diagonal within $t_{2g}^{k_1} \rightleftarrows t_{2g}^{k_1}$ collective channel.

3. *Effective exchange Hamiltonian in the kinetic approximation*

Let us start with the orbital operators problem. We want to express our unit operators $V_q^\lambda(\Gamma)$ in the basis of orbital ground functions $|\Gamma\mu\rangle$. Using equivalence (18) from Part I we find

$$V_q^\lambda(\Gamma) = \sum_{\mu\mu'} [\lambda]^{-1/2} \langle \Gamma\mu'\Gamma\mu|\lambda q\rangle \, \langle \Gamma \| V^\lambda(\Gamma) \, \| \Gamma\rangle \, |\Gamma\mu\rangle \, \langle \Gamma\mu'|. \tag{7}$$

One can notice that due to the Wigner–Eckart theorem for cubic symmetry [1] the tensor operators $V^{A_2}(\Gamma)$ and $V^{T_1}(\Gamma)$ should be purely imaginary, so

$$\langle \Gamma \| V^{A_2}(\Gamma) \, \| \Gamma\rangle = \langle \Gamma \| \, V^{T_1}(\Gamma) \, \| \Gamma\rangle = i. \tag{8}$$

We shall first consider the case when each ion has a double degenerate ground orbital state. So, we find

$$V_{e_1}^{A_1}(E) = \frac{1}{\sqrt{2}} \mathscr{A}_1, \qquad V_\theta^E(E) = \tfrac{1}{2} \mathscr{U}_\theta,$$

$$V_{e_2}^{A_2}(E) = -\frac{1}{\sqrt{2}} \mathscr{A}_2, \quad V_\varepsilon^E(E) = \tfrac{1}{2} \mathscr{U}_\varepsilon, \tag{9}$$

where

$$\mathscr{A}_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathscr{A}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \mathscr{U}_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \mathscr{U}_\varepsilon = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{10}$$

(i.e., $\langle E\theta|\mathscr{U}_\theta|E\theta\rangle = -1$, etc.). These operators form Ham's basis [5] within the four-dimensional space of linear operators acting in the orbital doublet. We note that apart from the sign of $\mathscr{U}_\theta$ the matrices (10) are simply the Pauli matrices.

We now turn to the orbital triplet state. Let us start from the type T_1. Using formula (7) we find

$$V_{e_1}^{A_1}(T_1) = \frac{1}{\sqrt{3}} \mathscr{A}_1, \qquad V_x^{T_1}(T_1) = \frac{1}{\sqrt{6}} \mathscr{L}_x, \qquad V_\xi^{T_2}(T_1) = \frac{1}{\sqrt{6}} \mathscr{Q}_\xi,$$

$$V_\theta^E(T_1) = -\frac{1}{\sqrt{3}} \mathscr{E}_\theta, \qquad V_y^{T_1}(T_1) = \frac{1}{\sqrt{6}} \mathscr{L}_y, \qquad V_\eta^{T_2}(T_1) = \frac{1}{\sqrt{6}} \mathscr{Q}_\eta,$$

$$V_\varepsilon^E(T_1) = -\frac{1}{\sqrt{3}} \mathscr{E}_\varepsilon, \qquad V_z^{T_1}(T_1) = \frac{1}{\sqrt{6}} \mathscr{L}_z, \qquad V_\zeta^{T_2}(T_1) = \frac{1}{\sqrt{6}} \mathscr{Q}_\zeta, \tag{11}$$

where

$$\mathscr{A}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \mathscr{E}_\theta = \begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}, \quad \mathscr{E}_\varepsilon = \begin{pmatrix} -\frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & \frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\mathscr{L}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad \mathscr{L}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}, \quad \mathscr{L}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$\mathscr{Q}_\xi = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix}, \quad \mathscr{Q}_\eta = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix}, \quad \mathscr{Q}_\zeta = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{12}$$

