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Two-Centre Exchange Interactions between Orbitally Degenerate Ions

I. One Ion in Orbitally Degenerate State

By

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A multielectron theory of exchange interactions in transition metal ion pairs in cubic matrices and ions in orbitally degenerate states is developed. The orbitally dependent part of the exchange Hamiltonian is expressed by Pauli operators determined in the orbital space for the case of an orbital doublet and by fictitious orbital operators $\tilde{L} = 1$ in the case of a triplet state. It is shown that the anisotropic exchange parameters may be estimated from isotropic ones. The theory described is compared with experiment.

Развита многоэлектронная теория обменных взаимодействий в парах ионов переходных металлов, находящихся в кубических кристаллах в орбитально-вырожденных состояниях. Орбитально-зависимая часть обменного гамильтониана в случае орбитального дублета выражена через матрицы Паули, определенные на орбитальных функциях вырожденных ионов, а в случае орбитального триплета — через операторы фиктивного орбитального момента $\tilde{L} = 1$. Показано, что параметры анизотропного обмена можно оценить, используя известные значения параметров изотропного обмена. Развита теория сравнивается с экспериментом.

1. Introduction

It is understood at present that the Heisenberg-Dirac-Van Vleck Hamiltonian $J(\hat{S}_a\hat{S}_b)$ does not provide an adequate description of exchange interactions, particularly in the case of orbitally degenerate states. With non-quenched orbital motion, the exchange Hamiltonian (EH) depends not only on the spin moments, but also on the orbital moments of interacting atoms (see [1 to 5] and references cited therein). The experimental determination of EH parameters is a difficult task because of their large number. Thus, even with only one d-electron per centre, the number of independent EH parameters amounts to 22 [2, 5]. The general theory includes so many parameters because of consideration of all ion states arising from ground electron configurations. As intraatomic electrostatic interactions and crystal field effects are, as a rule, far more important than interion exchange couplings, several energy levels prove to be well separated from each other so that many of them may be disregarded, which essentially reduces the number of independent parameters in the effective EH.

Two methods may be applied to solve this problem in which local symmetry restrictions are introduced at different stages. According to the first approach, EH is constructed for a pair of interacting free ions [1 to 5]. Ion symmetries may then be taken into consideration at subsequent stages of analysis. The other method (the strong crystal field scheme) takes into consideration local symmetry requirements prior to constructing EH [6 to 10]. The latter approach is more effective because it is naturally related to the exchange channel model [10, 11]. It is shown below that using this approach one cannot only determine the form of the effective EH but also estimate its parameters from known values of isotropic spin exchange parameters.

2. The General Form of the Exchange Hamiltonian

Consider a pair of exchange coupled ions with open d-subshells. Let the local environment of the ions be approximately O_h (cubic) so that the energies of non-cubic components of the crystal field and of spin-orbit coupling are sufficiently small and do not cause any considerable mixing of the cubic levels.

The basis functions of the irreducible representations are chosen as follows:

$$u = d_{r^2-3z^2}, \quad v = d_{y^2-x^2}, \quad \zeta = d_{xy}, \quad \xi = d_{yz}, \quad \eta = d_{zx}.$$

As the basis is real, the 3γ -symbols are real too and, consequently, the EH derived in [9, 10] may be written in the form

$$\hat{H}_{\text{ex}} = \sum_{\substack{\kappa\pi\gamma_1\gamma_2q_1q_2 \\ \gamma_a\gamma'_a\gamma_b\gamma'_b}} (-1)^\pi W_{\pi q_1}^{(\kappa\gamma_1)}(\gamma_a\gamma'_a) W_{-\pi q_2}^{(\kappa\gamma_2)}(\gamma_b\gamma'_b) J_{q_1q_2}^{\gamma_1\gamma_2}(\gamma_a\gamma'_a\gamma_b\gamma'_b), \quad (1)$$

where the quantities $J_{q_1q_2}^{\gamma_1\gamma_2}$ are defined by

$$J_{q_1q_2}^{\gamma_1\gamma_2}(\gamma_a\gamma'_a\gamma_b\gamma'_b) = \sum_{\substack{q_aq'_a \\ q_bq'_b}} \sqrt{[\gamma_1][\gamma_2]} \left\langle \gamma'_a\gamma_1\gamma_a \right\rangle \left\langle \gamma'_b\gamma_2\gamma_b \right\rangle J_{\gamma_aq_a\gamma_bq_bq'_aq'_bq'_b}. \quad (2)$$

