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ON SUPEREXCHANGE IN MAGNETIC INSULATORS. I. GENERAL THEORY

By M. Błaszak

Institute of Physics, A. Mickiewicz University, Poznań*

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The problem of superexchange interaction between orbitally degenerate ions is considered in the case of ground state resulting from different configurations. A new kind of exchange contributions due to the configurational mixing is found. The general effective Hamiltonian is given, using the tensor operator formalism. The concept of general channels is used to describe the microscopic theory of its parameters. It is shown that in the case of orbitally nondegenerate ground state for the strong crystal field, the Heisenberg form of the exchange Hamiltonian can be expressed as a sum of simple channels (pairs of interacting half-filled orbitals). In the other cases (orbital degeneracy or mixing of configurations) we can decompose the exchange Hamiltonian into the sum of collective channels (pairs of interacting subconfigurations or configurations). The second order correlations are taken into account.

1. *Introduction*

The purpose of this work is to give the detail theory of isotropic superexchange interaction in the transition metal compounds, in the case of orbital degeneracy and configurational mixing. The theory takes into account all contributions to isotropic superexchange up to the second order perturbation theory, so the considerations include correlation effects.

The superexchange problem was studied several times, however mainly very limited cases have been considered till now. If authors considered this problem taking into account orbital degeneracy, they restricted to the kinetic exchange mechanism [1–3] or to the mean-field coupling scheme [4, 5] and they neglected the configurational mixing. Most generally the problem was treated by Eremin and Rokitin [6, 7] but these authors started from a different Hamiltonian in comparison with the one studied in the present work and they did not take into account the interaction between configurations.

The theory presented here deals with the isotropic spin superexchange. All anisotropic contributions which may appear here come from the orbital part of the effective Hamiltonian. Anisotropic, antisymmetric, and biquadratic exchange are generally smaller

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* Address: Instytut Fizyki, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

effects than the isotropic exchange, so we omit them in this work. The general theory of these interactions makes another nontrivial problem.

To describe the physical properties of transition metal compounds, the effective Hamiltonian, expressed in terms of irreducible tensor operators, will be constructed. To find them we apply the perturbation theory and make use of the isomorphism between the Lee algebra of the angular momentum operators and the algebra of Fermi-Dirac operators (Section 2 and 3). In the particular case it led us to the simple Heisenberg form $H_{ex} = -2\sum_{i,j} J_{ij} S_i S_j$.

In the transition metal compounds the Coulomb interaction between electrons from the same ion is comparable with the crystal field energy. So, we can start either from the mean-field coupling scheme, or from the strong-field one. However, having in mind the microscopic character of the theory, the strong-field approximation seems to be more natural due to the dominating role of covalency for the exchange parameter, mixing the central ion d-orbitals with ligand p- and s-orbitals. Unfortunately, this approach is not always correct from the physical point of view and we have to take into account also a mixing of the crystal configurations (within the same d^n configuration). It leads to a new kind of electron transfers and to the renormalization of the effective Hamiltonian parameters and we will discuss it in Section 3.

To give a physical interpretation for the new parameters, a concept of general channels is introduced (Section 4). This concept is useful for better understanding of nature of the superexchange interaction in the case of orbital degeneracy or the configurational mixing.

2. *Effective superexchange Hamiltonian*

One of the most important problems in the microscopic theory of superexchange is a proper choice of one-electron states. We start from the localized-electron model.

In the strong crystal field approximation, d-electron wave functions can be approximated by antibonding orbitals of the cluster and each d-electron localized state has the form

$$|\gamma\nu\rangle = N_\gamma(|d\gamma\nu\rangle - \lambda_p|p\gamma\nu\rangle - \lambda_s|s\gamma\nu\rangle), \tag{1}$$

where $|d\gamma\nu\rangle$ is a state of a central magnetic ion, $|p\gamma\nu\rangle$, $|s\gamma\nu\rangle$ are linear combinations of atomic $2p$ and $2s$ states of ligands surrounding them, and λ is a function of the covalency parameter as well as the overlap integral [8]. After orthogonalisation of orbitals (1) from different ions we get the basic set of one-electron states $|i\gamma\nu\sigma\rangle$ of magnetic insulator. The index i labels magnetic ion sites, γ and ν denote irreducible representations of the point group and their basic vectors, respectively, and σ is the spin component.

The Hamiltonian of the d-electrons in the second quantized form, with respect to this basic set of states, is

$$H = \sum_{\{i\gamma\nu\}\sigma} \langle i_1\nu_1\gamma_1|\hat{h}|i_2\gamma_2\nu_2\rangle a^\dagger_{i_1\gamma_1\nu_1\sigma} a_{i_2\gamma_2\nu_2\sigma}$$

$$+\tfrac{1}{2}\sum_{\{i\gamma\nu\sigma\}} \langle i_1\gamma_1\nu_1 i_3\gamma_3\nu_3|\hat{g}|i_2\gamma_2\nu_2 i_4\gamma_4\nu_4\rangle a^\dagger_{i_1\gamma_1\nu_1\sigma} a^\dagger_{i_3\gamma_3\nu_3\sigma'} a_{i_4\gamma_4\nu_4\sigma'} a_{i_2\gamma_2\nu_2\sigma} = H(\hat{h}) + H(\hat{g}), \tag{2}$$