These operators form Ham's basis [5] within the nine-dimensional space of linear operators acting in the orbital triplet T_1. It is easy to show that for T_2 state we have the following relation

$$V_q^\lambda(T_2) = \pm V_q^\lambda(T_1). \tag{13}$$

The values of phase factors of the Clebsch–Gordan coefficients are defined according to [7]. It is interesting that matrices of $\hat{\mathscr{L}}_x, \hat{\mathscr{L}}_y$ and $\hat{\mathscr{L}}_z$ are the same as matrices of orbital operator $\hat{\mathscr{L}} = 1$ in the p-state of free atom. So, we can call $\hat{\mathscr{L}} = 1$ the fictitious orbital moment operator. On the other hand we can express all other operators $V_q^\lambda(\Gamma)$ via components of $V^{T_1}(T_1) = \hat{\mathscr{L}}$. Thus, we have

$$\begin{aligned} \mathscr{A}_1 &= \tfrac{1}{2}\hat{\mathscr{L}}^2, & \mathscr{Q}_\xi &= \mathscr{L}_y\mathscr{L}_z + \mathscr{L}_z\mathscr{L}_y, \\ \mathscr{E}_\theta &= \tfrac{1}{2}(3\mathscr{L}_z^2 - 2), & \mathscr{Q}_\eta &= \mathscr{L}_z\mathscr{L}_x + \mathscr{L}_x\mathscr{L}_z, \\ \mathscr{E}_\varepsilon &= \tfrac{1}{2}[\sqrt{3}\,(\mathscr{L}_x^2 - \mathscr{L}_y^2)], & \mathscr{Q}_\zeta &= \mathscr{L}_x\mathscr{L}_y + \mathscr{L}_y\mathscr{L}_x. \end{aligned} \tag{14}$$

Now, we may pass to the effective Hamiltonian (1). In the first approximation we will restrict ourselves to kinetic contributions only, and we neglect all the others (i.e. potential contributions and second order correlation contributions). Let us ignore for a moment the configurational mixing. In our Hamiltonian we will have only two parameters A and B (4) resulting from $e_g^{k1} \rightleftarrows e_g^{k1}$ and $t_{2g}^{k_2} \rightleftarrows t_{2g}^{k_2}$ collective channels. Moreover, the only one simple channel $e_g\theta \rightleftarrows e_g\theta$ contributes to the collective channel $e_g^{k_1} \rightleftarrows e_g^{k_1}$. Because of our restriction $\nu_1, \nu_2, \nu_1', \nu_2'$ in (24) Part I are not independent but $\nu_1 = \nu_1'$ and $\nu_2' = \nu_1$. If we consider the orbital doublet $d^n \to \Gamma = E$ the effective Hamiltonian takes the form

$$\begin{aligned} H_{ex}^{ij} &= (\tilde{I}_{e_1e_1}^{A_1A_1} + I_{e_1e_1}^{A_1A_1}\mathbf{S}_i\mathbf{S}_j)\mathscr{A}_1^i\mathscr{A}_1^j \\ &+ (\tilde{I}_{e_1\theta}^{A_1E} + I_{e_1\theta}^{A_1E}\mathbf{S}_i\mathbf{S}_j)(\mathscr{A}_1^i\mathscr{U}_\theta^j + \mathscr{U}_\theta^i\mathscr{A}_1^j) \\ &+ (\tilde{I}_{\theta\theta}^{EE} + I_{\theta\theta}^{EE}\mathbf{S}_i\mathbf{S}_j)\mathscr{U}_\theta^i\mathscr{U}_\theta^j + (\tilde{I}_{\varepsilon\varepsilon}^{EE} + I_{\varepsilon\varepsilon}^{EE}\mathbf{S}_i\mathbf{S}_j)\mathscr{U}_\varepsilon^i\mathscr{U}_\varepsilon^j, \end{aligned} \tag{15}$$

where

$$I^{A_1A_1}_{e_1e_1} = \tfrac{1}{4}A\left(\frac{\langle ES\|W^{1A_1}(ee)\,\|ES\rangle}{\langle S\|S\|S\rangle}\right)^2 + \tfrac{1}{3}B\left(\frac{\langle ES\|W^{1A_1}(tt)\,\|ES\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{A_1E}_{e_1\theta} = \frac{1}{4\sqrt{2}}A\langle S\|S\|S\rangle^{-2}\langle ES\|W^{1A_1}(ee)\,\|ES\rangle\,\langle ES\|W^{1E}(ee)\,\|ES\rangle$$

$$+\frac{1}{2\sqrt{3}}B\langle S\|S\|S\rangle^{-2}\langle ES\|W^{1A_1}(tt)\,\|ES\rangle\,\langle ES\|W^{1E}(tt)\,\|ES\rangle,$$

$$I^{EE}_{\theta\theta} = \tfrac{1}{8}A\left(\frac{\langle ES\|W^{1E}(ee)\,\|ES\rangle}{\langle S\|S\|S\rangle}\right)^2 + \tfrac{1}{12}B\left(\frac{\langle ES\|W^{1E}(tt)\,\|ES\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{EE}_{\varepsilon\varepsilon} = \tfrac{1}{4}B\left(\frac{\langle ES\|W^{1E}(tt)\,\|ES\rangle}{\langle S\|S\|S\rangle}\right)^2. \tag{16}$$

