ON THE ACCOUNT OF ORBITAL STATES IN THE THEORY OF INDIRECT EXCHANGE

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Abstract

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ON THE ACCOUNT OF ORBITAL STATES IN THE THEORY OF INDIRECT EXCHANGE

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There exists a large class of magnetically ordered crystals in which paramagnetic ions are surrounded by nonmagnetic ions, for example crystals of the MnO type. The magnetic properties of this type of crystal may be described by the magnetic properties of the linear chain Mn–O–Mn*. For the first time such a model was considered by Kramers ([1]), Anderson ([2]), and Shimizu ([3]). In work ([3]) it was shown that the effective exchange integral is a quantity of third order of smallness in the parameter $(E_0-E_1)^{-1}$, if virtual transitions of one of the anion electrons to the unoccupied s-orbital of the cation are considered as the excited state (here E_0 and E_1 are the average energies of the ground and excited states, respectively)

$$I_{\text{eff}} = -4\rho^2(I_{pd} - I_{ds})I_{pd}/(E_0 - E_1)^3, \tag{1}$$

where ρ is the one-particle transfer integral,

$$\rho = \int \Psi_s^*(r_1)\hat{H}_1(r_1)\Psi_d(r_1)\,d\tau, \quad I_{pd} = \int \Psi_p^*(r_1)\Psi_d^*(r_2)\frac{1}{r_2}\Psi_p(r_2)\Psi_d(r_1)\,d\tau,$$

$$I_{sd} = \int \Psi_s^*(r_1)\Psi_d^*(r_2)\frac{1}{r_{12}}\Psi_s(r_2)\Psi_d(r_1)\,d\tau,$$

s, d denote the empty and singly occupied orbitals of the cation, and p is the occupied orbital of the anion.

In the present note an attempt is made to take into account the orbital states of the electrons within the same model of a linear chain of 3 centers–4 electrons. The purely ionic configuration is described by the antisymmetric wave function $|[\lambda]k;\Gamma_1\mu_1[\lambda_1]\Gamma_2\mu_2[\lambda_2]\Gamma_3\mu_3[\lambda_3]\rangle$, where $[\lambda]$ is an irreducible representation of the permutation group of 4 electrons, $[\lambda] = [2^2]$ for the singlet state of the chain and $[\lambda] = [21^2]$ for the triplet; k is the Yamanouchi symbol; Γ_1 is an irreducible

representation of the cubic group obtained from the d-state of the electron, μ_1 is a row of this representation; Γ_2 is an irreducible representation of the cubic group obtained from the $(p^2\,{}^1S)$-state of the anion, μ_2 is a row of this representation. The excited configurations, analogously to Anderson et al., are considered as transitions of one electron of the anion to the cation, the transferred electron being placed on the unoccupied s-orbital. The wave functions of the excited configurations have the form: $|[\lambda]k;\Gamma_1\mu_1[\lambda_1]\Gamma_2\mu_2[\lambda_2]\Gamma_3 s\mu_1[\lambda_3]\rangle$ (the notation is analogous).

The wave functions of the ground and excited configurations may be represented in the form

$$|[\lambda]k;\Gamma_1\mu_1[\lambda_1]\Gamma_2\mu_2[\lambda_2]\Gamma_3\mu_3[\lambda_3]\rangle =$$

$$= \sum_{M_1M_2M_3} P^{\mu_1\mu_2\mu_3 k}_{M_1M_2M_3}\,|[\lambda]k;\ L_1M_1[\lambda_1]L_2M_2[\lambda_2]L_3M_3[\lambda_3]\rangle^{**},$$

where $P^{\mu_1\mu_2\mu_3}_{M_1M_2M_3}$ is the matrix of the projection operator ([5]).

* The available neutron-diffraction experiment to some extent justifies this approximation ([4]).

** For the ground configuration only the functions of the d-electron formed according to the e_g-representation are taken into account, and for the excited configurations (the (sd)-configuration) only functions of E_g-symmetry.

