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## Exchange integrals in Mn- and Co-doped II-VI semiconductors

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Exchange integrals between nearest-neighbor (NN) transition metal ions in II-VI diluted magnetic semiconductors (DMSs) are calculated within a local superexchange model, which includes orbital-dependent transfer, on-site Coulomb repulsion and Hund's exchange between  $3d$  electrons, and ligand field effects. This extended model gives a quantitative account for the available experimental data on the NN exchange constants in all II-VI DMS family (wurtzite and zinc-blende) doped by cobalt or manganese. As expected, all obtained exchange integrals are antiferromagnetic. Remarkably, the model input parameters are taken directly from the photoemission spectroscopy. We show that in the case of Co-doped compounds, as compared to Mn-doped ones, the exchange process has at least two salient features. The first one is that the electron transfer between NN  $\text{Co}^{2+}$   $3d$  orbitals strongly depends on their symmetry positions in the crystal lattice. The second one is related to a peculiar virtual process, involving empty and occupied  $\text{Co}^{2+}$   $3d$  orbitals, which leads to an additional *ferromagnetic* contribution to the exchange constant. We argue that our systematic study of the superexchange opens a pathway toward an understanding of other exchange mechanisms occurring in DMSs.

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### I. INTRODUCTION

Diluted magnetic semiconductors (DMSs), that is binary semiconductors in which a fraction  $x$  of cations is replaced by transition metal ions (TMIs), are promising materials for spin electronics [1,2]. Room-temperature carrier-induced ferromagnetism (FM) in these materials remains a great challenge. While it is clear that long-range magnetic ordering involves delocalized carriers to couple distant TMIs by a Zener-like FM exchange process [3,4], several exchange mechanisms can occur at shorter distances, enhancing or inhibiting this long-range FM order. Therefore, exchange interactions at a short distance, and in particular nearest-neighbors (NN) exchange, deserve to be studied deeply to understand conditions enabling room-temperature FM in DMS. To this end, the undoped II-VI DMS are of particular interest because the isovalent substitution of host cations by TMIs prevents carrier-induced spin interactions.

Experimentally, many works have been devoted during the last three decades to measurement and identification of NN, next nearest-neighbors (NNN), and sometimes more distant [5], exchange constants in DMSs, principally by magnetization step (MST) [6] and inelastic neutron scattering (INS) experiments [5,7]. In all cases, NN and NNN pairs of TMIs have been found to be antiferromagnetically coupled.

On the theoretical side, recent *ab initio* calculations, using the supercell method, have proved that LSDA can reproduce NN exchange constants ( $J_{dd}$ ) [8–12], provided that the localized character of the TMI  $d$  shell is taken into account via an adjustable Hubbard parameter  $U$  in the so-called LSDA+ $U$  approach. However, these calculations do not say much about the involved mechanisms, so that quantitative analytic calculations remain highly desirable.

Since the pioneering work of Spalek *et al.* [13] and Larson *et al.* [14,15], it is commonly admitted that coupling between NN TMIs in DMS mainly stems from the superexchange [16], that is, from a high order process of virtual hole hopping from

valence band to open  $d$  shell. Therefore, analytical calculations have been based on a perturbative treatment of  $p$ - $d$  transfer (hybridization) in  $k$  space. In this case, the calculation of  $J_{dd}$  involves a double integration over the Brillouin zone [14,15], which makes it rather complex and dependent on a lot of band-structure parameters [17–19]. While thus obtained exchange constants take into account the contribution of all ions of the host lattice, the local character of the  $d$ - $d$  interaction is clearly ignored. This seems contrary to the fact that even in highly covalent tellurides the exchange between nearest Mn ions involves principally a single intermediate Te anion [15].

In this work we present the results of analytical calculations of a NN exchange constant, within a local superexchange model, for *all* common II-VI DMSs doped by cobalt and manganese. This is done by a generalization of a model which has been successfully applied for  $J_{dd}$  estimation in wurtzite Mn-doped II-VI DMS [20]. In this model,  $k$ -space description of hybridization is discarded in favor of a purely local transfer between  $d$  and  $p$  electrons (flat-band or dispersionless limit). This simplification, which is *a posteriori* justified, allows us to take into account: (1) all details of  $p$ - $d$  hybridization, and in particular its orbital dependence (see below), (2) on-site Coulomb repulsion and Hund's exchange between  $d$  electrons, and (3) ligand field terms in the TMI Hamiltonian.

Our approach reveals an important difference between  $\text{Mn}^{2+}$ - $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ - $\text{Co}^{2+}$  superexchange interactions. In the high-spin state of the  $\text{Mn}^{2+}$  ion (or other TMI with  $d^5$  configuration), all  $d$  orbitals are singly occupied and the state has a spherical symmetry. In this case, in the expression for the superexchange  $J_{dd}$  [Eqs. (9) and (10) of Ref. [20], also Eq. (2) below], the sum over occupied state runs over all  $d$  orbitals and the orientation of the coordinate system does not matter. In the  $\text{Co}^{2+}$  ion, in tetrahedral coordination, three holes in the  $d$  shell occupy  $t_2$  orbitals. The ligand field thus fixes the orientation of the coordinate system, with respect

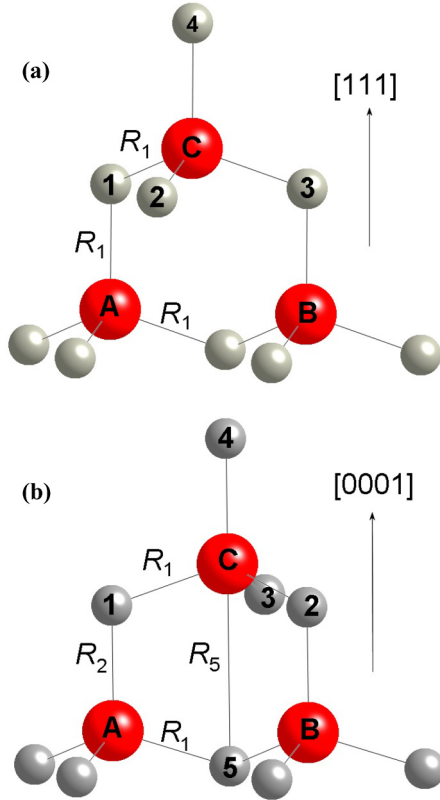


FIG. 1. (Color online) Analogous cluster of (a) zinc-blende and (b) wurtzite DMS. A, B, and C (red) denote cationic sites possibly occupied by transition metal ions, and 1, 2, 3, . . . (gray) denote anionic sites. A-B and A-C pairs are equivalent in the zinc-blende structure but not in the wurtzite structure: The C surrounding anion tetrahedron is rotated by  $60^\circ$  compared to the A and B ones.

to which the  $d$  orbitals are defined. This has an important consequence for the superexchange between lattice sites which are not simply related by translation: Local coordinate systems of different TMIs may be *rotated* with respect to each other [see Fig. 1(b)], and we should take this rotation into account in the  $J_{dd}$  calculation if the  $d$ -shell filling differs from 5.