For orbital triplet $d^n \to \Gamma = T_{1(2)}$ the effective Hamiltonian is

$$H^{ij}_{ex} = (\tilde{I}^{A_1A_1}_{e_1e_1} + I^{A_1A_1}_{e_1e_1}\mathbf{S}_i\mathbf{S}_j)\mathscr{A}^i_1\mathscr{A}^j_1 + (\tilde{I}^{A_1E}_{e_1\theta} + I^{A_1E}_{e_1\theta}\mathbf{S}_i\mathbf{S}_j)(\mathscr{A}^i_1\mathscr{E}^j_\theta + \mathscr{E}^i_\theta\mathscr{A}^j_1) + (\tilde{I}^{EE}_{\theta\theta} + I^{EE}_{\theta\theta}\mathbf{S}_i\mathbf{S}_j)\mathscr{E}^i_\theta\mathscr{E}^\theta_j$$
$$+(\tilde{I}^{EE}_{\varepsilon\varepsilon} + I^{EE}_{\varepsilon\varepsilon}\mathbf{S}_i\mathbf{S}_j)\mathscr{E}^i_\varepsilon\mathscr{E}^j_\varepsilon + (\tilde{I}^{T_1T_1}_{zz} + I^{T_1T_1}_{zz}\mathbf{S}_i\mathbf{S}_j)\mathscr{L}^i_z\mathscr{L}^j_z + (\tilde{I}^{T_2T_2}_{\zeta\zeta} + I^{T_2T_2}_{\zeta\zeta}\mathbf{S}_i\mathbf{S}_j)\mathscr{Q}^i_\zeta\mathscr{Q}^j_\zeta, \tag{17}$$

where

$$I^{A_1A_1}_{e_1e_1} = \tfrac{1}{6}A\left(\frac{\langle TS\|W^{1A_1}(ee)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2 + \tfrac{2}{9}B\left(\frac{\langle TS\|W^{1A_1}(tt)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{A_1E}_{e_1\theta} = \tfrac{1}{6}A\langle S\|S\|S\rangle^{-2}\langle TS\|W^{1A_1}(ee)\,\|TS\rangle\,\langle TS\|W^{1E}(ee)\,\|TS\rangle$$

$$\mp\frac{\sqrt{2}}{9}B\langle S\|S\|S\rangle^{-2}\langle TS\|W^{1A_1}(tt)\,\|TS\rangle\,\langle TS\|W^{1E}(tt)\,\|TS\rangle,$$

$$I^{EE}_{\theta\theta} = \tfrac{1}{6}A\left(\frac{\langle TS\|W^{1E}(ee)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2 + \tfrac{1}{9}B\left(\frac{\langle TS\|W^{1E}(tt)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{EE}_{\varepsilon\varepsilon} = \tfrac{1}{3}B\left(\frac{\langle TS\|W^{1E}(tt)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{T_1T_1}_{zz} = -\tfrac{1}{6}B\left(\frac{\langle TS\|W^{1T_1}(tt)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right)^2,$$

$$I^{T_2T_2}_{\zeta\zeta} = \tfrac{1}{6}B\left(\frac{\langle TS\|W^{1T_2}(tt)\,\|TS\rangle}{\langle S\|S\|S\rangle}\right). \tag{18}$$

The coefficients $\tilde{I}^{\lambda\lambda'}_{qq'}$ are obtained by changing

$$\frac{\langle \Gamma S\|W^{1\lambda}(\gamma\gamma)\,\|\Gamma S\rangle}{\langle S\|S\|S\rangle} \to \frac{\langle \Gamma S\|W^{0\lambda}(\gamma\gamma)\,\|\Gamma S\rangle}{\sqrt{[S]}}, \tag{19}$$

and the diagonal reduced matrix elements of the double cubic irreducible tensor operators are tabulated in [6].