Here $\gamma_a(\gamma_b)$ is the irreducible representation of the point group symmetry of magnetic ion a(b), $q_a(q_b)$ the representation row, $\langle \dots \rangle$ the 3γ -symbols of the cubic groups (see [12]), $[\gamma]$ the representation dimension. The quantities $J_{\gamma_aq_a\gamma_bq_bq'_aq'_bq'_b}$ are invariant under point group symmetry operations of the pair. They are also invariant with respect to permutations of primed and unprimed indices. $W_{\pi q}^{(\kappa\gamma)}(\gamma_3\gamma_4)$ is the double cubic irreducible tensor with the matrix elements calculated by the Wigner-Eckart theorem

$$\begin{aligned} & \langle \Gamma Q S M_S | W_{\pi q}^{(\kappa\gamma)}(\gamma_3\gamma_4) | \Gamma' Q' S' M'_S \rangle = \\ & = (-1)^{S-M_S} \begin{pmatrix} S & \kappa & S' \\ -M_S & \pi & M'_S \end{pmatrix} \left\langle \begin{matrix} \Gamma' & \gamma & \Gamma \\ Q' & q & Q \end{matrix} \right\rangle \langle \Gamma S || W^{(\kappa\gamma)}(\gamma_3\gamma_4) || \Gamma' S' \rangle, \end{aligned} \quad (3)$$

where S is the total ion spin, Γ the irreducible representation according to which the multielectron wave function transforms, Q the representation row.

For one subshell containing n equivalent electrons the reduced matrix element in (3) is calculated using the formula

$$\begin{aligned} & \langle \gamma_1^n \Gamma S || W^{(\kappa\gamma)}(\gamma_3\gamma_4) || \gamma_1^n \Gamma' S' \rangle = \\ & = n(-1)^{\gamma_1+1/2+\Gamma+S+\gamma+\kappa} \{ [\Gamma] [S] [\Gamma'] [S'] [\kappa] [\gamma] \}^{1/2} \delta_{\gamma_1\gamma_3} \delta_{\gamma_1\gamma_4} \times \\ & \times \sum_{\Gamma'' S''} (-1)^{\Gamma''+S''} \begin{bmatrix} \Gamma & \Gamma' & \gamma \\ \gamma_1 & \gamma_1 & \Gamma'' \end{bmatrix} \left\{ \begin{matrix} S & S' & \kappa \\ 1/2 & 1/2 & S'' \end{matrix} \right\} \times \\ & \times \langle \gamma_1^n \Gamma S | \gamma_1^{n-1} \Gamma'' S'' \rangle \langle \gamma_1^n \Gamma' S' | \gamma_1^{n-1} \Gamma'' S'' \rangle. \end{aligned} \quad (4)$$

The values of phase factors $(-1)^\gamma$, $(-1)^{\Gamma'}$, of 6γ -symbols $\left\langle \begin{matrix} \Gamma & \Gamma' & \gamma \\ \gamma_1 & \gamma_1 & \Gamma'' \end{matrix} \right\rangle$, and of fractional parentage coefficients $\langle | \rangle$ are defined according to [12].

With two subshells containing n_1 and n_2 equivalent electrons and having quantum numbers $\Gamma_1 S_1$ and $\Gamma_2 S_2$, respectively, the reduced matrix element may be calculated

as follows:

$$\begin{aligned}
 & \langle \gamma_1^{n_1}(I_1 S_1) \gamma_2^{n_2}(I_2 S_2) I S || W^{(\kappa\gamma)}(\gamma_3 \gamma_4) || \gamma_1^{n_1}(I'_1 S'_1) \gamma_2^{n_2}(I'_2 S'_2) I' S' \rangle = \\
 & = \delta_{I_1 I'_1} \delta_{S_1 S'_1} (-1)^{I_1 + I_2 + I' + \gamma + S_1 + S_2 + S' + \kappa} \times \\
 & \times \{ [I] [I'] [S] [S'] \}^{1/2} \begin{bmatrix} I_1 & I_2 & I \\ I' & \gamma & I'_1 \end{bmatrix} \begin{Bmatrix} S_1 & S_2 & S \\ S' & \kappa & S'_1 \end{Bmatrix} \times \\
 & \times \langle \gamma_1^{n_1} I_1 S_1 || W^{(\kappa\gamma)}(\gamma_3 \gamma_4) || \gamma_1^{n_1} I'_1 S'_1 \rangle + \delta_{I_1 I'_1} \delta_{S_1 S'_1} (-1)^{I + I'_2 + \gamma + I_1 + S + S'_2 + \kappa + S_1} \times \\
 & \times \{ [I] [I'] [S] [S'] \}^{1/2} \begin{bmatrix} I_2 & I' & I_1 \\ I' & I'_2 & \gamma \end{bmatrix} \begin{Bmatrix} S_2 & S & S_1 \\ S' & S'_2 & \kappa \end{Bmatrix} \times \\
 & \times \langle \gamma_2^{n_2} I_2 S_2 || W^{(\kappa\gamma)}(\gamma_3 \gamma_4) || \gamma_2^{n_2} I'_2 S'_2 \rangle, \quad (5)
 \end{aligned}$$

where one-subshell reduced matrix elements are calculated by (4).