Another advantage of our approach is that its input parameters are unequivocally related to the parameters used in the interpretation of photoemission experiments [21–24]. This connects our consideration of the superexchange with the ligand field theory, where  $p$ - $d$  hybridization appears in second order virtual hopping [25–27]. Moreover, the quantitative agreement of our model allows us to use the measurement of  $J_{dd}$  to determine the  $p$ - $d$  hybridization in addition or replacement of  $J_{sp-d}$  [28].

After having presented the model in Sec. II, we discuss in some detail the structures and input parameters in Sec. III. The two following sections focus, respectively, on Mn-doped and Co-doped compounds. They are followed by a discussion about general trends in the II-VI series, and about the involved magnetic mechanisms. Two detailed Appendices supplement the main part of this work, and are displayed after our conclusions.

## II. MODEL

The local superexchange model between two NN TMIs (denoted A, B, or C) presented here is an extension to the case  $N \leq 5$  ( $N$  is the number of  $d$  holes in the TMIs ground state) of a previously described model [20] developed for Mn ions ( $N = 5$ ). This model treats  $p$ - $d$  transfer between two TMIs and  $\mathcal{L}$  ligands as a perturbation to on-site Hamiltonians for TMIs and surrounding anions. On-site Hamiltonians contain on-site energy (TMIs and ligands), Coulomb repulsion, and a ligand field (for TMIs only). For  $N \neq 5$ , a ligand field cannot be ignored and an intra- $d$  Coulomb Hamiltonian gives rise to the FM process.

The first point is accounted for by writing all operators in a basis which diagonalizes the ligand field. The second one is a consequence of the off-diagonal part of the intra- $d$  Hund's exchange. Following Ref. [20], we use the approximate intra- $d$  Coulomb operator introduced by Kanamori [29,30]:

$$W = \left( U_d - \frac{5}{2} J_H \right) \frac{\hat{N}(\hat{N} - 1)}{2} - J_H \left( \hat{\mathbf{S}}^2 - \frac{3}{4} \hat{N} \right) + J_H \hat{P}^\dagger \hat{P}, \quad (1)$$

where  $U_d$  is the Hubbard parameter,  $J_H$  is the Hund exchange constant, and  $\hat{\mathbf{S}}$  and  $\hat{N}$  are the total spin and the total number of  $d$  holes operators, respectively.  $P^\dagger = \sum_m d_{m\uparrow}^\dagger d_{m\downarrow}^\dagger$  ( $d_{m\sigma}^\dagger$  creates a fermion in which quantum numbers are  $m$  for the orbital index, and  $\sigma$  for the spin degree of freedom).  $\hat{P}^\dagger \hat{P}$  couples empty orbitals to doubly occupied ones such that, for  $N \neq 5$ , occupied and unoccupied  $d$  orbitals of A and B can be connected via  $p$ - $d$  transfer over an intermediate ligand. Note that the Hamiltonian (1) is strictly equivalent to Eq. (7) of Ref. [20] when the condition for the spherical symmetry  $U'_d = U_d - 2J_H$  is satisfied (see Appendix A for the proof). The explicit spherically symmetric form (1) of the interaction Hamiltonian is close to the form obtained in Ref. [31], which was used for superexchange calculations in Ref. [19]. In Ref. [31] the so-called double hopping term of Hund's exchange [last term in Eq. (A2)]  $J'_H \sum_{m \neq m'} d_{m,\uparrow}^\dagger d_{m',\uparrow}^\dagger d_{m,\downarrow}^\dagger d_{m',\downarrow}^\dagger$  was neglected ( $J'_H \approx 0$ ), then the spherical symmetry was achieved via the relation  $U'_d = U_d - J_H$ , and the last term of Eq.(1) is absent.

Repeating the calculation scheme depicted in Ref. [20], with the additional difficulty that  $W$  is no longer diagonal in some intermediate states, a general expression for  $J_{dd}$  coupling between TMIs of the same kind is obtained (see Appendix B for details):

$$J_{dd} = K_1 \sum_{m_A, m_B}^{\text{occ.}} \mathcal{R}_{m_A m_B} + K_2 \sum_{m_A}^{\text{occ.}} \sum_{m_B}^{\text{unocc.}} (\mathcal{R}_{m_A m_B} + \mathcal{R}_{m_B m_A}), \quad (2)$$

where  $K_1$  and  $K_2$  are constants defined below and  $\mathcal{R}$  is the  $5 \times 5$  matrix whose elements are the resulting coupling, to fourth order, between  $d$  orbital  $m_A$  of A and  $d$  orbital  $m_B$  of B,  $m_A$  and  $m_B$  spanning the basis which diagonalize ligand fields (not necessarily identical) of A and B. Elements of the  $\mathcal{R}$  matrix can be written as the square modulus of a sum on the  $\mathcal{L}$  ligands involved in the superexchange process, this ensures

their positivity:

$$\mathcal{R}_{m_A m_B} = \left| \sum_{\beta=1}^{\mathcal{L}} \mathbf{T}_{m_A m_B}^{\beta} \right|^2, \quad (3)$$

$\mathcal{T}^{\beta}$  is the  $5 \times 5$  matrix which couples, to second order, A and B via the  $\beta$  ligand:

$$\mathcal{T}^{\beta} = \mathbf{T}_{\beta A}^{\dagger} \times \mathbf{T}_{\beta B}, \quad (4)$$

where  $\mathbf{T}_{\beta A}$  ( $\mathbf{T}_{\beta B}$ ) is the  $3 \times 5$  matrix of the Slater-Koster coefficients [32] between ligand  $\beta$  and A (B) written in the suitable basis (see Appendix C),  $\times$  denotes the matrix product, and  $\dagger$  is the hermitic conjugate.  $\mathbf{T}_{\beta\alpha}$  matrix ( $\alpha = A, B, C$ ) depends on relative orientation of  $\alpha$  TMI and  $\beta$  ligand, as well as on two transfer parameters for  $p$ - $d$  hopping,  $V_{pd\sigma}(\beta, \alpha)$  and  $V_{pd\pi}(\beta, \alpha)$ . We then note  $\eta = V_{pd\sigma}(\beta, \alpha)/V_{pd\pi}(\beta, \alpha)$  ( $\forall \beta, \alpha$ ) and adopt the value of  $\eta = -2.16$  from Ref. [33] in order to keep a connection with the model used in Refs. [21–24], which provides us input parameters. So far there is still as many transfer parameters as there is  $(\beta, \alpha)$  couples, so that we make two common assumptions: (1)  $V_{pd\sigma}(\beta, \alpha)$  depends only on the distance between the  $\beta$  ligand and  $\alpha$  TMI,  $R_{\beta, \alpha}$ , and (2) this dependence is given by Harrison formula [33], that is,  $V_{pd\sigma}(\beta, \alpha) \propto R_{\beta, \alpha}^{-7/2}$ .