If we now take into account the configurational mixing new features appear. First, we have to renormalize $I_{qq'}^{\lambda\lambda'}$ coefficients in consistence with (29) in Part I. So, we change

$$\langle \Gamma S \| W^{\omega\lambda}(\gamma\gamma) \| \Gamma S \rangle \langle \Gamma S \| W^{\omega\lambda'}(\gamma'\gamma') \| \Gamma S \rangle$$

$$\to \sum_{m,n} \alpha_m^2 \alpha_n^2 \langle m\Gamma S \| W^{\omega\lambda}(\gamma\gamma) \| m\Gamma S \rangle \langle n\Gamma S \| W^{\omega\lambda'}(\gamma'\gamma') \| n\Gamma S \rangle, \tag{20}$$

where

$$\langle m\Gamma S \| W^{\omega\lambda}(\gamma\gamma) \| m\Gamma S \rangle \equiv \langle (t_{2g}^{k_1-m} e_g^{k_2+m}) \Gamma S \| W^{\omega\lambda}(\gamma\gamma) \| (t_{2g}^{k_1-m} e_g^{k_2+m}) \Gamma S \rangle. \tag{21}$$

Secondly, new terms in exchange Hamiltonian will appear due to configuration-configuration interaction (the last term of the Hamiltonian (37) in Part I). Note, that in our approximation the second and the third term of this Hamiltonian does not exist. Generally, all elements of the Hamiltonian (37) from Part I, except the first one, result from the interaction between terms and because of the coefficient $\langle t_{2g} v e_g v' | \lambda q \rangle$ they are nonzero only for the orbital triplet. Thus, for the orbital singlet or doublet the configurational mixing does not change the form of the Hamiltonian but only renormalizes its coefficients (see (20)). In our approximation new terms appear for the orbital triplet

$$(\tilde{I}_{xx}^{T_1T_1} + I_{xx}^{T_1T_1} \mathbf{S}_i \mathbf{S}_j) \mathcal{L}_x^i \mathcal{L}_x^j + (\tilde{I}_{yy}^{T_1T_1} + I_{yy}^{T_1T_1} \mathbf{S}_i \mathbf{S}_j) \mathcal{L}_y^i \mathcal{L}_y^j$$

$$+ (\tilde{I}_{\xi\xi}^{T_2T_2} + I_{\xi\xi}^{T_2T_2} \mathbf{S}_i \mathbf{S}_j) \mathcal{Q}_\xi^i \mathcal{Q}_\xi^j + (\tilde{I}_{\eta\eta}^{T_2T_2} + I_{\eta\eta}^{T_2T_2} \mathbf{S}_i \mathbf{S}_j) \mathcal{Q}_\eta^i \mathcal{Q}_\eta^j, \tag{22}$$

where

$$I_{xx}^{T_1T_1} = I_{yy}^{T_1T_1} = \tfrac{1}{4} \sqrt{A \cdot B} \sum_{m,n} \alpha_m \alpha_{m+1} \alpha_n \alpha_{n+1} \langle S \| S \| S \rangle^{-2} RM(m) RM(n),$$

$$I_{\xi\xi}^{T_2T_2} = I_{\eta\eta}^{T_2T_2} = \tfrac{1}{12} \sqrt{A \cdot B} \sum_{m,n} \alpha_m \alpha_{m+1} \alpha_n \alpha_{n+1} \langle S \| S \| S \rangle^{-2} RM(m) RM(n), \tag{23}$$

and

$$RM(m) = \langle mTS \| W^{1T}(et) \| m+1TS \rangle. \tag{24}$$

4. *Conclusions*

More detail considerations of the theory of superexchange, developed in Part I, was performed. Symmetry considerations allow us to reduce a great number of dependent exchange parameters to only a few independent ones. It was shown that the second order Coulomb correlations contribute to $t_{g2}v \to t_{2g}v$ and $e_g v \to e_g v'$ transfers and that $t_{2g} \to e_g$ interaction results from the potential exchange and second order exchange correlations.

The effective Hamiltonian for arbitrary $d^n - d^n$ pair was found in the kinetic approximation. In this case we were able to express all coefficients by the two parameters. Simultaneously, it was shown that in the case of ground orbital singlet or doublet the configurational mixing does not change the form of the Hamiltonian but renormalizes its coefficients. If

we consider the orbital triplet, the configurational mixing renormalizes the coefficients in the Hamiltonian and also produces new significant terms.

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