The reduced matrix elements non-diagonal with respect to configuration are given by [12]

$$\begin{aligned}
 & \langle \gamma_1^{n_1}(I_1 S_1) \gamma_2^{n_2-1}(I_2 S_2) I S || W^{(\kappa\gamma)}(\gamma_3 \gamma_4) || \gamma_1^{n_1-1}(I'_1 S'_1) \gamma_2^{n_2}(I'_2 S'_2) I' S' \rangle = \\
 & = \sqrt{n_1 n_2} (-1)^{n_2 + \gamma_1 + 1/2 + I_1 - S_1 + I - S + \gamma - \kappa + I'_1 + S'_1 + I' + S'} \times \\
 & \times \{ [I_1] [S_1] [I] [S] [I'_2] [S'_2] [I'] [S'] [\gamma] [\kappa] \}^{1/2} \times \\
 & \times \begin{bmatrix} I_1 & \gamma_1 & I'_1 \\ I_2 & \gamma_2 & I'_2 \\ I & \gamma & I' \end{bmatrix} \begin{Bmatrix} S_1 & 1/2 & S'_1 \\ S_2 & 1/2 & S'_2 \\ S & \kappa & S' \end{Bmatrix} \times \\
 & \times \langle \gamma_1^{n_1} I_1 S_1 | \gamma_1^{n_1-1} I'_1 S'_1 \rangle \langle \gamma_2^{n_2} I'_2 S'_2 | \gamma_2^{n_2-1} I_2 S_2 \rangle \delta_{\gamma_1 \gamma_2} \delta_{\gamma_3 \gamma_4}, \quad (6)
 \end{aligned}$$

where $[\cdot \cdot \cdot \cdot \cdot]$ is the 9γ -symbol.

On the assumption that there is no interaction between the terms (the restriction introduced in the beginning of this section) the matrix elements non-diagonal with respect to the quantum numbers I and S may be neglected. The general EH (1) may therefore be replaced by an effective one written in terms of the operators of fictitious moments. As is known, these may be represented by Pauli matrices for the orbital doublet state and by the operator of fictitious orbital moment $\tilde{L} = 1$ for the triplet state. The derivation of fictitious moment operators will be exemplified.

3. Exchange Interaction in the Case of Quenched Orbital Motion of One of the Ions

Let ion "b" be in an orbitally non-degenerate state. Taking into consideration (5), (16) derived in Part II of [10] we may write EH (1) in the form

$$\begin{aligned}
 \hat{H}_{\text{ex}} = & \sum_{\gamma_1 q_1 \gamma_a \gamma'_a \gamma_b} \frac{n_{\gamma_b}}{\sqrt{2} [\gamma_b]} W_{q_1}^{(0\gamma_1)}(\gamma_a \gamma'_a) J_{q_1}^{\gamma_1 A_1}(\gamma_a \gamma'_a \gamma_b \gamma'_b) + \\
 & + \sum_{\pi \gamma_1 q_1 \gamma_a \gamma'_a \gamma'_b} \sqrt{\frac{2}{[\gamma_b]}} (-1)^\pi W_{\pi q_1}^{(1\gamma_1)}(\gamma_a \gamma'_a) S_{-\pi}(\gamma_b) J_{q_1}^{\gamma_1 A_1}(\gamma_a \gamma'_a \gamma_b \gamma'_b), \quad (7)
 \end{aligned}$$

where

$$J_{q_a q_b}^{\gamma_1 A_1}(\gamma_a \gamma'_a \gamma_b \gamma_b) = \sum_{q_a q'_a q_b} \sqrt{\frac{[\gamma_1]}{[\gamma_b]}} \left\langle \begin{matrix} \gamma'_a & \gamma_1 & \gamma_a \\ q'_a & q_1 & q_a \end{matrix} \right\rangle J_{\gamma_a q_a \gamma_b q_b \gamma'_a q'_a \gamma_b q_b} . \quad (8)$$

Let us consider a frequently occurring case of an ion pair having C_{4v} point group symmetry with the fourfold axis coinciding with the pair axis. The condition of invariance of $J_{\gamma_a q_a \gamma_b q_b \gamma'_a q'_a \gamma_b q_b}$ with respect to pair point group symmetry operations gives $\gamma_a = \gamma'_a$, $q_a = q'_a$.

Further we shall use the notations

$$J_{q_a q_b} = J_{\gamma_a q_a \gamma_b q_b \gamma_a q_a \gamma_b q_b}; \quad J_{q_1}^{\gamma_1}(\gamma_a \gamma_b) = J_{q_1}^{\gamma_1 A_1}(\gamma_a \gamma_a \gamma_b \gamma_b) .$$

As we have confined our discussion to the d-metals only, γ_a may take on two values: e and t_2 .