As a result, for a given ligand number and positions, knowing the basis which diagonalize ligand fields of A and B, the  $\mathcal{R}$  matrix is unambiguously determined by only one transfer parameter, namely  $V_{pd\sigma}$ , which appears to fourth order. We choose it to be the transfer between a TMI and its nearest ligand. Sums in Eq. (2) then only depend on the set of basis orbitals which are holes occupied in A and B ground states.

Constants  $K_1$  and  $K_2$  contain energy differences related to intermediates states of the fourth order processes:

$$K_1 = -\frac{1}{2S^2\Delta_{\text{eff}}^2} \left( \frac{1}{\Delta_{\text{eff}}} + \frac{r^2}{U_{\text{eff}}} \right), \quad (5)$$

$$K_2 = +\frac{r^2 J_H}{2S\Delta_{\text{eff}}^2(U_d - 3J_H)[U_d + (N - 2)J_H]}, \quad (6)$$

where  $r$  is a reduction factor that is caused by dependence of the transfer integrals on the number of  $d$  holes: The transfer integrals between configurations  $d^{N+1}$  and  $d^N p^1$  are smaller by the factor  $r$  than the integrals between  $d^N$  and  $d^{N-1} p^1$ , where  $N$  is the number of holes on TMI [22,24]. The effective charge transfer  $\Delta_{\text{eff}}$  and effective Coulomb repulsion parameter  $U_{\text{eff}}$  are defined as follows (see Sec. III):

$$\Delta_{\text{eff}} \equiv \Delta + \frac{7}{9}(N - 1)J_H, \quad (7)$$

$$U_{\text{eff}} \equiv (U_d + 4J_H)[U_d + (N - 2)J_H]/(U_d + 3J_H). \quad (8)$$

Here we have neglected the tetrahedral ligand field (CF) splitting  $10D_q$  ( $\sim 0.5$  eV) compared to  $\Delta_{\text{eff}}$  ( $\sim 5$ – $9$  eV) in the denominators. By doing this, we still take into account the most important effect of CF, namely, the local symmetry dependence of  $p$ - $d$  transfer.

We see that, due to the positive sign of  $\mathcal{R}$  matrix elements,  $K_1$  implies an antiferromagnetic (AFM) contribution from the

first term of Eq. (2), while  $K_2$  implies an FM one from the second term. As  $|K_2/K_1| \sim 0.1$ , the resulting  $J_{dd}$  coupling remains AFM. It can be checked that for  $N = 5$  we get back to the results previously obtained for Mn ions: The first term of Eq. (2) becomes exactly Eq. (9) of Ref. [20]. Also, the cross terms of Eq. (3), involving different ligands, gives rise to the ring exchange discussed in Ref. [20].

Equation (3) clearly shows that coupling between occupied orbitals is AFM (because of the Pauli principle), while coupling between occupied and unoccupied ones is FM because of Hund's exchange. In some special cases, the AFM contribution is suppressed (e.g.,  $90^\circ$  bond angle,  $N = 1$ ) and the resulting superexchange may be ferromagnetic [34].

### III. INPUT PARAMETERS

The model giving  $J_{dd}$  exchange integrals is supplied by three kinds of parameters: crystallographic data of host semiconductors, free TMIs parameters, and energetic couplings between both.

First, structures of II-VI semiconductors are well known and, provided that TMI concentrations are not too high, lattice parameters of the corresponding DMS are assumed to be globally identical, although slight local deformations around TMIs certainly take place. We then dispose of all geometrical data needed, namely, relative orientation and distance of each ligand-TMI couple. Figure 1 shows the clusters for zinc-blende (ZB) and wurtzite (W) structures.

In unstressed ZB structure, characterized by one lattice parameter ( $a$ ), all distances are equal so that we simplify notations and write  $R_{\beta, \alpha} = R_1$ .

On the contrary, W structure is defined by two lattice ( $a, c$ ) and one displacement ( $u$ ) parameters. For  $u = 3/8 = a^2/c^2$ , the ligands surrounding a TMI form a perfect tetrahedron ( $R_1 = R_2 = 3c/8$  on Fig. 1), and the W structure is said to be ideal. Even in this case, it can be seen that there exists two kinds of NN pairs (A-B  $\neq$  A-C), which will be referred to as *in-plane* (A-B) and *out-of-plane* (A-C) pairs [20]. To keep generality (nonideal W) and simplify notation, W structure cluster will be characterized by three distances,  $R_1$ ,  $R_2$ , and  $R_5$  [see Fig. 1(b)]. Note that the A-1-C-5 ring lies in a single plane.

Second, exact Coulomb interaction of free TMIs is fully defined by three Racah parameters  $\mathcal{A}$ ,  $\mathcal{B}$ , and  $\mathcal{C}$ , which reduce to two in the approximated form (1):  $U_d = \mathcal{A} + 4\mathcal{B} + 3\mathcal{C}$  and  $J_H = 5\mathcal{B}/2 + \mathcal{C}$ . While  $\mathcal{B}$  and  $\mathcal{C}$  are relatively well known from the study of intra- $d$  optical transitions in a single  $d^N$  configuration,  $\mathcal{A}$  (and so  $U_d$ ) characterizes transitions between different configurations and is not so well known. Then, following Bocquet *et al.* [21], we use  $U = U_d - 20J_H/9$  which is experimentally accessible from the fit of photoemission (PE) spectroscopy on each DMS. This has been made in Ref. [20]. In the following,  $J_H$  will be regarded as constant for a given TMI while  $U$  will vary a little from one host to another.

Finally, energetic parameters coupling TMIs and ligands are logically the most important in the resulting TMI-TMI interaction. There are two such parameters:  $\Delta$ , the energetic barrier to be overcome by a hole to be transferred from a TMI  $d$  shell to a ligand  $p$  shell [see Eq. (6) of Ref. [20] and Eq. (B10)], and  $V_{pd\sigma}$ , the corresponding transfer integral.

$\Delta = \epsilon_p - \epsilon_d - U(N - 1)$ , where  $\epsilon_l$  ( $l = p, d$ ) and  $N$  refer to hole energies and number, respectively. In terms of electron energies ( $\epsilon_{l,el}$ ) and number ( $N_{el}$ ), the energetic barrier reads  $\Delta = \epsilon_{d,el} - \epsilon_{p,el} + UN_{el}$ .

In many cases,  $\Delta$  and  $V_{pd\sigma}$  are available from the fit of PE experiment, and if not, their values can be reasonably extrapolated or interpolated from the known ones in a given series of II-VI DMS. For example, it is clear that the  $V_{pd\sigma}$  parameter must decrease as the TMI-ligand distance increases because of the minor resulting overlapping. Similarly, the  $\Delta$  parameter must decrease, for a given cation of the host (Zn or Cd), as the ligand goes down in the periodic table (O, S, Se, ...), because of the decreasing electronegativity. Note that the examination of the density of states from *ab initio* calculations fully supports these qualitative trends.