where $H(\hat{h})$ and $H(\hat{g})$ correspond to one- and two-particle terms, respectively. We restrict ourselves to the terms with one-electron states $|i_n\gamma_n\nu_n\rangle$, $n = 1, 2, 3, 4$ localized on the same or the nearest neighbouring magnetic ions. Interactions and transfers between more distant neighbours will be neglected for their relative smallness. The Hamiltonian (2) contains one- and two-electron operators (denoted by $\hat{h}$ and $\hat{g}$, respectively) that are spin independent. Spin dependent operators contribute to anisotropic, antisymmetric and biquadratic interactions and we omit them in this work.

Now, using our basic one-electron states, we construct the many-electron states $|m\rangle$ of the whole crystal. First, let us define a subspace Ω_0 of states which preserve the number of electrons as well as the ground term on each ion. The many-electron state $|m_0\rangle$ of this subspace has the form

$$|m_0\rangle = \mathscr{A} \bigotimes_{i=1}^{N} |i\Gamma\mu SM\rangle, \tag{3}$$

where $\mathscr{A}$ is the antisymmetrizing operator and $|i\Gamma\mu SM\rangle$ is a many-electron state of the ground term of the i-th ion. The state $|i\Gamma\mu SM\rangle$ is assumed to be constructed from the one-electron states $|i\gamma\nu\sigma\rangle$ as it is usually in the crystal-field theory. The index m_0 denotes a set of quantum numbers $\{\Gamma_i\mu_iS_iM_i\}_{i=1,2,\ldots,N}$. Ω_0 contains $\prod_{i=1}^{N}(2\Gamma_i+1)(2S_i+1)$ many-electron states $|m_0\rangle$. Next, applying once or twice the pairs of creation and annihilation operators, we obtain excited states of the form

$$|m_1\rangle = a^{\dagger}_{\xi_2}a_{\xi_1}|m_0\rangle, \tag{4}$$

or

$$|m_1'\rangle = a^{\dagger}_{\xi_4}a_{\xi_3}a^{\dagger}_{\xi_2}a_{\xi_1}|m_0'\rangle, \tag{5}$$

where $\xi_n = (i_n\gamma_n\nu_n\sigma_n)$. We assume $i_1 \neq i_2$ in Eq. (4) and $i_1 \neq i_2$ or $i_3 \neq i_4$ in Eq. (5) and denote a subspace of these states by Ω_1.

Let us introduce the operators P_0 and P_1 of projection on subspaces Ω_0 and Ω_1

$$P_0 = \sum_{\Omega_0} |m_0\rangle\langle m_0|,$$

$$P_1 = \sum_{\Omega_1} |m_1\rangle\langle m_1|, \tag{6}$$

and define the unperturbed Hamiltonian as

$$H_0 = P_0HP_0+P_1HP_1. \tag{7}$$

The perturbation V is the difference $H-H_0$, i.e. the part of H which couples states from different subspaces. Using the perturbation theory for degenerate states [9], we obtain the effective Hamiltonian for H in the ground subspace Ω_0 up to the second order as

$$H_{\mathrm{eff}} = P_0HP_0+P_0VP_0-P_0VKVP_0 = P_0HP_0-P_0HKHP_0, \tag{8}$$

where the operator K has the form

$$K = \sum_{\Omega_1} \frac{|m_1\rangle \langle m_1|}{U_{m_1 m_0}}, \tag{9}$$

and

$$U_{m_1 m_0} = E_{m_1} - E_{m_0} = \langle m_1|H_0|m_1\rangle - \langle m_0|H_0|m_0\rangle \tag{10}$$

are the energy differences between states from Ω_1 and Ω_0 subspaces, respectively.

Contributions to the isotropic exchange interaction result from the terms that change the spin direction of occupied one-electron states [5]. So, we are looking for the isotropic superexchange Hamiltonian in the form

$$H_{\text{ex}} = \sum_{i,j} \sum_{\{\gamma\nu\sigma\}} J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_3\nu_3\gamma_4\nu_4) P_0 a^\dagger_{i\gamma_1\nu_1\sigma} a_{i\gamma_2\nu_2\sigma'} a^\dagger_{j\gamma_3\nu_3\sigma'} a_{j\gamma_4\nu_4\sigma} P_0, \tag{11}$$

with

$$\begin{aligned} J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_3\nu_3\gamma_4\nu_4) &= \frac{\langle j\gamma_3\nu_3|\hat{h}|i\gamma_2\nu_2\rangle \langle i\gamma_1\nu_1|\hat{h}|j\gamma_4\nu_4\rangle}{U(i\gamma_1\nu_1, j\gamma_4\nu_4)} \\ &\quad -\tfrac{1}{2}\langle i\gamma_1\nu_1 j\gamma_3\nu_3|\hat{g}|j\gamma_4\nu_4 i\gamma_2\nu_2\rangle + \text{second order correlation contributions,} \end{aligned} \tag{12}$$

where

$$U(i\gamma_1\nu_1, j\gamma_4\nu_4) \equiv U_{m_1 m_0}, \; |m_1\rangle = a^\dagger_{j\gamma_4\nu_4} a_{i\gamma_1\nu_1}|m_0\rangle.$$