After substituting the numerical 3γ -symbol values into (8) and bearing in mind that $\gamma_1 \neq A_1$ (the case of $\gamma_1 = A_1$ corresponds to isotropic exchange and has been considered in [10]) we obtain for $\gamma_a = e$:

$$J_u^E(e, \gamma_b) = \frac{1}{\sqrt{2[\gamma_b]}} \sum_{q_b} (J_{vq_b} - J_{uq_b}) . \quad (9)$$

All the other $J_{q_1}^{\gamma_1}(e\gamma_b)$ values reduce to zero.

With $\gamma_a = t_2$, we also have only one non-zero value:

$$J_u^E(t, \gamma_b) = \frac{1}{\sqrt{6[\gamma_b]}} \sum_{q_b} (J_{\eta q_b} + J_{\xi q_b} - 2J_{\zeta q_b}) . \quad (10)$$

The orbitally dependent exchange may thus be described in terms of four independent parameters at most.

The values entering expressions (9) and (10) can be estimated from the values of exchange parameters J_{ee} , J_{tt} , J_{te} suggested in [10]. These are related to the $J_{q_a q_b}$ values as follows:

$$\left. \begin{aligned} J_{ee} &= 2(J_{uu} + J_{uv} + J_{vu} + J_{vv}) , \\ J_{te} &= 2(J_{\eta u} + J_{\eta v} + J_{\xi u} + J_{\xi v} + J_{\zeta u} + J_{\zeta v}) , \\ J_{et} &= 2(J_{u\eta} + J_{v\eta} + J_{u\xi} + J_{v\xi} + J_{u\zeta} + J_{v\zeta}) , \\ J_{tt} &= 2(J_{\eta\eta} + J_{\xi\xi} + J_{\zeta\zeta} + J_{\xi\eta} + J_{\eta\xi} + J_{\eta\zeta} + J_{\zeta\eta} + J_{\xi\zeta} + J_{\zeta\xi}) . \end{aligned} \right\} \quad (11)$$

The number of $J_{\alpha\beta}$ parameters on the right-hand side of (11) is exceedingly large. However, in a number of practically important cases, most of these may be neglected. For example, consider a perovskite-type crystal with superexchange mainly along bridge one-atom ligands lying on the fourfold axis between the magnetic ions. In this case, all the $J_{\alpha\beta}$ having α or β equal to $\eta = d_{xy}$ or $v = d_{y^2-x^2}$ may be neglected because the corresponding metal orbitals overlap with ligand orbitals to a far lesser extent than the remaining three d-orbitals. Bearing in mind this and (9) to (11) we may write

$$\left. \begin{aligned} J_u^E(ee) &\approx -\frac{1}{4} J_{ee} , & J_u^E(te) &\approx \frac{1}{4\sqrt{3}} J_{te} , \\ J_u^E(et) &\approx -\frac{\sqrt{2}}{4\sqrt{3}} J_{et} , & J_u^E(tt) &\approx \frac{1}{6\sqrt{2}} J_{tt} . \end{aligned} \right\} \quad (12)$$

Substitution of the known values $J_{ee} \approx 248 \text{ cm}^{-1}$, $J_{te} \approx J_{et} \approx -50 \text{ cm}^{-1}$, and $J_{tt} = 40.5 \text{ cm}^{-1}$ (these were determined in [10], Part III, for KMf_3) into (12) readily yields the estimates for the orbitally dependent exchange parameters.

Ion "a" may be either in the doubly degenerate E or in triply degenerate T_1 or T_2 states.

We shall first consider the orbital doublet. Using (3), it is easy to show that in the orbital space, the matrix elements of $W_u^{(0E)}(ee)$ entering (7) and of $\tau_z^{(a)}$, operating in the orbital space of the basis functions $|Ev\rangle$, $|Eu\rangle$ of atom "a" as follows:

$$\tau_z = \begin{vmatrix} v & 1 & 0 \\ u & 0 & -1 \end{vmatrix} \quad (13)$$

coincide with the exception of a factor.

The effective EH for a doublet-singlet pair may thus be written in the form

$$\hat{H}_{\text{ex}} = J(\hat{S}_a \hat{S}_b) + [J_1^b + J_2^b(S_a S_b)] \tau_z^{(a)}. \quad (14)$$

The isotropic part of EH (14) is considered in detail in [10].