Notation: $A_1 = E_0 - \frac{2}{3}I^{02}_{pd} - \frac{4}{3}I^{12}_{pd} - E$; $\quad A_4 = E_0 - \frac{2}{3}I^{00}_{pd} - \frac{4}{3}I^{10}_{pd}$;

$$A_2 = A_3 = E_0 - \frac{1}{3}I^{00}_{pd} - \frac{1}{3}I^{10}_{pd} - \frac{2}{3}I^{02}_{pd} - \frac{2}{3}I^{12}_{pd}.$$

For singlet states:

$$B_m = \begin{vmatrix} E_1 + I^{02}_{sd} + \frac{1}{2}I^{m2}_{pd} - \frac{1}{2}I^{m0}_{ps} - E & \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m2}_{pd}) \\ \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m2}_{pd}) & E_1 - I^{02}_{sd} - \frac{1}{2}I^{m2}_{pd} + \frac{1}{2}I^{m0}_{ps} - E \end{vmatrix},$$

$$C_m = \begin{vmatrix} E_1 + I^{00}_{sd} + I^{m2}_{pd} - \frac{1}{2}I^{m2}_{pd} - \frac{1}{2}I^{m0}_{ps} - E & \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m0}_{pd}) \\ \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m0}_{pd}) & E_1 - I^{00}_{sd} - I^{m2}_{pd} + \frac{1}{2}I^{m0}_{pd} + \frac{1}{2}I^{m0}_{ps} - E \end{vmatrix},$$

$$D_m = \begin{vmatrix} E_1 + I^{02}_{sd} + I^{m0}_{pd} - \frac{1}{2}I^{m2}_{pd} - \frac{1}{2}I^{m0}_{ps} - E & \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m2}_{pd}) \\ \frac{1}{2}\sqrt{3}\,(I^{m0}_{ps} - I^{m2}_{pd}) & E_1 - I^{02}_{sd} - I^{m0}_{pd} + \frac{1}{2}I^{m2}_{pd} + \frac{1}{2}I^{m0}_{ps} - E \end{vmatrix},$$

$$F_m = \begin{vmatrix} E_1 + I_{sd}^{00} + \frac{1}{2} I_{pd}^{m0} - \frac{1}{2} I_{ps}^{m0} - E & \frac{1}{2}\sqrt{3}\,(I_{ps}^{m0} - I_{pd}^{m0}) \\ \frac{1}{2}\sqrt{3}\,(I_{ps}^{m0} - I_{pd}^{m0}) & E_1 - I_{sd}^{00} - \frac{1}{2} I_{pd}^{m0} + I_{ps}^{m0} - E \end{vmatrix},$$

$$L = \begin{vmatrix} \frac{1}{2}\sqrt{2}\,\tilde{I}_{pd} & 0 \\ 0 & -\frac{1}{2}\sqrt{2}\,\tilde{I}_{pd} \end{vmatrix}, \qquad K = \begin{vmatrix} -\frac{1}{4}\sqrt{2}\,\tilde{I}_{pd} & -\frac{1}{4}\sqrt{6}\,\tilde{I}_{pd} \\ -\frac{1}{4}\sqrt{6}\,\tilde{I}_{pd} & \frac{1}{4}\sqrt{2}\,\tilde{I}_{pd} \end{vmatrix},$$

$$\tilde{I}_{pd} = \int \Psi_{d2}^{*}(r_1)\Psi_{p-1}^{*}(r_2)\frac{1}{r_{12}}\Psi_{d0}(r_2)\Psi_{p1}(r_1)\,d\tau.$$