The second order correlation contributions result from a part of Eq. (2) of the form

$$\tfrac{1}{2}\sum_{i,j} \sum_{\{\gamma\nu\sigma\}} \langle j\gamma_1\nu_1 i\gamma_3\nu_3|\hat{g}|j\gamma_2\nu_2\, j\gamma_4\nu_4\rangle a^\dagger_{j\gamma_1\nu_1\sigma} a^\dagger_{i\gamma_3\nu_3\sigma'} a_{j\gamma_4\nu_4\sigma'} a_{j\gamma_2\nu_2\sigma} + \text{h.c. terms.} \tag{13}$$

If we neglect effects of these terms, the expression (11) represents a generalization of Anderson's mechanism of kinetic and potential exchange [10] that allows one to treat the orbital degeneracy of magnetic ions.

Generally, second order correlation contributions are accompanied by eight creation and annihilation operators

$$\mathrlap{\overbrace{\phantom{a^\dagger_{j\gamma_1\nu_1\sigma} a^\dagger_{i\gamma_3\nu_3\sigma'} a_{j\gamma_4\nu_4\sigma'}}}^{1}} a^\dagger_{j\gamma_1\nu_1\sigma} \underbrace{a^\dagger_{i\gamma_3\nu_3\sigma'} a_{j\gamma_4\nu_4\sigma'} \mathrlap{\underbrace{\phantom{a_{j\gamma_2\nu_2\sigma} a^\dagger_{i\gamma_5\nu_5\sigma'}}}_{2}} a_{j\gamma_2\nu_2\sigma} \overbrace{a^\dagger_{i\gamma_5\nu_5\sigma'} a^\dagger_{j\gamma_7\nu_7\sigma} a_{i\gamma_8\nu_8\sigma} a_{i\gamma_6\nu_6\sigma'}}^{1}}_{2} \tag{14}$$

and they contribute to higher order interactions as biquadratic exchange, for example. Bilinear exchange terms are accompanied by four second quantized operators (11) so in the second order correlation terms two pairs of these operators should give unite operators. There are two ways to do it.

1. First way consists in replacing one pair of second quantized operators from each ion by a unite operator, where each pair proceeds from the term of form (13) i.e. $\gamma_1\nu_1 = \gamma_2\nu_2$ and $\gamma_5\nu_5 = \gamma_6\nu_6$ (14), and we refer to these terms as the second order Coulomb correlation terms.

2. Second way consists in replacing one pair of second quantized operators from each ion by a unite operator, where each pair proceeds from different terms of form (13) i.e. $\gamma_2\nu_2 = \gamma_7\nu_7$ and $\gamma_3\nu_3 = \gamma_6\nu_6$, and we refer to these terms as the second order exchange correlation terms.

Note, that the second order Coulomb correlations are antiferromagnetic in sign and second order exchange correlations are ferromagnetic in sign.

Let us consider for a moment the problem of a linearization of the two-electron terms in (13) by the Hartree–Fock approximation. If we perform the averaging over ground spin-unordered state of one pair operators from the same ion $\langle a^{\dagger}_{i\gamma\nu\sigma}\, a_{i\gamma'\nu'\sigma'}\rangle$, we pass to the concept of the Coulomb and exchange one-ion fields resulting from e_g- and t_{2g}-electrons. The Coulomb field arises from averaging over $\langle a^{\dagger}_{j\gamma_1\nu_1\sigma}\, a_{j\gamma_2\nu_2\sigma}\rangle$ and the exchange field arises from averaging over $\langle a^{\dagger}_{j\gamma_1\nu_1\sigma}\, a_{j\gamma_4\nu_4\sigma'}\rangle$. Now, from (14) one can find that the Hartree–Fock approximation does not change the second order Coulomb terms but do not take into account second order exchange correlations in the Hamiltonian (11) [11].

3. *Tensor operators technique*

The effective Hamiltonian (11) can be expressed as a series of irreducible tensor operators. For this purpose, let us note that both the creation operators $a^{\dagger}_{i\gamma\nu\sigma}$ and annihilation operators $\tilde{a}_{i\gamma\nu\sigma} = (-1)^{s-\sigma}\, a_{i\gamma\nu-\sigma}$ are tensor operators [12]. The product of them, expressed in terms of double tensor operators, takes the form

$$a^{\dagger}_{i\gamma\nu\sigma} a_{i\gamma'\nu'\sigma'} = \sum_{\substack{\omega\lambda \\ \pi q}} (-1)^{s-\sigma} \langle \gamma\nu\gamma'\nu'|\lambda q\rangle\, \langle s\sigma s-\sigma|\omega\pi\rangle W^{\omega\lambda}_{\pi q}(\gamma\gamma'), \tag{15}$$

where the double tensor operators $W^{\omega\lambda}(\gamma\gamma')$ are the sum of the one-electron double tensor operators

$$W^{\omega\lambda}(\gamma\gamma') = \sum_{k} w^{\omega\lambda}(k)\,(\gamma\gamma'), \tag{16}$$

with reduced matrix element

$$\langle \gamma s\|w^{\omega\lambda}(k)\,(\gamma\gamma')\,\|\gamma' s'\rangle = \delta_{\gamma\gamma'}\delta_{ss'}[\omega,\, \lambda]^{1/2}. \tag{17}$$

The index k labels the electron of a given ion. The coefficients in Eq. (15) are the Clebsch–-Gordan coefficients and the notation $[\omega] = 2\omega+1$ is used.