The anisotropic exchange parameters J_1^b and J_2^b (index b indicates quenching of orbital motion on b) are related to the values defined by (9), (10) as follows:

$$J_1^b = \frac{1}{2} \sum_{\gamma_a \gamma_b} \frac{n_{\gamma_b}}{\sqrt{2[\gamma_b]}} \frac{\langle S_a E || W^{(0E)}(\gamma_a \gamma_a) || S_a E \rangle}{\sqrt{[S_a]}} J_u^E(\gamma_a \gamma_b), \quad (15)$$

$$J_2^b = \sum_{\gamma_a \gamma_b} \sqrt{\frac{1}{2[\gamma_b]}} \frac{\langle S_a E || W^{(1E)}(\gamma_a \gamma_a) || S_a E \rangle}{\langle S_a || S_b || S_a \rangle} \frac{\langle S_b || S_{\gamma_b} || S_b \rangle}{\langle S_b || S_b || S_b \rangle} J_u^E(\gamma_a \gamma_b). \quad (16)$$

Like with isotropic exchange (see [10], Part II), the expressions for anisotropic exchange parameters J_1^b and J_2^b may be generalized to include states resulting from superposition of configurations. This can be done by replacing the occupancies n_{γ_b} of subshells γ on b by

$$N_{\gamma_b} = \sum_j |C_j^b|^2 n_{\gamma_b}^{(j)},$$

where C_j^b are the coefficients in the expansion of the wave function of ion b in terms of wave functions corresponding to definite electronic configurations.

As in [10], Part III, the quantities

$$g_{\gamma_b} = \frac{\langle S_b || S_{\gamma_b} || S_b \rangle}{\langle S_b || S_b || S_b \rangle}$$

should be replaced by

$$\tilde{g}_{\gamma_b} = \sum_j |c_j^b|^2 \frac{\langle S_b || S_{\gamma_b}^{(j)} || S_b \rangle}{\langle S_b || S_b || S_b \rangle}.$$

Similarly, the reduced matrix element of the operator $W^{(\kappa\gamma)}(\gamma_a \gamma_a)$ for ion "a" is replaced by

$$\sum_i |C_i^a|^2 \langle n_{\gamma_a}^{(i)} S_a \Gamma_a || W^{(\kappa\gamma)}(\gamma_a \gamma_a) || n_{\gamma_a}^{(i)} S_a \Gamma_a \rangle,$$

where $n_{\gamma_a}^{(i)}$ are introduced to differentiate between the contributions from various configurations.

With all these substitutions we have

$$J_1^b = \frac{1}{2} \sum_{\gamma_a \gamma_b} \frac{N_{\gamma_b}}{\sqrt{2[\gamma_b]}} \left(\sum_i |C_i^a|^2 \frac{\langle n_{\gamma_a}^{(i)} S_a E || W^{(0E)}(\gamma_a \gamma_a) || n_{\gamma_a}^{(i)} S_a E \rangle}{\sqrt{[S_a]}} \right) J_u^E(\gamma_a \gamma_b), \quad (15')$$

$$J_2^b = \sum_{\gamma_a \gamma_b} \sqrt{\frac{1}{2[\gamma_b]}} \left(\sum_i |C_i^a|^2 \frac{\langle n_{\gamma_a}^{(i)} S_a E || W^{(1E)}(\gamma_a \gamma_a) || n_{\gamma_a}^{(i)} S_a E \rangle}{\langle S_a || S_a || S_a \rangle} \right) \tilde{g}_{\gamma_b} J_u^E(\gamma_a \gamma_b). \quad (16')$$

In order to estimate the order of magnitude of J_1^b and J_2^b we shall consider the doping pair $\text{Mn}^{2+}({}^6A_{1g})\text{--Cu}^{2+}({}^2E_g)$ in the KZnF_3 host lattice. Using the numerical values of the $n\gamma$ -symbols and fractional parentage coefficients given in [12] we obtain from (4)

$$\langle e^3 {}^2E_g || W^{(0E)}(ee) || e^3 {}^2E_g \rangle = -\sqrt{2}, \quad \langle e^3 {}^2E_g || W^{(1E)}(ee) || e^3 {}^2E_g \rangle = \sqrt{6}.$$

Equation (15) then gives

$$J_1^b = -\frac{3}{2\sqrt{6}} J_u^E(et) - \frac{1}{2} J_u^E(ee).$$

Using (12), we have eventually

$$J_1^b \approx \frac{1}{8} (J_{ee} + J_{te}) \approx 25 \text{ cm}^{-1}.$$

The value of J_2^b may be estimated in a similar way:

$$J_2^b = \frac{\sqrt{6}}{5} J_u^E(et) + \frac{2}{5} J_u^E(ee) \approx -\frac{1}{10} (J_{te} + J_{ee}) \approx -20 \text{ cm}^{-1}.$$

It should be noted for comparison that according to our estimate, the isotropic exchange parameter for the same pair is equal to

$$J = \frac{1}{10} (J_{te} + J_{ee}) \approx 20 \text{ cm}^{-1}.$$

It thus follows that anisotropic and isotropic exchange parameters may, generally speaking, have comparable values.

The energy level scheme for the $\text{Mn}^{2+}\text{--Cu}^{2+}$ ion pair agrees qualitatively with the one suggested in [13] on the basis of the optical spectrum.

One more point should be mentioned. According to [13], the Cu^{2+} nearest environment suffers Jahn-Teller distortion with the tetragonal axis directed towards Mn^{2+} , and this agrees with predictions from our theory.