We are now able to apply our model to the reproduction of experimental NN exchange integrals in all II-VI DMS, of W and ZB structures, doped by cobalt and manganese with a minimum number (and sometimes none) of adjustable parameters.

#### IV. Mn-DOPED COMPOUNDS

The case of manganese NN pairs in II-VI semiconductors has been the most studied and is the simplest one. Because all five  $d$  orbitals are singly occupied in the ground state of the ground configuration ( $N = 5$ ,  $S = 5/2$ ,  $L = 0$ ), any basis change has no effect so that the tetrahedral ligand field can be ignored and the sum over unoccupied orbitals, second term of Eq. (2), disappears. For both W and ZB structures, we have used a reduction factor  $r = 0.8$ , and free ion values of Racah parameters ( $B = 0.119$  eV,  $C = 0.412$  eV), leading to a Hund exchange constant  $J_H = 0.710$  eV.

In ZB structure, where there is only one type of NN pair to consider, only one anion (labeled as 1) is involved. Noting that this pair is equivalent to the *in-plane* pair of an ideal W structure, we have  $J_{dd}(ZB) \equiv J_{dd}^{\text{in}}(W)$ . Only  $J_{dd}^{\text{in}}(W)$  and  $J_{dd}^{\text{out}}(W)$  for the ideal W structure will be given in the following.

By injecting input parameters (Sec. III) into the generalized superexchange model for  $\mathcal{L} = 1$  (Sec. II), we obtain the  $\mathcal{R}$  matrix for which we sum all 25 elements. The resulting superexchange integral is then

$$\frac{J_{dd}^{\text{in}}}{V_{pd\sigma}^4} = \frac{K_1}{9} \left( 1 + \frac{16}{\eta^2} + \frac{10}{\eta^4} \right). \quad (9)$$

In this expression we have kept the  $\eta$  dependence (although it finally results in a numerical value) in order to see the contribution of  $V_{pd\sigma}^4$ ,  $V_{pd\sigma}^2 V_{pd\pi}^2$ , and  $V_{pd\pi}^4$  processes as well as to facilitate comparison with other past or future works. We stress that this expression is exact for ZB and ideal W cases, but that for nonideal W, weights of each process (1, 16, 10) are slightly modified and odd-power processes (e.g.,  $V_{pd\sigma}^3 V_{pd\pi}$ ) appear.

In the same spirit, we give an expression for *out-of-plane* pairs of ideal W structure for which two different lengths,  $R_1$  and  $R_5$ , are involved (see Fig. 1). In the ideal W structure, their ratio is simply  $\rho = R_1/R_5 = 3/5$ . Now that two ligands are involved in the superexchange process ( $\mathcal{L} = 2$ ), Eq. (3) gives rise to a FM cross term, that is, the ring-exchange contribution

TABLE I. Calculated  $J_{dd}$  (ZB) and  $J_{dd}^{\text{in}}$ ,  $J_{dd}^{\text{out}}$  (W) (in K) for Mn-doped II-VI DMS as a function of input parameters  $V_{pd\sigma}$ ,  $U$ ,  $\Delta$  (in eV). The table also enables comparison with experimental  $J_1$  and  $J_2$ .

| Host                         | ZnO                | ZnS                | ZnSe               | ZnTe              | CdS                | CdSe               | CdTe              |
|------------------------------|--------------------|--------------------|--------------------|-------------------|--------------------|--------------------|-------------------|
| Struct.                      | W                  | ZB                 | ZB                 | ZB                | W                  | W                  | ZB                |
| $V_{pd\sigma}$               | -1.8 <sup>a</sup>  | -1.34              | -1.09              | -0.92             | -1.22 <sup>a</sup> | -0.98 <sup>a</sup> | -0.92             |
| $\Delta$                     | 4.7 <sup>a</sup>   | 3 <sup>b</sup>     | 2 <sup>b</sup>     | 1.5 <sup>b</sup>  | 3 <sup>a</sup>     | 2 <sup>a</sup>     | 2 <sup>c</sup>    |
| $U$                          | 5 <sup>d</sup>     | 4 <sup>b</sup>     | 4 <sup>b</sup>     | 4 <sup>b</sup>    | 4 <sup>c</sup>     | 4 <sup>c</sup>     | 4 <sup>c</sup>    |
| $J_{dd}^{\text{in}}, J_{dd}$ | -24.1              | -16.1              | -12.6              | -9.1              | -11.1              | -8.3               | -6.4              |
| $J_{dd}^{\text{out}}$        | -18.7              |                    |                    |                   | -9.4               | -7.2               |                   |
| $J_1$                        | -24.3 <sup>e</sup> | -16.1 <sup>f</sup> | -12.6 <sup>g</sup> | -9.0 <sup>h</sup> | -11.0 <sup>i</sup> | -8.1 <sup>j</sup>  | -6.2 <sup>h</sup> |
| $J_2$                        | -18.2 <sup>e</sup> |                    |                    |                   | -9.6 <sup>i</sup>  | -7.0 <sup>j</sup>  |                   |

<sup>a</sup>Reference [20].

<sup>b</sup>Reference [24].

<sup>c</sup>Reference [22].

<sup>d</sup>References [9,24,35].

<sup>e</sup>Reference [36].

<sup>f</sup>Reference [7].

<sup>g</sup>Reference [37].

<sup>h</sup>Reference [38].

<sup>i</sup>References [6,39].

<sup>j</sup>References [38,40,41].

discussed in Ref. [20]:

$$\frac{J_{dd}^{\text{out}}}{V_{pd\sigma}^4} = \frac{K_1}{9} \left[ \left( 1 + \frac{16}{\eta^2} + \frac{10}{\eta^4} \right) (1 + \rho^7) - \frac{2\rho^{7/2}}{81} \left( 9 + \frac{768}{\eta^2} + \frac{130}{\eta^4} \right) \right]. \quad (10)$$

The  $7/2$  exponent comes from the Harrison bond-length dependence of  $V_{pd\sigma}$  transfer discussed in Sec. III. We see that Eq. (9) is a special case of Eq. (10): it just results from the strict equivalence of A-5-B and A-1-C superexchange paths. Other contributions to  $J_{dd}^{\text{out}}$  are the A-5-C and A-1-C-5 paths.

We remark that, if Eq. (9) and (10) are only valid for ideal W structures,  $J$  values for nonideal cases can be simply numerically obtained by changing orientation and bond length in the appropriate Slater-Koster transfer matrix  $\mathbf{T}_{\beta i}$  (Sec. II).

We now apply this model to the seven II-VI Mn-doped DMS for which the measurement of the largest exchange integrals ( $J_1$ ,  $J_2$ ) is available. The three W compounds have already been treated in a previous work [20] and will not be discussed here.