One should notice that, in expression (11), the only components that do not vanish are operators $|m_0\rangle\langle m'_0|$ for which the states $|m_0\rangle$ and $|m'_0\rangle$ differ only by states on j-th and i-th ion. So, using the relation

$$|\Gamma\mu SM\rangle\, \langle \Gamma\mu' SM'| = \sum_{\substack{\omega\lambda \\ \pi q}} (-1)^{S-M}[\omega,\, \lambda]^{1/2} \langle \Gamma\mu'\Gamma\mu|\lambda q\rangle\, \langle SM'S-M|\omega\pi\rangle V^{\lambda}_{q}(\Gamma) V^{\omega}_{\pi}(S), \tag{18}$$

where $V^{\omega}_{\pi}(S)$ and $V^{\lambda}_{q}(\Gamma)$ are unite irreducible tensor operators in the space of a ground crystal term of the i-th cation with the full spin S and pseudomomentum Γ

$$\langle SM|V^{\omega}_{\pi}(S)\,|SM'\rangle = (-1)^{S-M}[\omega]^{-1/2}\langle SM'S-M|\omega\pi\rangle,$$

$$\langle \Gamma\mu|V^{\lambda}_{q}(\Gamma)\,|\Gamma\mu'\rangle = [\lambda]^{-1/2}\langle \Gamma\mu'\Gamma\mu|\lambda q\rangle, \tag{19}$$

and orthogonality relation for the Clebsch–Gordan coefficients we obtain

$$P_0 a^{\dagger}_{i\gamma_1 v_1 \sigma} a_{i\gamma_2 v_2 \sigma'} a^{\dagger}_{j\gamma_3 v_3 \sigma'} a_{j\gamma_4 v_4 \sigma} P_0$$

$$= \sum_{\substack{\lambda\lambda' \\ qq'}} \sum_{\substack{\omega \\ \pi}} (-1)^{\pi} \langle \gamma_1 v_1 \gamma_2 v_2 | \lambda q \rangle \, \langle \gamma_3 v_3 \gamma_4 v_4 | \lambda' q' \rangle \, \langle i\Gamma S \| W^{\omega\lambda}(\gamma_1\gamma_2) \, \| i\Gamma S \rangle$$

$$\times \langle j\Gamma S \| W^{\omega\lambda'}(\gamma_3\gamma_4) \, \| j\Gamma S \rangle V^{\lambda}_{iq}(\Gamma) V^{\lambda'}_{jq'}(\Gamma) V^{\omega}_{i\pi}(S) V^{\omega}_{j-\pi}(S). \tag{20}$$

After some algebra we find the following form of the exchange Hamiltonian

$$H^{ij}_{\text{ex}} = \sum_{\substack{\lambda\lambda' \\ qq'}} (\tilde{I}^{\lambda\lambda'}_{qq'}(i,j) + I^{\lambda\lambda'}_{qq'}(i,j) S_i S_j) V^{\lambda}_{iq}(\Gamma) V^{\lambda'}_{jq'}(\Gamma). \tag{21}$$

The coefficients $\tilde{I}^{\lambda\lambda'}_{qq'}(i,j)$ and $I^{\lambda\lambda'}_{qq'}(i,j)$ result from terms with $\omega = 0$ and $\omega = 1$, respectively, and are dependent on the form of the ground crystal term on each ion.

For the ground states of the i-th ion $|i\Gamma\mu SM\rangle$ resulting from $t^{k_1}_{2g}e^{k_2}_{g}$ configuration (the case of the strong octahedral crystal field),

$$|i\Gamma\mu SM\rangle \equiv |t^{k_1}_{2g}(\Gamma_1 S_1) e^{k_2}_{g}(\Gamma_2 S_2); i\Gamma\mu SM\rangle, \tag{22}$$

the parameters $I^{\lambda\lambda'}_{qq'}(i,j)$ are found to be of the form

$$I^{\lambda\lambda'}_{qq'}(i,j) = \sum_{\gamma\gamma'} I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma'), \qquad \gamma, \gamma' = t_{2g}, e_g, \tag{23}$$

where

$$I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma') = \sum_{\{v\}} J(i\gamma v_1 \gamma v_2, j\gamma' v'_1 \gamma' v'_2) \, \langle \gamma v_1 \gamma v_2 | \lambda q \rangle \, \langle \gamma' v'_1 \gamma' v'_2 | \lambda' q' \rangle$$

$$\times \langle S \| S \| S \rangle^{-2} \langle i\Gamma S \| W^{1\lambda}(\gamma\gamma) \, \| i\Gamma S \rangle \, \langle j\Gamma S \| W^{1\lambda'}(\gamma'\gamma') \, \| j\Gamma S \rangle. \tag{24}$$