We now turn to the orbital triplet state. Let L_z be the operator of fictitious moment $\tilde{L} = 1$ defined as usual in [14]:

$$\langle \hat{L}_z | \rangle = \begin{array}{c} -\frac{1}{\sqrt{2}}(x+iy) \\ z \\ \frac{1}{\sqrt{2}}(x-iy) \end{array} \left| \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{array} \right| \begin{array}{c} -\frac{1}{\sqrt{2}}(\xi+i\eta) \\ \xi \\ \frac{1}{\sqrt{2}}(\xi-i\eta) \end{array}, \quad (17)$$

where the symbols on the left-hand side correspond to representations of the type T_1 and on the right-hand side to T_2 .

Comparison of the matrix elements of the operator $W_u^{(0E)}$ and of $3L_z^2 - 2$ shows that these coincide within a factor. We have therefore

$$H_{\text{ex}} = J(\hat{S}_a \hat{S}_b) + [J_3^b + J_4^b(\hat{S}_a \hat{S}_b)](3\hat{L}_z^2 - 2). \quad (18)$$

The anisotropic exchange parameters are related to the values entering (9), (10) as follows:

$$J_3^b = \mp \frac{1}{2} \sum_{\gamma_a \gamma_b} \frac{n_{\gamma_b}}{\sqrt{6[\gamma_b]}} \frac{\langle S_a T || W^{(0E)}(\gamma_a \gamma_b) || S_a T \rangle}{\sqrt{[S_a]}} J_u^E(\gamma_a \gamma_b), \quad (19)$$

$$J_4^b = \mp \sum_{\gamma_a \gamma_b} \sqrt{\frac{1}{6[\gamma_b]}} \frac{\langle S_a T || W^{(1E)}(\gamma_a \gamma_b) || S_a T \rangle}{\langle S_a || S_a || S_a \rangle} \frac{\langle S_b || S_{\gamma_b} || S_b \rangle}{\langle S_b || S_b || S_b \rangle} J_u^E(\gamma_a \gamma_b), \quad (20)$$

where the signs $-$ and $+$ correspond to representations T_1 and T_2 , respectively.

These expressions can be generalized to include configuration interactions, just as it has been done with the orbital doublet:

$$J_3^b = \mp \frac{1}{2} \sum_{\gamma_a \gamma_b} \frac{N_{\gamma_b}}{\sqrt{6[\gamma_b]}} \left(\sum_i |C_i^a|^2 \frac{\langle n_{\gamma_a}^{(i)} S_a T || W^{(0E)}(\gamma_a \gamma_b) || n_{\gamma_a}^{(i)} S_a T \rangle}{\sqrt{[S_a]}} \right) J_u^E(\gamma_a \gamma_b), \quad (19')$$

$$J_4^b = \mp \sum_{\gamma_a \gamma_b} \sqrt{\frac{1}{6[\gamma_b]}} \left(\sum_i |C_i^a|^2 \frac{\langle n_{\gamma_a}^{(i)} S_a T || W^{(1E)}(\gamma_a \gamma_b) || n_{\gamma_a}^{(i)} S_a T \rangle}{\langle S_a || S_a || S_a \rangle} \right) \tilde{g}_{\gamma_b} J_u^E(\gamma_a \gamma_b). \quad (20')$$

4. Conclusive Remarks

The theory described provides a means to determine anisotropic exchange parameters for ion pairs with arbitrary occupancies of subshells. To do this, one must substitute the reduced matrix elements of operators $W^{(\kappa\gamma)}(\gamma_3 \gamma_3)$ into the expressions for J_i^b . All the reduced matrix elements calculated by (4) and (5) are given in the Appendix.

It should be pointed out that anisotropic exchange interactions with one of the ions in an orbitally degenerate state only depend on four parameters which have the meaning of anisotropic exchange parameters between the subshells. We have shown earlier (see [10]) that with isotropic exchange in a given host lattice, the parameters $J_{\gamma_a \gamma_b}$ vary only slightly from one 3d-ion pair to another. It is reasonable to expect that the same rule will hold with the anisotropic exchange parameters $J_u^E(\gamma_a \gamma_b)$. On this assumption, one may use the J_i^b values determined from experimental data on several ion pairs to predict their values for other doping pairs in the same host lattice.