Concerning ZB compounds, Refs. [22] and [24] give all three energetic input parameters,  $V_{pd\sigma}$ ,  $\Delta$ , and  $U$ . As the  $J_{dd}$  expression is highly sensitive to  $V_{pd\sigma}$ , we choose to let it vary a little within its uncertainty. The uncertainty of  $V_{pd\sigma}$  resulting from PE modeling is of the order of a few tenths of an eV [24], while our adjustment is of the order of a hundredth of an eV around the same central value. For example, concerning Mn-doped ZnS,  $V_{pd\sigma}$  is given to be -1.3 eV [24], leading to  $J_{dd} = -14.2$  K. By letting  $V_{pd\sigma}$  grow up to -1.34 eV, we reach the experimental value of  $J_1 = -16.1$  K. Doing the same for other ZB compounds, we are able to reproduce with a very good agreement all experimental  $J_1$  values (Table I).

The resulting uncertainty in  $J_{dd}$  value deserves some words. As  $J_{dd} \propto V_{pd\sigma}^4$ , an uncertainty of about 10% on  $V_{pd\sigma}$  results

in a huge uncertainty for  $J_{dd}$ . However, the problem must not be taken in this way. Indeed, the better experimentally known value is  $J_{dd}$ , which has an uncertainty of about a few percent and, moreover, which is almost raw data due to the simplicity of the fitting model (Heisenberg Hamiltonian). As a consequence, it is more relevant to consider the very weak resulting uncertainty for  $V_{pd\sigma}$ . The conclusion is that only a very narrow range around the central  $V_{pd\sigma}$  PE modeling value is compatible with the experimental  $J_{dd}$  value, and this very narrow range is entirely contained in the wide one of PE modeling.

Having only to adjust the  $V_{pd\sigma}$  parameter to reproduce NN exchange integrals, we can say that, in this model, measurement of  $J_{dd}$  is a measure of a  $p$ - $d$  transfer integral.

Concerning spatial anisotropy, formulas (9) and (10) show that  $\xi = (J_{dd}^{\text{in}} - J_{dd}^{\text{out}})/J_{dd}^{\text{in}}$  (defined in Ref. [20]) does not depend on energetic parameters, but only on  $\eta$  value and geometrical configuration.

## V. Co-DOPED COMPOUNDS

We now consider the case of a  $\text{Co}^{2+}$  pair in II-VI DMS. In tetrahedral coordination, ground state representation of the ground configuration of each TMI is  $^4A_2$ , that is,  $N = 3$  holes,  $S = 3/2$ , and  $L = 0$ . As for Mn-doped compounds (Sec. IV), we use free ion values of Racah parameters ( $B = 0.138$  eV,  $C = 0.541$  eV), leading to a Hund exchange constant  $J_H = 0.886$  eV.

As pointed in Sec. II, the essential difference between Mn and Co cases is that for Co,  $e$  orbitals are unoccupied by holes in the ground state, this implies two important modifications.

First, the ligand field symmetry of  $d$  holes cannot be ignored anymore in the Slater-Koster transfer matrix appearing in Eq. (4), so that we replace the  $\mathbf{T}_{\beta i}$  transfer matrix (whose matrix elements are given in Ref. [32] and Table III for tetragonal basis) by  $\mathbf{T}_{\beta i} \times \mathbf{B}_i^{-1}$  ( $i = A, B, C$ ), where  $\mathbf{B}_i^{-1}$  is the matrix passing from tetragonal  $d$  basis to the trigonal  $d$  basis of  $i$  TMI [Eq. (A5)], namely to the basis with  $z$  axis parallel to the threefold axis  $C_3$ . The  $p$  basis of the transfer matrix is indifferent because the ligand  $p$  shell is empty of holes.

Second, neglecting the ligand field splitting, one-particle  $d$  level of each TMI is degenerate and the ground state can be denoted, in hole occupation, as  $e^0 t_2^3$ , so that occupied- $t_2$ -hole state of a TMI can be coupled to an unoccupied- $e$ -hole (electron-occupied) state of the other. This makes the second term of Eq. (2) nonzero by summing elements of  $e/t_2$  and  $t_2/e$  subspaces of the  $\mathcal{R}$  matrix with the  $K_2$  prefactor, while the first term is a sum over  $t_2/t_2$  subspace with the  $K_1$  prefactor. Due to the  $K_2$  sign, the second term of Eq. (2) (specific to cobalt pairs) results in a FM contribution to the superexchange constant.

Concerning ZB compounds, A-B and A-C pairs [see Fig. 1(a)] are strictly the same and are equivalent to an A-B (in-plane) pair of ideal W structure. As for the Mn case (Sec. IV), we then give the  $J_{dd}^{\text{in}}$  formula, valid for ZB compounds and the in-plane pair of ideal W ones:

$$\frac{J_{dd}^{\text{in}}}{V_{pd\sigma}^4} = \frac{K_1}{81} \left( 9 + \frac{48}{\eta^2} + \frac{10}{\eta^4} \right) + 8 \frac{K_2}{81} \left( \frac{12}{\eta^2} + \frac{5}{\eta^4} \right). \quad (11)$$

The number of AFM processes [first term of Eq. (11)] is reduced when passing from the Mn to Co case because the number of occupied  $d$ -states pairs changes from 25 to 9. The FM process [second term of Eq. (11)] is a small correction to the AFM one ( $|K_2/K_1| \sim 0.1$ ) and involves only 12  $d$ -states pairs. We note that FM contributions imply only  $V_{pd\sigma}^2 V_{pd\pi}^2$  and  $V_{pd\pi}^4$  processes. As for the Mn case (Sec. IV), nonideal W compounds slightly modify the weight of each process and give rise to odd power transfer processes.

An out-of-plane pair of W structure is more complicated because, taking into account the ligand field, A-B and A-C pairs are not equivalent [Fig. 1(b)]. This difference has to be accounted for in the appropriate Slater-Koster transfer matrix (see Appendix C). Moreover, for the out-of-plane pair A-C, two ligands (1 and 5) have to be considered and the following expression for  $J_{dd}^{\text{out}}$  of ideal W structure is obtained:

$$\begin{aligned} \frac{J_{dd}^{\text{out}}}{V_{pd\sigma}^4} = & \frac{K_1}{81} \left[ \left( 9 + \frac{48}{\eta^2} + \frac{10}{\eta^4} \right) (1 + \rho^7) \right. \\ & \left. - \frac{2\rho^{7/2}}{9} \left( 9 + \frac{480}{\eta^2} + \frac{82}{\eta^4} \right) \right] \\ & + \frac{8K_2}{81} \left[ \left( \frac{12}{\eta^2} + \frac{5}{\eta^4} \right) (1 + \rho^7) \right. \\ & \left. - \frac{2\rho^{7/2}}{3} \left( \frac{12}{\eta^2} - \frac{13}{\eta^4} \right) \right]. \quad (12) \end{aligned}$$

This expression for  $J_{dd}^{\text{out}}$  for the  $\text{Co}^{2+}$ - $\text{Co}^{2+}$  pair concentrates all the difficulties encountered before, that is, FM and AFM processes due to empty ground state orbitals, each of these processes containing bridged and loop exchange paths due to the two involved ligands.