For triplet states:

$$B_m = \begin{vmatrix} E_1 + I_{sd}^{02} - \frac{3}{2} I_{pd}^{m2} - \frac{1}{2} I_{sp}^{0m} - E & \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m2}) & 0 \\ \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m2}) & E_1 - I_{sd}^{02} + \frac{1}{6} I_{pd}^{m2} + \frac{1}{2} I_{sp}^{0m} - E & \frac{2}{3}\sqrt{2}\,I_{pd}^{m2} \\ 0 & \frac{2}{3}\sqrt{2}\,I_{pd}^{m2} & E_1 - I_{sd}^{02} - \frac{2}{3} I_{pd}^{m2} - I_{sp}^{0m} - E \end{vmatrix},$$

$$C_m = \begin{vmatrix} E_1 + 2I_{sd}^{02} - I_{pd}^{m2} - \frac{1}{2} I_{sp}^{0m} - \frac{1}{2} I_{pd}^{m2} - E & \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m0}) & \\ \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m0}) & E_1 - I_{sd}^{02} + \frac{1}{2} I_{pd}^{m0} + \frac{1}{2} I_{sp}^{0m} - \frac{2}{3}\sqrt{2}\,I_{pd}^{m2} - \frac{1}{3} I_{pd}^{m2} - E & \\ 0 & \frac{2}{3}\sqrt{2}\,I_{pd}^{m2} & E_1 - I_{sd}^{00} - \end{vmatrix},$$

$$D_m = \begin{vmatrix} E_1 + I_{sd}^{02} - I_{pd}^{m0} - \frac{1}{2} I_{sp}^{0m} - \frac{1}{2} I_{pd}^{m2} - E & \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m2}) & 0 \\ \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m2}) & E_1 - I_{sd}^{02} + \frac{1}{2} I_{pd}^{m2} + \frac{2}{3}\sqrt{2}\,I_{pd}^{m0} + \frac{1}{2} I_{sp}^{0m} - E & \frac{2}{3}\sqrt{2}\,I_{pd}^{m0} \\ 0 & \frac{2}{3}\sqrt{2}\,I_{pd}^{m0} & E_1 - I_{sd}^{00} - \frac{2}{3} I_{pd}^{0m} - \end{vmatrix},$$

$$F_m = \begin{vmatrix} E_1 + I_{sd}^{02} - \frac{3}{2} I_{pd}^{m0} - \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m0}) - \frac{1}{2} I_{sp}^{0m} - E & 0 & \\ \frac{1}{2}\sqrt{3}\,(I_{sp}^{0m} - I_{pd}^{m0}) & E_1 - I_{sd}^{00} + \frac{1}{6} I_{pd}^{m0} + \frac{2}{3}\sqrt{2}\,I_{pd}^{m0} + \frac{1}{2} I_{sp}^{0m} - E & \\ 0 & \frac{2}{3}\sqrt{2}\,I_{pd}^{m0} & E_1 - I \end{vmatrix},$$

$$L = \begin{vmatrix} -\frac{1}{4}\sqrt{2}\,\tilde{I}_{pd} & -\frac{1}{4}\sqrt{6}\,\tilde{I}_{pd} & 0 \\ -\frac{1}{4}\sqrt{6}\,\tilde{I}_{pd} & \frac{1}{2}\sqrt{2}\,\tilde{I}_{pd} & 0 \\ 0 & 0 & -\frac{1}{2}\sqrt{2}\,\tilde{I}_{pd} \end{vmatrix},$$

$$K = \begin{vmatrix} -\frac{1}{2}\sqrt{2}\,\tilde{I}_{pd} & 0 & 0 \\ 0 & -\frac{1}{6}\sqrt{2}\,\tilde{I}_{pd} & \frac{2}{3}\tilde{I}_{pd} \\ 0 & \frac{2}{3}\tilde{I}_{pd} & \frac{1}{6}\sqrt{2}\,\tilde{I}_{pd} \end{vmatrix}.$$

$$\alpha = \frac{1}{6}\sqrt{6}\,\rho_1, \qquad \beta = \frac{1}{2}\sqrt{2}\,\rho_1, \qquad \gamma = \frac{1}{6}\sqrt{6}\,\rho_2, \qquad \delta = \frac{1}{2}\sqrt{2}\,\rho_2.$$

$\sigma = 0$ for triplet states; for singlet states, the rows and columns containing σ need not be taken into account.