The explicit form of reduced matrix element $\langle \Gamma S \| W^{1\lambda}(\gamma\gamma) \| \Gamma S \rangle$ is expressed by 6-j, 6-Γ symbols and fractional parentage coefficients and can be found in Ref. [13]. If the ground state is orbitally nondegenerate, the spin dependent part of the exchange Hamiltonian takes the form

$$H^{ij}_{\text{ex}} = I^{A_1 A_1}_{e_1 e_1}(i,j) S_i S_j = \sum_{\gamma\gamma'} I^{A_1 A_1}_{e_1 e_1}(i\gamma, j\gamma') \frac{S_{i\gamma} S_{j\gamma'}}{g_{i\gamma} g_{j\gamma'}}, \tag{25}$$

where $S_{i\gamma}$ is the spin of subconfiguration $i\gamma^k$ and the g-factors are as follows

$$g_{i\gamma} = \frac{S_i(S_i+1) + S_{i\gamma}(S_{i\gamma}+1) - S_{i\gamma'}(S_{i\gamma'}+1)}{2S_i(S_i+1)}. \tag{26}$$

For the crystal field energy comparable with the Coulomb energy on the i-th ion, the ground crystal term results from different configurations

$$|i\Gamma\mu SM\rangle = \sum_{n} \alpha_n |i\Gamma\mu SM(t^{k_1-n}_{2g} e^{k_2+n}_{g})\rangle, \tag{27}$$

with $\sum_n \alpha_n^2 = 1$. The configurational mixing does not change the general form of the Hamiltonian (21), but renormalizes its parameters, only. Now, the coefficients $I_{qq'}^{\lambda\lambda'}(i,j)$ take the form

$$I_{qq'}^{\lambda\lambda'}(i,j) = \sum_{\substack{\gamma_1\gamma_2 \\ \gamma_3\gamma_4}} I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_4), \tag{28}$$

where for $\gamma_1 = \gamma_2 = \gamma$ and $\gamma_3 = \gamma_4 = \gamma'$

$$I_{qq}^{\lambda\lambda'}(i\gamma, j\gamma') = \sum_{\{\nu\}} J(i\gamma\nu\gamma\nu', j\gamma'\nu'\gamma'\nu'') \langle\gamma\nu\gamma\nu'|\lambda q\rangle \langle\gamma'\nu'\gamma'\nu''|\lambda'q'\rangle \langle S\|S\|S\rangle^{-2}$$
$$\times \sum_{m,n} \alpha_m^2\alpha_n^2 \langle in\|W^{1\lambda}(\gamma\gamma)\|in\rangle \langle jm\|W^{1\lambda'}(\gamma'\gamma')\|jm\rangle, \tag{29}$$

for $\gamma_3 = \gamma_4 = \gamma$ and $\gamma_1 \neq \gamma_2$

$$I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma\gamma) = \sum_{\{\nu\}} J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma\nu\gamma\nu') \langle\gamma_1\nu_1\gamma_2\nu_2|\lambda q\rangle \langle\gamma\nu\gamma\nu'|\lambda'q'\rangle \langle S\|S\|S\rangle^{-2}$$
$$\times \sum_{m,n} \alpha_m^2\alpha_n\alpha_{n+1} \langle in\|W^{1\lambda}(\gamma_1\gamma_2)\|in+1\rangle \langle jm\|W^{1\lambda'}(\gamma\gamma)\|jm\rangle, \tag{30}$$

similar for $\gamma_3 \neq \gamma_4$ and $\gamma_1 = \gamma_2 = \gamma$, and for $\gamma_1 \neq \gamma_2$ and $\gamma_3 \neq \gamma_4$

$$I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_4) = \sum_{\{\nu\}} J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_3\nu_3\gamma_4\nu_4) \langle\gamma_1\nu_1\gamma_2\nu_2|\lambda q\rangle \langle\gamma_3\nu_3\gamma_4\nu_4|\lambda'q'\rangle$$
$$\langle S\|S\|S\rangle^{-2} \sum_{m,n} \alpha_m\alpha_{m+1}\alpha_n\alpha_{n+1} \langle in\|W^{1\lambda}(\gamma_1\gamma_2)\|in+1\rangle \langle jm\|W^{1\lambda'}(\gamma_3\gamma_4)\|jm+1\rangle. \tag{31}$$

For simplicity we have denoted

$$\|in\rangle \equiv \|t_{2g}^{k_1-n}(\Gamma_nS_n)e_g^{k_2+n}(\Gamma'_nS'_n);\, i\Gamma S\rangle. \tag{32}$$

The explicit form of nondiagonal reduced matrix element of double tensor operators is to be found in Ref. [13].

4. *Interpretation — general channels in superexchange*

To explain the physical meaning of the contributions which appeared in formulas (28)–(32), it is convenient to improve the concept of simple and collective channels in superexchange.