We then apply our formulas to the six Co-doped II-VI DMS for which NN exchange constants have been measured (Table II).

TABLE II. Calculated  $J_{dd}$  (ZB) and  $J_{dd}^{\text{in}}$ ,  $J_{dd}^{\text{out}}$  (W) (in K) for Co-doped II-VI DMS as a function of input parameters  $V_{pd\sigma}$ ,  $U$ ,  $\Delta$  (in eV). Comparisons with experimental  $J_1$  and  $J_2$  are provided. Nonreferenced input parameters have been extrapolated or interpolated.

| Host                            | ZnO                | ZnS                | ZnSe               | ZnTe               | CdS              | CdSe             |
|---------------------------------|--------------------|--------------------|--------------------|--------------------|------------------|------------------|
| Struct.                         | W                  | ZB                 | ZB                 | ZB                 | W                | W                |
| $V_{pd\sigma}$                  | -1.6 <sup>a</sup>  | -1.11              | -1.01              | -0.92              | -1.01            | -0.9             |
| $\Delta$                        | 5 <sup>a</sup>     | 1.5 <sup>b</sup>   | 1.1 <sup>b</sup>   | 1                  | 1.5              | 1.06             |
| $U$                             | 6 <sup>a</sup>     | 5.5                | 5                  | 5                  | 5                | 5                |
| $J_{dd}^{\text{in}}$ , $J_{dd}$ | -25.5              | -47.6              | -49.9              | -38.7              | -33.7            | -33.3            |
| $J_{dd}^{\text{out}}$           | -13.7              |                    |                    |                    | -24.3            | -25.8            |
| $J_1$                           | -25.6 <sup>c</sup> | -47.5 <sup>d</sup> | -49.5 <sup>e</sup> | -38.0 <sup>e</sup> | -33 <sup>f</sup> | -33 <sup>f</sup> |
| $J_2$                           | -8.5 <sup>e</sup>  |                    |                    |                    | -27 <sup>f</sup> | -27 <sup>f</sup> |

<sup>a</sup>Reference [42].

<sup>b</sup>Reference [22].

<sup>c</sup>Reference [5].

<sup>d</sup>Reference [43].

<sup>e</sup>Reference [7].

<sup>f</sup>Reference [44].

For reproducing  $J$  values, we proceed as follows: We first obtain the ZnO:Co  $J_1$  exchange constant by only adjusting the reduction factor  $r$ , other input parameters being given by Ref. [42]. A very good agreement is obtained for  $r = 0.95$ , a value that we keep constant for the rest of the series. Concerning the next two compounds, ZnS:Co and ZnSe:Co, Ref. [22] gives  $V_{pd\sigma} = 1.1$  and  $1.0$  eV, respectively. These values lead to slightly underestimated  $J_1$  constants. As the remaining free parameter  $U$  cannot resolve this discrepancy, we choose to slightly increase  $V_{pd\sigma}$  (1.11 and 1.01) in order to match the experimental value. For the remaining compounds, as no input parameters have been found in literature, we extrapolate them from the precedent ones.

In all cases,  $J_1$  values are well reproduced by  $J_{dd}^{\text{in}}$  (for W) or  $J_{dd}$  (for ZB) with the available input parameters or reasonably extrapolated ones. Again, the predominance of superexchange mechanism is supported by these results, and a quantitative link between  $J_{dd}$  and  $V_{pd\sigma}$  is made.

More interesting is the  $J_2$  constant for W compounds ( $J_{dd}^{\text{out}}$  integral), resulting from the fitting of  $J_1$ : We see that  $J_{dd}^{\text{out}}$  gives an overestimated  $J_2$  value for ZnO, a slightly underestimated one for CdS, and an almost exact one for CdSe.

The ZnO:Co case discrepancy has been discussed in previous work in terms of possible  $K_{pd}$  FM process [5], which would reduce the AFM  $J_{dd}^{\text{out}}$ , thereby allowing us to reach the  $J_2$  value. Work in this direction in the context of DMS is in progress.

Concerning CdS and CdSe cases, experimental exchange constants call for some remarks: MST peaks corresponding to  $J_1$  and  $J_2$  are barely resolved in CdS, and not at all in CdSe. Foner *et al.* [44] then only give average  $J$ :  $-30.6 \pm 1.7$  K and  $-31.0 \pm 2$  K for CdS and CdSe, respectively. Consequently,  $J_1$  and  $J_2$  constants for these two compounds are not known with precision but should be almost identical in both cases. However, accepting the values given in Table II is a good approximation, we remark that CdSe:Co, an almost perfect W structure, is very close to the experimental value while CdS:Co, a less ideal W structure, is a bit farther. In fact, experimental  $J_1$  and  $J_2$  values for these two compounds can be exactly reproduced by assuming ideal W structure, that is, using formulas (11) and (12). A possible explanation would be that in these compounds, around the Co impurities, W structure tends to be ideal.

We end this section by noting that the greater spatial anisotropy of Co-doped compounds (compared to the Mn-doped ones) can be qualitatively understood as follows: Both  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  ions in tetrahedral coordination have a zero orbital momentum ground state, but while  $\text{Mn}^{2+}$  is fully symmetric ( $A_1$  representation),  $\text{Co}^{2+}$  is not ( $A_2$  representation). The ground state wave function changes sign by  $S_4$  and  $\sigma_d$  operations of the  $T_d$  point group. The ground state being less symmetric for  $\text{Co}^{2+}$  ions, a greater anisotropy can be expected for these ions.

## VI. DISCUSSION

The understanding of how localized spins of TMIs couple in matter is a longstanding and still open problem. While it is clear that many different mechanisms can occur according to the particular situation (TMIs type, distance and concentration,

host carrier doping, etc.), it is valuable to examine the simplest situation, that is NN TMIs pair in insulating materials, as a basis for more elaborate cases.

First, by reproducing  $J_1$  value for 13 different compounds, this work supports the common idea that NN exchange is largely dominated by superexchange mechanism but in a quantitative and systematic way, within the frame of a single model linked to independent experimental data. More precisely, the success of this cluster model indicates that, for such a NN pair, a  $k$ -space approach is not relevant because of the highly localized character of superexchange. The problem will then be to describe how superexchange contribution gradually decreases as the distance between TMIs increases (due to the increasing order of superexchange processes) and is gradually relayed by other exchange mechanisms, carrier mediated or not: In fact, even in insulating materials, some distant pairs have been found to be ferromagnetically coupled (e.g., in ZnO:Co [5]), indicating that noncarrier-mediated exchange mechanisms, other than superexchange, can occur.

