ON SUPEREXCHANGE IN MAGNETIC INSULATORS. III. THE EFFECTIVE HAMILTONIAN FOR AN ARBITRARY d^n–d^n PAIR

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(Received January 8, 1980; revised version received April 28, 1980)

New contributions to the orbital part of the effective Hamiltonian coming from the Coulomb part of the electrostatic interaction were found. The explicit connection between the parameters $I^{\lambda\lambda'}_{qq'}$ and $\tilde{I}^{\lambda\lambda'}_{qq'}$ of the exchange Hamiltonian is demonstrated. The effective Hamiltonian parameters for an arbitrary d^n-d^n pair are given calculated on the bases of the previously formulated theory and their relative magnitudes are estimated.

PACS numbers: 75.30.Et, 75.50.Dd, 75.10.-b

1. Introduction

In previous papers, Part I [1] and II [2], the general theory of exchange interaction in magnetic insulators was given based on the localized-electron model. The exchange Hamiltonian takes the general form:

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

and

$$I^{\lambda\lambda'}_{qq'}(i,j) = \sum_{\{\gamma\}} I^{\lambda\lambda'}_{qq'}(i\gamma_1\gamma_2, j\gamma'_1\gamma'_2) = \sum_{\{\gamma\}}\sum_{\{\nu\}} J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma'_1\nu'_1\gamma'_2\nu'_2)$$
$$\times \langle S\|S\|S\rangle^{-2} \langle\gamma_1\nu_1\gamma_2\nu_2|\lambda q\rangle \langle\gamma'_1\nu'_1\gamma'_2\nu'_2|\lambda' q'\rangle \langle\Gamma S\|W^{1\lambda}(\gamma_1\gamma_2)\|\Gamma S\rangle$$
$$\times \langle\Gamma S\|W^{1\lambda'}(\gamma'_1\gamma'_2)\|\Gamma S\rangle, \tag{2}$$

where $\langle\Gamma S||W^{\omega\lambda}(\gamma\gamma')||\Gamma S\rangle$ are reduced matrix elements of the double tensor operators (the diagonal elements are tabulated in [3, 4] and non-diagonal ones are tabulated in [5]), $\langle\gamma\nu\gamma'\nu'|\lambda q\rangle$ are the Clebsch-Gordan coefficients and $J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma'_1\nu'_1\gamma'_2\nu'_2)$ contains a great

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number of contributions proceeding from potential exchange, kinetic exchange and second order correlations [1]. $\tilde{I}^{\lambda\lambda'}_{qq'}(i,j)$ parameters are found in a similar way by substituting $\omega = 1 \to \omega = 0$ and $\langle S||S||S\rangle \to [S]^{1/2} = (2S+1)^{1/2}$.

In this paper we determine the explicit relation between the $I^{\lambda\lambda'}_{qq'}$ and $\tilde{I}^{\lambda\lambda'}_{qq'}$ parameters (Section 2), new contributions to the orbital part of the effective Hamiltonian, which arise from the Coulomb part of the electrostatic interaction (Section 3), and we find the effective Hamiltonian parameters for an arbitrary $d^n - d^n$ pair, which allows us to estimate their relative magnitudes (Section 4).

2. *The relation between the $I^{\lambda\lambda'}_{qq'}$ and $\tilde{I}^{\lambda\lambda'}_{qq'}$ parameters*

At first, we should note that for a given ion the ground state of each sub-configuration has a maximum spin (high spin) due to the Hund rule. The same occurs for the whole spin of an ion resulting from spins of sub-configurations. However, this means that $S = k/2$, $S_\gamma = k_\gamma/2$ and $g_\gamma = k_\gamma/k$, where k is the number of unpaired electrons of sub-configuration γ.

Using the above, the explicit forms of reduced matrix elements and algebraic formulas of 3-j symbols we find the following relations:

$$\frac{\langle \Gamma S\|W^{0\lambda}(\gamma\gamma')\|\Gamma S\rangle}{\langle \Gamma S\|W^{1\lambda}(\gamma\gamma')\|\Gamma S\rangle} = \left(\frac{S}{S+1}\right)^{1/2} = \frac{k}{2}\,\frac{[S]^{1/2}}{\langle S\|S\|S\rangle} \tag{3}$$

and

$$\frac{\langle \Gamma S\|W^{1\lambda}(\gamma\gamma')\|\Gamma S\rangle}{\langle S\|S\|S\rangle} = \frac{\sqrt{2}}{k}\langle \Gamma S\|W^{\lambda}(\gamma\gamma')\|\Gamma S\rangle, \tag{4}$$

where $W^\lambda(\gamma\gamma')$ is the crystal field tensor operator which acts on the orbital part of wave functions.