Appendix

Diagonal reduced matrix elements of the double cubic irreducible tensor operator $W^{(\kappa E)}(\gamma_3 \gamma_3)$ for states consistent with the Pauli principle. The following notation is used in tables:

$$\langle e^n \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S || W^{(\kappa E)}(\gamma_3 \gamma_3) || e^n \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S \rangle \equiv W^{(\kappa E)}(\gamma_3 \gamma_3) || e^n \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S \rangle.$$

configurations of equivalent electrons	states ΓS allowed
e^2	$A_1 0 \ E 0 \ A_2 1$
t^2	$A_1 0 \ E 0 \ T_2 0 \ T_1 1$
t^3	$E \frac{1}{2} \ T_1 \frac{1}{2} \ T_2 \frac{1}{2} \ A_2 \frac{3}{2}$

$$W^{(0E)}(ee) \parallel e^2 E 0 \rangle = 0$$

$$W^{(0D)}(tt) \parallel t_2^2 E 0 \rangle = 2/\sqrt{3} \quad W^{(0E)}(tt) \parallel t_2^2 T_1 1 \rangle = \sqrt{3}$$

$$W^{(0E)}(tt) \parallel t_2^2 T_2 0 \rangle = -1 \quad W^{(1E)}(tt) \parallel t_2^2 T_1 1 \rangle = \sqrt{6}$$

$W^{(\kappa E)}(ee) \parallel e^1 E \frac{1}{2} t_2^1 T_2 \frac{1}{2} \Gamma S \rangle$		
κ	S	Γ T_1, T_2
0	0	$\sqrt{3}/2$
0	1	$3/2$
1	1	$3/\sqrt{2}$

$W^{(\kappa E)}(tt) \parallel e^1 E \frac{1}{2} t_2^1 T_2 \frac{1}{2} \Gamma S \rangle$			
κ	S	Γ	
		T_1	T_2
0	0	-1	1
0	1	$-\sqrt{3}$	$\sqrt{3}$
1	1	$-\sqrt{6}$	$\sqrt{6}$

$W^{(\kappa E)}(tt) \parallel t_2^3 \Gamma \frac{1}{2} \rangle$			
κ	Γ		
	E	T_1	T_2
0	0	0	0
1	$2/\sqrt{2}$	$-\sqrt{6}$	$\sqrt{6}$

$W^{(\kappa E)}(ee) \parallel e^1 E \frac{1}{2} t_2^2 \Gamma_2 0 \Gamma \frac{1}{2} \rangle$			
κ	$\Gamma_2 \Gamma$		
	$A_1 E$	EE	$T_2 T_1, T_2 T_2$
0	$\sqrt{2}$	0	$\sqrt{3}/\sqrt{2}$
1	$\sqrt{6}$	0	$3/\sqrt{2}$

$W^{(\kappa E)}(ee) \parallel e^1 E \frac{1}{2} t_2^2 T_1 1 \Gamma S \rangle$		
κ	S	Γ T_1, T_2
0	1/2	$-\sqrt{3}/\sqrt{2}$
0	3/2	$-\sqrt{3}$
1	1/2	$1/\sqrt{2}$
1	3/2	$-\sqrt{5}$

$W^{(\kappa E)}(tt) \parallel e^1 E \frac{1}{2} t_2^2 T_1 1 \Gamma S \rangle$			
κ	S	Γ	
		T_1	T_2
0	1/2	$\sqrt{2}$	$-\sqrt{2}$
0	3/2	2	-2
1	1/2	$2\sqrt{2}/\sqrt{3}$	$-2\sqrt{2}/\sqrt{3}$
1	3/2	$2\sqrt{5}/\sqrt{3}$	$-2\sqrt{5}/\sqrt{3}$

$W^{(0E)}(tt) \parallel e^1 E \frac{1}{2} t_2^2 \Gamma_2 0 \Gamma \frac{1}{2} \rangle$			
$\Gamma_2 \Gamma$	EE	$T_2 T_1$	$T_2 T_2$
	0	$\sqrt{2}$	$-\sqrt{2}$

$W^{(\kappa E)}(tt) \parallel e^2 A_2 1 t_2^1 T_2 \frac{1}{2} T_1 S \rangle$		
κ	S	
	1/2	3/2
0	$-\sqrt{2}$	-2
1	$\sqrt{2}/\sqrt{3}$	$-2\sqrt{5}/\sqrt{3}$

$$W^{(0E)}(ee) \parallel e^2 E 0 t_2^1 T_2 \frac{1}{2} \Gamma \frac{1}{2} \rangle = 0$$

$W^{(\kappa E)}(tt) e^2 \Gamma_1 0 t_2^1 T_2 \frac{1}{2} \Gamma \frac{1}{2}\rangle$			
κ	$\Gamma_1 \Gamma$		
	$A_1 T_2, E T_2$	$E T_1$	
0	$\sqrt{2}$	$-\sqrt{2}$	
1	$\sqrt{6}$	$-\sqrt{6}$	

$W^{(\kappa E)}(ee) e^1 E \frac{1}{2} t_2^3 \Gamma_2 \frac{1}{2} \Gamma S\rangle$				
κ	S	$\Gamma_2 \Gamma$		
		EE	$T_1 T_1, T_1 T_2$	$T_2 T_1, T_2 T_2$
0	0	0	$-\sqrt{3}/2$	$\sqrt{3}/2$
0	1	0	$-3/2$	$3/2$
1	1	0	$-3/\sqrt{2}$	$3/\sqrt{2}$

$$W^{(0E)}(tt) ||e^1 E \frac{1}{2} t_2^3 \Gamma_2 \frac{1}{2} \Gamma S\rangle = 0$$