Table 1

Subtable	Column headings visible	Row sequence visible	Entries visible on the main stepped diagonal
A_1	$\alpha\beta\sigma$, $\alpha\beta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$	$\alpha, \beta, \sigma;$ $\alpha, \beta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ γ, δ, σ	$B_0, B_0, B_1, B_1, B_1, B_1$
A_2	$\alpha\beta\sigma$, $\alpha\beta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$	$\alpha, \beta, \sigma;$ $\alpha, \beta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ γ, δ, σ	$C_0, C_0, C_1, C_1, C_1, C_1$
A_3	$\alpha\beta\sigma$, $\alpha\beta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$	$\alpha, \beta, \sigma;$ $\alpha, \beta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ γ, δ, σ	$D_0, D_0, D_1, D_1, D_1, D_1$
A_4	$\alpha\beta\sigma$, $\alpha\beta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$, $\gamma\delta\sigma$	$\alpha, \beta, \sigma;$ $\alpha, \beta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ $\gamma, \delta, \sigma;$ γ, δ, σ	$F_0, F_0, F_1, F_1, F_1, F_1$

Visible off-diagonal stepped blocks in the surrounding part of the table are labeled K and L.

For the calculation of the energy matrix, the method of genealogical coefficients was used ([6]). Without dwelling on the details of the calculation, we give the energy matrix (see Table 1). The form of the energy matrix is the same both for the triplet and for the singlet states (for the singlet the order of the matrix is 52, for the triplet 76).

We do not set ourselves the task of finding all the roots of the energy matrix; rather, as previous authors did, we seek only the lowest levels by Löwdin' s method ([7]). The solution averaged over the orbital states of the cations has the form:

$$I_{\text{eff}} = \frac{E_s - E_t}{2} = -\frac{1}{3}(E_0 - E_1)^{-3}\{\rho_1^2[I_{pd}^{02}(I_{pd}^{02} + I_{pd}^{00} - 2I_{sd}^{02}) +$$

$$+ I_{pd}^{00}(I_{pd}^{00} + I_{pd}^{02} - 2I_{sd}^{00})] +$$

$$+ \rho_2^2[I_{pd}^{12}(I_{pd}^{12} + I_{pd}^{10} - 2I_{sd}^{02}) + I_{pd}^{10}(I_{pd}^{10} + I_{pd}^{12} - 2I_{sd}^{00})]\}, \tag{2}$$

where $I_{pd}^{\alpha\beta}$, $I_{sd}^{\alpha\beta}$ have the same meaning as in formula (1), and the upper indices denote projections of the orbital moments, for example,

$$I_{pd}^{12} = \int \Psi_{p1}^*(r_1)\Psi_{d2}^*(r_2)\frac{1}{r_{12}}\Psi_{p1}(r_2)\Psi_{d2}(r_1)\,d\tau;$$

$$\rho_1 = \int \Psi_s^*(r_1)\hat{H}_1(r_1)\Psi_{p0}(r_1)\,d\tau, \qquad \rho_2 = \int \Psi_s^*(r_1)\hat{H}_1\Psi_{p1}(r_1)\,d\tau.$$

If in formula (2) we assume that all $I_{pd}^{\alpha\beta} = I_{pd}^{00}$, $I_{sd}^{\alpha\beta} = I_{sd}^{00}$, $\rho_1 = \rho_2$, then we obtain the formula

$$I_{\text{eff}} = -\frac{4\rho_1^2(I_{pd}^{00} - I_{sd}^{00})I_{pd}^{00}}{(E_0 - E_1)^3},$$

which coincides with (1), if I_{pd}, I_{sd}, and ρ are understood as I_{pd}^{00}, I_{sd}^{00}, and ρ_1. The formula obtained, (2), makes it possible to carry out numerical estimates of the effective exchange interaction as a function of the orbital states.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.