Applying the above formulas, the exchange Hamiltonian without configurational mixing becomes:

$$H^{ij}_{\mathrm{ex}} = \frac{2}{k_i k_j}\left(\frac{k_i k_j}{4} + \boldsymbol{S}_i\boldsymbol{S}_j\right)\sum_{\substack{\lambda\lambda'\\ qq'}} I^{\lambda\lambda'}_{qq'}(i,j)V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma)$$

$$= \sum_{\gamma\gamma'}\frac{2}{k_{i\gamma}k_{j\gamma'}}\left(\frac{k_{i\gamma}k_{j\gamma'}}{4} + \boldsymbol{S}_{i\gamma}\boldsymbol{S}_{j\gamma'}\right)\sum_{\substack{\lambda\lambda'\\ qq'}} I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma')V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma), \tag{5}$$

where

$$I^{\lambda\lambda'}_{qq'}(i\gamma, j\gamma') = \sum_{\{\nu\}} J(i\gamma\nu_1\gamma\nu_2, j\gamma'\nu_1'\gamma'\nu_2')\,\langle \gamma\nu_1\gamma\nu_2|\lambda q\rangle\,\langle \gamma'\nu_1'\gamma'\nu_2'|\lambda' q'\rangle$$

$$\times \langle \Gamma S\|W^{\lambda}(\gamma\gamma)\|\Gamma S\rangle\,\langle \Gamma S\|W^{\lambda'}(\gamma'\gamma')\|\Gamma S\rangle. \tag{6}$$

The case of configurational interacting in our Hamiltonian (5) appears to be a part which we cannot decompose, that is:

$$\frac{2}{k_i k_j}\left(\frac{k_i k_j}{4}+\boldsymbol{S}_i\boldsymbol{S}_j\right)\sum_{\substack{\lambda\lambda'\\ qq'}} I^{\lambda\lambda'}_{qq'}(i\gamma\gamma', j\gamma\gamma')V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma). \tag{7}$$

3. *Coulomb orbital terms in the effective Hamiltonian*

Till now, we considered only the exchange part of the effective Hamiltonian. Although, if the orbital degeneracy does exist, the effective Hamiltonian should contain orbital terms not only from the exchange interaction. Using the perturbation procedure [1], we find new terms in the effective Hamiltonian proceeding from Coulomb interaction within ground subspace having the form:

$$H^{ij}_{\text{Coul}} = \sum_{\{\gamma\nu\}} \langle i\gamma_2\nu_2\gamma_2'\nu_2'|\hat{g}|i\gamma_1\nu_1 j\gamma_1'\nu_1'\rangle \sum_{\sigma} a^{+}_{i\gamma_2\nu_2\sigma}a_{i\gamma_1\nu_1\sigma}\sum_{\sigma'} a^{+}_{j\gamma_2'\nu_2'\sigma'}a_{j\gamma_1'\nu_1'\sigma'}, \tag{8}$$

which in terms of crystal field tensor operators within ground crystal terms is as follows:

$$H^{ij}_{\text{Coul}} = \sum_{\substack{\lambda\lambda'\\ qq'}} \bar{I}^{\lambda\lambda'}_{qq'}(i,j)V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma), \tag{9}$$

where

$$\bar{I}^{\lambda\lambda'}_{qq'} = \sum_{\{\gamma\nu\}} \bar{J}(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_1'\nu_1'\gamma_2'\nu_2')\langle\gamma_1\nu_1\gamma_2\nu_2|\lambda q\rangle\langle\gamma_1'\nu_1'\gamma_2'\nu_2'|\lambda' q'\rangle$$
$$\langle\Gamma S\|W^{\lambda}(\gamma_1\gamma_2)\|\Gamma S\rangle\langle\Gamma S\|W^{\lambda'}(\gamma_1'\gamma_2')\|\Gamma S\rangle, \tag{10}$$

and

$$\bar{J}(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_1'\nu_1'\gamma_2'\nu_2') \equiv \langle i\gamma_2\nu_2 j\gamma_2'\nu_2'|\hat{g}|i\gamma_1\nu_1 j\gamma_1'\nu_1'\rangle, \tag{11}$$

which is the Coulomb integral. Thus, the whole effective Hamiltonian has the following form

$$H^{ij}_{\text{eff}} = H^{ij}_{\text{Coul}} + H^{ij}_{\text{ex}} = \sum_{\substack{\lambda\lambda'\\ qq'}} \bar{I}^{\lambda\lambda'}_{qq'}(i,j)V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma)$$
$$+\frac{2}{k_i k_j}\left(\frac{k_i k_j}{4}+\boldsymbol{S}_i\boldsymbol{S}_j\right)\sum_{\substack{\lambda\lambda'\\ qq'}} I^{\lambda\lambda'}_{qq'}(i,j)V^{\lambda}_{iq}(\Gamma)V^{\lambda'}_{jq'}(\Gamma). \tag{12}$$