This last idea is supported by the examination of the  $J_2$  exchange integral of W compounds: While this constant is well reproduced in Mn-doped compounds (all  $d$  orbital filled), this is not the case for Co-doped ones (not all  $d$  orbital filled). We can deduce from this fact that, even for NN pairs in insulating materials, additional exchange mechanisms involving TMI's empty orbital must take place. A candidate can be the FM  $K_{pd}$  exchange, which is a mix of second order superexchange and direct exchange [45], briefly discussed in Sec. III of Ref. [5]. This mechanism may account for  $J_2$  in ZnO:Co by adding a FM contribution.

We mention that the results presented in Tables I and II have been obtained within the Harrison approximation for  $V_{pd\sigma}(\beta, \alpha)$  transfer integrals (see Sec. III), which results in a single  $V_{pd\sigma}$  parameter, but that  $J_1$  and  $J_2$  for the three Co-doped W compounds can be simultaneously reproduced by letting  $V_{pd\sigma}(5, C)$ , the transfer integral involved in the looped exchange, vary. However, we are more interested in trends than in the illusory exact reproduction of all  $J$ . Moreover, the resulting  $V_{pd\sigma}(5, C)$  value is very far from the Harrison approximation and not consistent with the estimation of  $J_3$  in ZnO:Co, the third exchange integral which is believed to involve  $V_{pd\sigma}(5, C)$  in the 4-C-5 bridge [see Fig. 1(b) with anions and cations inverted].

At this stage, it is worthwhile to compare our cluster model to the  $k$ -space description developed by Larson *et al.* for Mn-doped ZB compounds. In his work, the authors finally express an exchange integral as a function of the distance between the two Mn ions:  $J(r) = J_0 f(r)$ , where  $f(r)$  is a material-independent dimensionless function of  $r = R/a$  ( $a$  being the ZB lattice constant and  $R$  the Mn-Mn distance) and  $J_0$  a constant. Being orbital independent, this formula uses  $V_{pd} = t_{pd}/\sqrt{2S}$ ,  $t_{pd} = V_{pd\sigma}/3 - 2\sqrt{3}V_{pd\pi}/9$  (see, e.g., Ref. [11]), a kind of *isotropic mean transfer*. For the NN pair  $r = 1/\sqrt{2}$ , the identification with Eq. (9) (taking care of the electron description of Larson) leads to

$$f(1/\sqrt{2}) = 9 \frac{10 + 16\eta^2 + \eta^4}{(2/\sqrt{3} - \eta)^4}. \quad (13)$$

These authors found that, for flat valence bands (dispersionless limit),  $f(1/\sqrt{2}) = 9$ . We see that we exactly find this result if the numerator and denominator of Eq. (13) are equal, that is, if we consider the same *mean transfer* expression as Larson. This confirms that our cluster description is, as expected, the dispersionless limit of the  $k$ -space description.

Another interesting comparison is the study of  $J(r)$  based on the spin-glass transition temperature of DMS [46] which gives  $f(r) = r^{-6.8}$ , that is, for the NN pair in ZB compounds,  $f(1/\sqrt{2}) = 10.56$ . By setting  $\eta = 2.16$  we obtain  $f(1/\sqrt{2}) = 7.93$ , a not so different value which again supports the local description. However, if our work points out the fact that superexchange is really the dominant mechanism in NN TMI coupling, it also points out that other exchange mechanisms should take place so that an expression of the kind  $J(r) = J_0 f(r)$  for any distance  $r$  and involving only one mechanism is certainly not relevant.

Finally, we remark that this cluster model of the NN superexchange can be applied to any TMIs pair coupled to fourth order with  $N \leq 5$  and an arbitrary number of ligands in any local symmetry, provided that input parameters are known or reasonably estimated. Formulas given for the  $J$  can then be incorporated in higher-level calculations such as Monte Carlo simulation of a set of randomly distributed TMIs over a given lattice.

Demonstration and generalization of the superexchange formula to a NN pair of different TMIs are given in the Appendix B.

## VII. CONCLUSION

Analytical calculation of NN superexchange integrals within a local model has allowed us to reproduce the experimental exchange constants for a wide range of II-VI DMS doped by cobalt and manganese.

First, our results quantitatively and systematically confirm a large predominance of superexchange mechanism in the magnetic coupling between NN localized spin of TMI embedded in an insulating host matrix.

Second, the importance of taking into account the off-diagonal Hund's exchange in the Coulomb operator has been pointed out by revealing an additional FM mechanism which occurs for  $N \neq 5$ . We show that the principal difference between Co and Mn cases consists in the possibility or not for this additional off-diagonal term to couple occupied and unoccupied  $d$  orbitals. The other difference resides in the ligand field which acts for nonfully symmetric ground states of TMIs and which results in an anisotropic transfer.

Finally, our model allows us to access the crucial parameter for DMS physics, namely  $V_{pd\sigma}$ , by means of magnetic measurements on a NN TMIs pair. This last point is of particular importance since the determination of  $V_{pd\sigma}$  from  $J_{sp-d}$  measurements encounters serious difficulties [3].

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## APPENDIX A: DETAILS OF THE MODEL

We consider a pair of TMIs, which can be different, and several ligand ions between them. The electronic Hamiltonian may be written as

$$\hat{H} = \sum_{\alpha} \hat{H}_{d,\alpha} + \sum_{\beta} \hat{H}_{p,\beta} + \hat{T}, \quad (\text{A1})$$

where  $\hat{H}_{d,\alpha}$  and  $\hat{H}_{p,\beta}$  are, respectively, on-site Hamiltonians for TMIs and ligands.  $\hat{T}$  describes electron hoppings between TMIs and ligands.

In the single ion Hamiltonian we include the diagonal one-particle terms and dominant Coulomb interactions

$$\begin{aligned} \hat{H}_{d,\alpha} &= \epsilon_{d,\alpha} \hat{N}_{d,\alpha} + \hat{H}_{LF,\alpha} + \hat{W}_{\alpha}, \\ \hat{W}_{\alpha} &= U_{d,\alpha} \sum_m \hat{n}_{\alpha,m,\uparrow} \hat{n}_{\alpha,m,\downarrow} + \frac{U'_{d,\alpha}}{2} \sum_{m \neq m'} \hat{n}_{\alpha,m} \hat{n}_{\alpha,m'} \\ &\quad - \frac{J_{H,\alpha}}{2} \sum_{m \neq m'} \left( 2\hat{s}_{\alpha,m} \hat{s}_{\alpha,m'} + \frac{1}{2} \hat{n}_{\alpha,m} \hat{n}_{\alpha,m'} \right) \\ &\quad + J'_{H,\alpha} \sum_{m \neq m'} d_{\alpha,m,\uparrow}^{\dagger} d_{\alpha,m',\uparrow} d_{\alpha,m,\downarrow}^{\dagger} d_{\alpha,m',\downarrow}, \end{aligned} \quad (\text{A2})$$