$W^{(1E)}(tt) e^1 E \frac{1}{2} t_2^3 \Gamma_2 \frac{1}{2} \Gamma 1\rangle$				
$\Gamma_2 \Gamma$	EE	$T_1 T_1, T_2 T_1$	$T_1 T_2, T_2 T_2$	
0	$-\sqrt{6}$	$\sqrt{6}$		

$$W^{(0E)}(ee) ||e^2 E 0 t_2^3 \Gamma_2 S_2 \Gamma S\rangle = 0$$

$$W^{(0E)}(tt) ||e^2 A_2 1 t_2^2 E 0 E 1\rangle = -2;$$

$W^{(\kappa E)}(tt) e^2 \Gamma_1 0 t_2^2 T_1 1 \Gamma 1\rangle$			
κ	$\Gamma_1 \Gamma$		
	$A_1 T_1, E T_1$	$E T_2$	
0	$\sqrt{3}$	$-\sqrt{3}$	
1	$\sqrt{6}$	$-\sqrt{6}$	

$$W^{(1E)}(tt) ||e^2 A_2 1 t_2^3 \Gamma_2 \frac{1}{2} \Gamma S\rangle$$

S	$\Gamma_2 \Gamma$		
	EE	$T_1 T_2$	$T_2 T_1$
1/2	$2\sqrt{2}/3$	$-\sqrt{2}/\sqrt{3}$	$\sqrt{2}/\sqrt{3}$
3/2	$-4\sqrt{5}/3$	$2\sqrt{5}/\sqrt{3}$	$-2\sqrt{5}/\sqrt{3}$

$W^{(\kappa E)}(ee) e^1 E \frac{1}{2} t_2^3 A_2 \frac{3}{2} E S\rangle$			
κ	S		
	1	2	
0	$-\sqrt{3}$	$-\sqrt{5}$	
1	$\sqrt{3}/\sqrt{2}$	$-\sqrt{15}/\sqrt{2}$	

$W^{(\kappa E)}(tt) e^2 A_2 1 t_2^2 T_1 1 T_2 S\rangle$			
κ	S		
	0	1	2
0	-1	$-\sqrt{3}$	$-\sqrt{5}$
1	-	$-\sqrt{3}/\sqrt{2}$	$-\sqrt{15}/\sqrt{2}$

$$W^{(0E)}(tt) ||e^2 A_2 1 t_2^2 T_2 0 T_1 1\rangle = \sqrt{3}$$

$$W^{(0E)}(tt) ||e^2 \Gamma_1 0 t_2^3 \Gamma_2 0 \Gamma 0\rangle$$

$\Gamma_1 \Gamma_2 \Gamma$	$A_1 EE$	EEE	$E T_2 T_1$	$A_1 T_2 T_2, E T_2 T_2$
	$2/\sqrt{3}$	0	1	-1

$$W^{(0E)}(ee) ||e^2 E 0 t_2^3 \Gamma_2 S_2 \Gamma S\rangle = 0$$

$$W^{(0E)}(tt) ||e^2 \Gamma_1 S_1 t_2^3 \Gamma_2 \frac{1}{2} \Gamma S\rangle = 0$$

$W^{(1E)}(tt) e^2\Gamma_1 0 t_2^3 \Gamma_2 \frac{1}{2} \Gamma \frac{1}{2}\rangle$				
$\Gamma_1 \Gamma_2 \Gamma$	$A_1 EE$	EEE	$A_1 T_1 T_1, ET_1 T_1, ET_2 T_1$	$A_1 T_2 T_2, ET_1 T_2, ET_2 T_2$
	$2/\sqrt{2}$	0	$-\sqrt{6}$	$\sqrt{6}$

The reduced matrix elements for more than half filled subshells may be calculated using these tables and the relationships

$$\begin{aligned}
 W^{(\kappa E)}(ee) ||e^n \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S\rangle &= W^{(\kappa E)}(ee) ||e^n \Gamma_1 S_1 t_2^{6-m} \Gamma_2 S_2 \Gamma S\rangle = \\
 &= (-1)^{\kappa+1} W^{(\kappa E)}(ee) ||e^{4-n} \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S\rangle, \\
 W^{(\kappa E)}(tt) ||e^n \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S\rangle &= W^{(\kappa E)}(tt) ||e^{4-n} \Gamma_1 S_1 t_2^m \Gamma_2 S_2 \Gamma S\rangle = \\
 &= (-1)^{\kappa+1} W^{(\kappa E)}(tt) ||e^n \Gamma_1 S_1 t_2^{6-m} \Gamma_2 S_2 \Gamma S\rangle.
 \end{aligned}$$

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