4. *Effective Hamiltonian parameters*

Let us consider the detail form of the $J(i\gamma_1\nu_1\gamma_2\nu_2, j\gamma_1'\nu_1'\gamma_2'\nu_2')$ parameters. At first, we must notice that significant contributions come from the η, ξ, θ-states [2], so we will take into account the electrons only from these states. The kinetic and potential contri-

butions result from the exchange of two electrons between neighbouring ions due to their kinetic and Coulomb energies, respectively (Fig. 1a). Second order Coulomb correlations result from electron hopping between magnetic ions under the influence of Coulomb interactions with another electron which does not change its state during the interaction

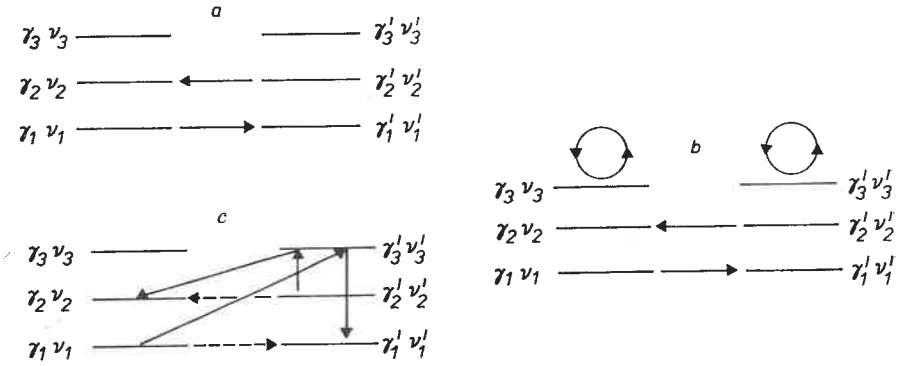

Fig. 1. Graphical description of different exchange contribution

(Fig. 1b). Second order exchange correlations result from the exchange of two electrons between magnetic ions due to Coulomb interaction through the intermediate states (Fig. 1c).

Previous symmetry considerations [2] allow us to state that the second order correlations do not generate any new terms in the effective Hamiltonian. Moreover, we have found that there are only two kinetic contributions — A and B, respectively. Now, let us consider the potential contributions. Without configurational mixing there are three kinds denoted by C, D and E. C contributes to the $e_g^{k_2} \rightleftarrows e_g^{k_2}$ channel, D — to the $t_{2g}^{k_1} \rightleftarrows t_{2g}^{k_1}$ channel and E — to the $t_{2g}^{k_1} \rightleftarrows e_g^{k_2}$ channel. E contributions are equal to each other due to symmetry demands and the D contributions we approximate by the same value because they should be of the same order of magnitude.

Applying our results from Parts I and II, and our present considerations, we may compute the effective Hamiltonian parameters $I_{qq'}^{\lambda\lambda'}(i,j)$ and $\bar{I}_{qq'}^{\lambda\lambda'}(i,j)$ (see Eq. (12)) for each d^n-d^n pair. All results are collected in Table I.

In this notation $J_{tt} = 2\tilde{B}-\tilde{D}$, $J_{ee} = \tilde{A}-\frac{1}{2}\tilde{C}$, $J_{et} = J_{te} = \tilde{E}$ and tylda over X means that X is renormalized due to the second order correlations. The $\bar{I}_{qq'}^{\lambda\lambda'}(i,j)$ parameters can be found by substituting:

$$J_{tt} \to \bar{J}_{tt} \equiv \bar{D}, \quad J_{ee} \to \bar{J}_{ee} \equiv \tfrac{1}{2}\bar{C}, \quad J_{et} \to \bar{J}_{et} \equiv -\bar{E}.$$

In the kinetic approximation all parameters except the kinetic ones vanish and we have:

$$J_{tt} = B, \quad J_{ee} = A, \quad J_{et} = 0, \quad \bar{J}_{tt} = \bar{J}_{ee} = \bar{J}_{et} = 0.$$

Because $A \gg B$, we find that for d^1-d^1, d^2-d^2, d^4-d^4 and d^5-d^5 pairs, in the kinetic approximation, the anisotropic parameters $I_{qq'}^{\lambda\lambda'}$ are of the same order of magnitude as the isotropic parameter $I_{e_1e_1}^{A_1A_1}$ and for the d^6-d^6 and d^7-d^7 pairs the anisotropic parameters are smaller than the isotropic ones by one order of magnitude.