Let us first consider the simplest case, when each ion is in orbitally nondegenerate state A_1. Because of this, coefficients $\langle\gamma\nu\gamma\nu'|A_1e_1\rangle$ do not vanish for $\nu = \nu'$ only, and Eq. (24) takes the form

$$I_{e_1e_1}^{A_1A_1}(i\gamma, j\gamma') = \frac{2g_{i\gamma}g_{j\gamma'}}{[\gamma]\,[\gamma']} \sum_{\nu\nu'} J(i\gamma\nu, j\gamma'\nu') \tag{33}$$

and

$$\tilde{I}_{e_1e_1}^{A_1A_1}(i\gamma, j\gamma') = \frac{k_{i\gamma}k_{j\gamma'}}{2[\gamma]\,[\gamma']} \sum_{\nu\nu'} J(i\gamma\nu, j\gamma'\nu'), \tag{34}$$

where $J(i\gamma v, j\gamma' v') \equiv J(i\gamma v\gamma v, j\gamma' v'\gamma' v')$ is given in Eq. (12). Assuming that the spin $\boldsymbol{S}_\gamma$ of each subconfiguration takes its maximum value due to Hund's rule, the exchange Hamiltonian can be written as

$$
\begin{aligned}
H_{\mathrm{ex}}^{ij} &= (\tilde{I}_{e_1e_1}^{A_1A_1}(i,j) + I_{e_1e_1}^{A_1A_1}(i,j)\boldsymbol{S}_i\boldsymbol{S}_j) \\
&= \sum_{\substack{\gamma\gamma' \\ vv'}} (\tilde{I}_{e_1e_1}^{A_1A_1}(i\gamma v, j\gamma' v') + I_{e_1e_1}^{A_1A_1}(i\gamma v, j\gamma' v')\boldsymbol{s}_{i\gamma v}\boldsymbol{s}_{j\gamma' v'}) \\
&= 2\sum_{\substack{\gamma\gamma' \\ vv'}} J(i\gamma v, j\gamma' v')\left(\tfrac{1}{4} + \frac{\boldsymbol{s}_{i\gamma v}\boldsymbol{s}_{jv'\gamma'}}{[\gamma]\,[\gamma']}\right),
\end{aligned}
\tag{35}
$$

where $\boldsymbol{s}_{i\gamma v}$ and $\boldsymbol{s}_{j\gamma' v'}$ are spin operators of one-electron states $|i\gamma v\rangle$ and $|j\gamma' v'\rangle$. So, we can decompose the exchange parameter $I_{e_1e_1}^{A_1A_1}(i,j)$ standing by the bilinear form $\boldsymbol{S}_i\boldsymbol{S}_j$ of the total spins of ions into the sum of simple contributions $I_{e_1e_1}^{A_1A_1}(i\gamma v, j\gamma' v')$, standing by the bilinear forms of the spins of one-electron states. We refer to these contributions as to the contributions from simple channels (Fig. 1) and they are analytical expressions for the Goodenough–Kanamori rules. Examples, where the simple channel picture can be applied, are transition metal compounds with the unpaired electrons on orbitals $t_{2g}(d^3)$,

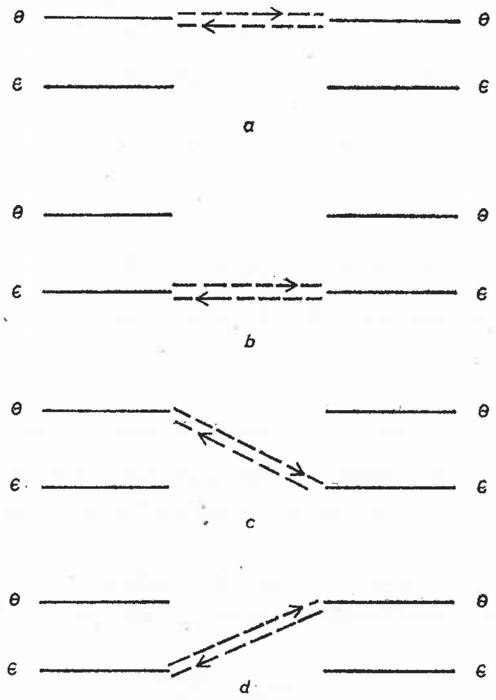

Fig. 1. Possible exchange paths between two e_g states

$e_g(d^8)$ and $t_{2g}+e_g(d^5)$. In the first case the summation runs over simple $t_{2g}\nu \rightleftarrows t_{2g}\nu'$ channels, in the second — over $e_g\nu \rightleftarrows e_g\nu'$ channels, in the third — over $t_{2g}\nu \rightleftarrows t_{2g}\nu'$, $e_g\nu \rightleftarrows e_g\nu'$ and $t_{2g}\nu \rightleftarrows e_g\nu'$ channels, respectively. This kind of simple channels approach was considered by Eremin and Rokitin [6], but these authors started from a different form of the Hamiltonian.