TABLE 1

$^{2S+1}\Gamma(t_{2g}^{k_1}e_g^{k_2})$	d^n-d^n	$I_{e_2e_1}^{A_1A_1}$	$I_{E_1\theta}^{A_1E}$	$I_{\theta\theta}^{EE}$	$I_{\varepsilon\varepsilon}^{EE}$	$I_{zz}^{T_1T_1}$	$I_{\xi\xi}^{T_2T_2}$
$^4A_2(t_{2g}^3)$	d^3-d^3	J_{tt}	—	—	—	—	—
$^3A_2(t_{2g}^6e_g^2)$	d^8-d^8	J_{ee}	—	—	—	—	—
$^6A_1(t_{2g}^3e_g^2)$	d^5-d^5	$J_{tt}+J_{ee}-2J_{et}$	—	—	—	—	—
$^2E\ (t_{2g}^6e_g^1)$ $(t_{2g}^6e_g^3)$	d^7-d^7 d^9-d^9	$\frac{1}{2}J_{ee}$	$-\frac{1}{\sqrt{2}}J_{ee}$	J_{ee}	—	—	—
$^5E(t_{2g}^2e_g^1)$	d^4-d^4	$2J_{tt}+\frac{1}{2}J_{ee}-2J_{et}$	$\frac{1}{\sqrt{2}}(J_{ee}-J_{et})$	J_{ee}	—	—	—
$^2T_2\ (t_{2g}^1)$ (t_{2g}^5)	d^1-d^1 d^5-d^5	$\frac{1}{3}J_{tt}$	$\frac{1}{3}J_{tt}$	$\frac{1}{3}J_{tt}$	$\tilde{B}$	$\frac{3}{2}\tilde{B}$	$\frac{3}{2}J_{tt}$
$^3T_1\ (t_{2g}^2)$ (t_{2g}^4)	d^2-d^2 d^4-d^4	$\frac{4}{3}J_{tt}$	$\frac{2}{3}J_{tt}$	$\frac{1}{3}J_{tt}$	$\tilde{B}$	$\frac{3}{2}\tilde{B}$	$\frac{3}{2}J_{tt}$
$^5T_2(t_{2g}^4e_g^2)$	d^6-d^6	$\frac{4}{3}J_{tt}+3J_{ee}-4J_{et}$	$\frac{2}{3}J_{tt}-J_{et}$	$\frac{1}{3}J_{tt}$	$\tilde{B}$	$\frac{3}{2}\tilde{B}$	$\frac{3}{2}J_{tt}$
$^4T_1(t_{2g}^5e_g^2)$	d^7-d^7	$\frac{1}{3}J_{tt}+3J_{ee}-2J_{et}$	$\frac{1}{3}J_{tt}-J_{et}$	$\frac{1}{3}J_{tt}$	$\tilde{B}$	$\frac{3}{2}\tilde{B}$	$\frac{3}{2}J_{tt}$

The exchange parameters for configurational mixing will be derived based on the example of the d^7-d^7 pair in the kinetic approximation and two configurations taken into account, that is $t_{2g}^5e_g^2$ and $t_{2g}^4e_g^3$. Applying the definition of the $I_{qq'}^{\lambda\lambda'}(i,j)$ parameters for configurational mixing [1] and by substituting $\alpha_0 = \cos\alpha$ and $\alpha_1 = \sin\alpha$ we find for example, that:

$$I_{e_1e_1}^{A_1A_1} = \tfrac{2}{3}B(\cos^2\alpha+2\sin^2\alpha)^2+3A(\cos^2\alpha+\tfrac{1}{2}\sin^2\alpha)^2. \tag{13}$$

In a similar way we can change the anisotropic parameters $I_{qq'}^{\lambda\lambda'}$. On the other hand, configurational interaction generates new terms in the Hamiltonian of the form:

$$I_{xx}^{T_1T_1} = I_{yy}^{T_1T_1} = I_{\xi\xi}^{T_2T_2} = I_{\eta\eta}^{T_2T_2} = \tfrac{9}{4}\sqrt{AB}\cos^2\alpha\sin^2\alpha. \tag{14}$$

Now, the relative values of the exchange parameters depend on the magnitude of configurational mixing. By substituting $\alpha = 0$ we come back to the d^7-d^7 pair without configurational mixing.

5. *Conclusions*

Using the properties of the $n-j$ symbols and the explicit forms of the reduced matrix elements of the double tensor operators, the connection between the $I_{qq'}^{\lambda\lambda'}$ and $\tilde{I}_{qq'}^{\lambda\lambda'}$ parameters of the exchange Hamiltonian was fixed. New spin-independent contributions to the effective Hamiltonian, which originate from the Coulomb part of the electrostatic interaction were found. The explicit forms of the 180°-effective Hamiltonian parameters for an arbitrary d^n-d^n pair, on the basis of the previous theory were calculated. This allowed us to

estimate their relative magnitudes and show the importance of anisotropic terms in superexchange.

All contributions up to the second order perturbation calculus were taken into account. The influence of configurational mixing on the effective Hamiltonian parameters was found. For strong ones they may change radically.

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