If we have deal with orbital degeneracy, the summation over simple channels only (Fig. 2a) is not valid. New contributions appear, like these in Fig. 2b, c, d which result

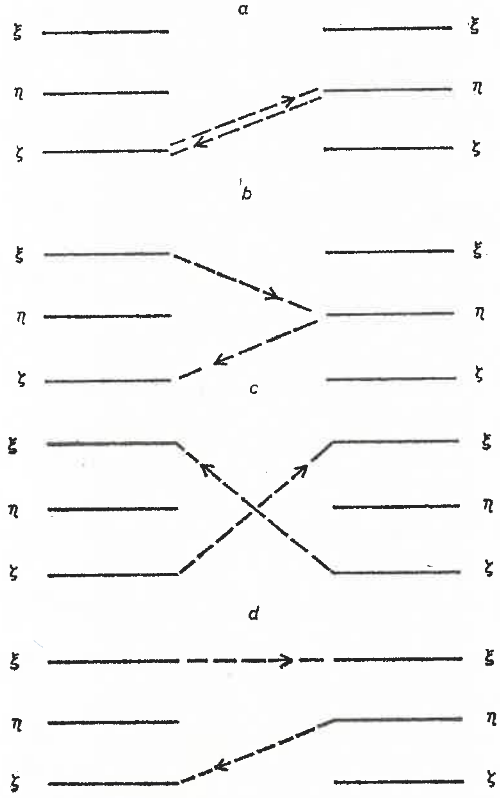

Fig. 2. Possible types of exchange paths between two t_{2g} states in the case of orbital degeneracy

from the potential exchange, kinetic exchange, second order Coulomb correlations and the second order exchange correlations. One can notice that, if ions are in their ground configuration $t_{2g}^{k_1}e_g^{k_2}$, all contributions described by diagrams from Fig. 2 do not change k_1 and k_2 on the same ion. Thus, also in this case the exchange Hamiltonian can be decomposed into the sum of contributions from some channels (Fig. 3)

$$H^{ij}_{\mathrm{ex}} = \sum_{\substack{\lambda\lambda' \\ qq'}} \Bigg[\sum_{\gamma\gamma'} \left(I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma') + I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma')\, \frac{\mathbf{S}_{i\gamma}\mathbf{S}_{j\gamma'}}{g_{i\gamma}g_{j\gamma'}}\right)\Bigg] V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma), \tag{36}$$

where $\boldsymbol{S}_{i\gamma}$ is the spin of subconfiguration γ^k and the parameter $I_{qq'}^{\lambda\lambda'}(i\gamma, j\gamma')$ is given in Eq. (24). Fig. 3 is very similar to Fig. 1, but now we deal with the collective channels between subconfigurations $\gamma_1^{k_1} \rightleftarrows \gamma_2^{k_2}$ that cannot be decomposed into the sum of simple channels without missing any significant terms.

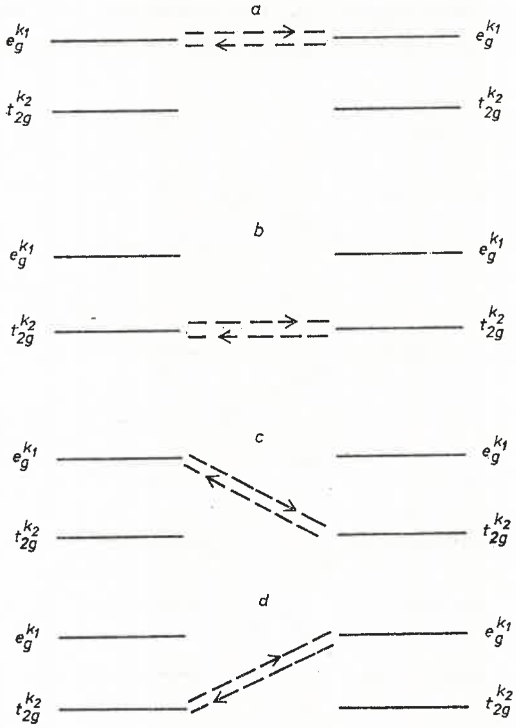

Fig. 3. Collective channels in the case of orbital degeneracy

Now, let us try to consider the configurational mixing. In this case, even in the absence of orbital degeneracy, simple channels picture is not valid for the description of exchange contributions. Diagrams which appear are similar to those in Fig. 2, but now paths connecting different subconfigurations from the same ion, i.e. k_1 and k_2 change. We can now decompose the exchange Hamiltonian as follows

$$H_{\mathrm{ex}}^{ij} = \sum_{\substack{\lambda\lambda' \\ qq'}} \left\{ \sum_{\gamma_1\gamma_3} \left[\tilde{I}_{qq'}^{\lambda\lambda'}(i\gamma_1, j\gamma_3) + I_{qq'}^{\lambda\lambda'}(i\gamma_1, j\gamma_3)\, \frac{\boldsymbol{S}_{i\gamma_1}\boldsymbol{S}_{j\gamma_3}}{g_{i\gamma_1}g_{j\gamma_3}} \right] \right.$$

$$+ \sum_{\substack{\gamma_1\gamma_3 \\ \gamma_2\neq\gamma_1}} \left[\tilde{I}_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_3) + I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_3)\, \frac{\boldsymbol{S}_i\boldsymbol{S}_{j\gamma_3}}{g_{j\gamma_3}} \right]$$

$$+\sum_{\substack{\gamma_1\gamma_3\\ \gamma_4\neq\gamma_3}}\left[\tilde{I}_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_1, j\gamma_3\gamma_4)+I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_1, j\gamma_3\gamma_4)\,\frac{S_{i\gamma_1}S_j}{g_{i\gamma_1}}\right]$$

$$+\sum_{\substack{\gamma_1\gamma_3\\ \gamma_2\neq\gamma_1\ \gamma_4\neq\gamma_3}}\left.[\tilde{I}_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_4)+I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_4)S_iS_j]\right\}V_{iq}^{\lambda}(\Gamma)V_{jq'}^{\lambda'}(\Gamma). \qquad (37)$$

The first term, as in the previous case, is a sum over collective channels of subconfiguration-subconfiguration interaction $\gamma_1^{k_1} \rightleftarrows \gamma_2^{k_2}$ where the parameter $I_{qq'}^{\lambda\lambda'}(i\gamma_1, j\gamma_3)$ is given in Eq. (29). The next two terms contain collective channels for subconfiguration-configuration interaction $\gamma_1^{k_1} \rightleftarrows (\gamma_2^{k_2} \xrightarrow{e-} \gamma_2^{k_3})$ with the configurational changing on the one ion, where the parameter $I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_1, j\gamma_3\gamma_4)$ is given in Eq. (30). In the same way one can obtain $I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_3)$. The last term in Eq. (37) is the collective channel for configuration-configuration interaction with the configurational changing on each ion $(\gamma_2^{k_1} \xrightarrow{e-} \gamma_2^{k_2}) \rightleftarrows (\gamma_3^{k_3} \xrightarrow{e-} \gamma_4^{k_4})$ where the parameter $I_{qq'}^{\lambda\lambda'}(i\gamma_1\gamma_2, j\gamma_3\gamma_4)$ is given in Eq. (31).

5. *Conclusions*

We have formulated theory of superexchange — in the case of orbital degeneracy and configurational mixing — based on the localized-electron model. The perturbation procedure in case of the Hamiltonian in the second quantized form and the irreducible tensor operators technique were used to obtain the effective Hamiltonian, expressed in terms of total spins S_i and pseudomomentum tensor operators $V_{iq}^{\lambda}(\Gamma)$ of the ground terms ${}^{2S_i+1}\Gamma_i$ from different ions. It has the properties of the second quantized one (electrons from different ions are undistinguishable), but the number of electrons on each ion is preserved. This additional condition restricts the application of the Hamiltonians of this kind to systems with a good localization of electrons.

In this work, we have started from the strong crystal-field coupling scheme and carried out the detail considerations of the configurational mixing. It implies the generation of a new type of electron transfers. To give the physical interpretation of all contributions, the general channels concept was developed. In the simplest case, when the ground crystal term is A_1 (A_2), we can decompose the exchange Hamiltonian into the sum of simple channels (34) — pairs of interacting half-filled orbitals. In the case of orbital degeneracy, it has been shown that the concept of simple channels is not valid, but we can decompose the exchange Hamiltonian into the sum of collective channels — pairs of interacting subconfigurations (36). For the configurational mixing yet another kind of collective channels has appeared (37). They contain interactions between subconfiguration and configuration with configurational changing on one ion and interaction between configurations with configurational changing on both ions, respectively. Thus, we have to add new terms to the exchange Hamiltonian (Eq. (37)). Simultaneously, the origin and influence of the electron-correlation effects in the microscopic theory were shown.

The typical compounds, which the theory is valid for, are XO, XO_2, KXF_3, $LaXO_3$, ... and a lot of others with X as impurities. The typical X i.e. d^n ions are

d^1(Ti^{3+}, V^{4+}, Cr^{5+}, Nb^{4+}, La^{2+}, Re^{6+}, Ta^{4+}, ...)
d^2(Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}, Fe^{6+}, ...)
d^3(V^{2+}, Cr^{3+}, Mn^{4+}, Nb^{2+}, Mo^{3+}, Tc^{4+}, Re^{4+}, ...)
d^4(Cr^{2+}, Mn^{3+}, Mo^{2+}, Tc^{3+}, Ru^{4+}, Os^{4+}, ...)
d^5(Cr^{1+}, Mn^{2+}, Fe^{3+}, Mo^{1+}, Tc^{2+}, Ru^{3+}, Rh^{4+}, Ir^{4+}, ...)
d^6(Te^{2+}, Co^{3+}, Ru^{2+}, Rh^{3+}, Ir^{3+}, Rt^{4+}, ...)
d^7(Co^{2+}, Ni^{3+}, Rh^{2+}, Pd^{3+}, Pt^{3+}, ...)
d^8(Co^{1+}, Ni^{2+}, Cu^{3+}, ...)
d^9(Cu^{2+}, Ni^{1+}, Ag^{2+}, ...)

Although, in this work the O_h symmetry has been used, the theory is valid for other symmetries.

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