$$\hat{H}_{p,\beta} = \epsilon_{p,\beta} \hat{N}_{p,\beta}, \quad (\text{A3})$$

where

$$\begin{aligned} \hat{N}_{l,i} &\equiv \sum_m \hat{n}_{i,m}, \quad \hat{n}_{i,m} \equiv \sum_s \hat{n}_{i,m,s}, \\ \hat{n}_{i,m,s} &= c_{i,m,s}^{\dagger} c_{i,m,s}, \\ \hat{s}_{i,m}^z &= (\hat{n}_{i,m,\uparrow} - \hat{n}_{i,m,\downarrow})/2, \\ \hat{s}_m^+ &= c_{i,m,\uparrow}^{\dagger} c_{i,m,\downarrow}, \\ \hat{H}_{LF,\alpha} &= \sum_s \sum_{m,m'} V_{\alpha,mm'} d_{\alpha,m,s}^{\dagger} d_{\alpha,m',s}, \\ U_{d,\alpha} &= \mathcal{A}_{\alpha} + 4\mathcal{B}_{\alpha} + 3\mathcal{C}_{\alpha}, \\ J_{H,\alpha} &= \frac{5}{2}\mathcal{B}_{\alpha} + \mathcal{C}_{\alpha}, \\ U'_{d,\alpha} &= U_{d,\alpha} - 2J_{H,\alpha} = \mathcal{A}_{\alpha} - \mathcal{B}_{\alpha} + \mathcal{C}_{\alpha}, \end{aligned}$$

$\epsilon_{d,\alpha}, \epsilon_{p,\beta}$  are the one-particle energies of  $d$  and  $p$  states, and  $\mathcal{A}_{\alpha}, \mathcal{B}_{\alpha}$ , and  $\mathcal{C}_{\alpha}$  are the Racah's parameters of TMI  $\alpha$ . It is convenient to use the *hole* notations, then the operator  $c_{i,m,s}^{\dagger} = d_{\alpha,m,s}^{\dagger} (p_{\beta,n,s}^{\dagger})$  creates a hole with the one-particle basis  $d(p)$  wave function and spin projections  $s$  on TMI ( $\alpha = A, B, C$ ) and ligand ( $\beta = 1, 2$ ) site, respectively;  $n = x, y, z$  for the ligand. For the  $d$  functions,  $m = x, y, z, v, w$  enumerates the functions that diagonalize the tetrahedral ligand field in trigonal axes [26]. The expression of the basis functions in terms of cubic harmonics  $m' = xy, yz, zx, x^2 - y^2, 3z^2 - r^2$ ,



is given by

$$\begin{aligned}
|x\rangle &= \sqrt{\frac{2}{3}}|x^2 - y^2\rangle - \sqrt{\frac{1}{3}}|zx\rangle, \\
|y\rangle &= -\sqrt{\frac{2}{3}}|xy\rangle - \sqrt{\frac{1}{3}}|zy\rangle, \\
|z\rangle &= |3z^2 - r^2\rangle, \\
|v\rangle &= \sqrt{\frac{1}{3}}|x^2 - y^2\rangle + \sqrt{\frac{2}{3}}|zx\rangle, \\
|w\rangle &= -\sqrt{\frac{1}{3}}|xy\rangle + \sqrt{\frac{2}{3}}|zy\rangle,
\end{aligned} \tag{A4}$$

written symbolically as

$$\begin{aligned}
\mathbf{d}_t &= \mathbf{B}\mathbf{d}_c, \\
\mathbf{d}_c &= \mathbf{B}^{-1}\mathbf{d}_t,
\end{aligned} \tag{A5}$$

where  $\mathbf{d}_t, \mathbf{d}_c$  denote the vectors in trigonal and cubic basis, respectively. In the ground state, the  $d$  shell of TMI  $\alpha$  contains  $N_\alpha \leq 5$  holes and ligand has the closed  $p$  shell with  $N = 0$  holes.

The hopping Hamiltonian reads

$$\hat{T} = \sum_{n,m,\alpha,\beta,s} t_{\alpha,m,\beta,n} (d_{\alpha,m,s}^\dagger p_{\beta,n,s} + \text{H.c.}), \tag{A6}$$

where  $t_{\alpha,m,\beta,n}$  coefficients are related to matrix elements of the Slater-Koster matrix,  $t_{\alpha,m,\beta,n} \equiv (\mathbf{T}_{\beta\alpha})_{nm}$ .  $\hat{T}$  couples configurations with different numbers of  $d$  and  $p$  holes. We will account for the coupling between the ground configuration  $d^{N_A} p^0 d^{N_B}$  and the following excited ones:  $d^{N_A-1} p^1 d^{N_B}$ ,  $d^{N_A-1} p^2 d^{N_B-1}$ ,  $d^{N_A-1} p^0 d^{N_B+1}$ , and those with  $N_A \leftrightarrow N_B$ .

The diagonal part of the LF Hamiltonian fixes the ground state of TMI, e.g., for the  $\text{Co}^{2+}$  for  $N = 3$ , it is  ${}^4A_2$ , and is given by single configuration  $e^0 t_2^3$  with the total spin  $S = 3/2$ .

Using the identities  $\hat{n}_{\alpha,m,s}^2 = \hat{n}_{\alpha,m,s}$ ,  $\hat{s}_{\alpha,m}\hat{s}_{\alpha,m} = \frac{3}{4} \sum_s \hat{n}_{\alpha,m,s}(1 - \hat{n}_{\alpha,m,-s})$ , the interaction term in (A2) may be written as

$$\begin{aligned}
\hat{W}_\alpha &= (U_{d,\alpha} - U'_{d,\alpha} - J_{H,\alpha}) \sum_m \hat{n}_{\alpha,m,\uparrow} \hat{n}_{\alpha,m,\downarrow} \\
&+ \left( U'_{d,\alpha} - \frac{J_{H,\alpha}}{2} \right) \frac{\hat{N}_{d,\alpha}^2 - \hat{N}_{d,\alpha}}{2} \\
&- J_{H,\alpha} \left( \hat{S}_\alpha^2 - \frac{3}{4} \hat{N}_{d,\alpha} \right) \\
&+ J'_{H,\alpha} \sum_{m \neq m'} d_{\alpha,m,\uparrow}^\dagger d_{\alpha,m',\uparrow} d_{\alpha,m,\downarrow}^\dagger d_{\alpha,m',\downarrow}, \tag{A7}
\end{aligned}$$

where  $\hat{S}_\alpha = \sum_m \hat{s}_{\alpha,m}$ . In Ref. [31] the double hopping term was neglected ( $J'_H \approx 0$ ), then the spherical symmetry was achieved via the relation  $U_d - U'_{d,\alpha} - J_H = 0$ . The spherical symmetry of full  $\hat{W}_\alpha$  (A7) demands the relations  $U'_{d,\alpha} = U_{d,\alpha} - 2J_{H,\alpha}, J_{H,\alpha} = J'_{H,\alpha}$ , and we obtain Eq. (1).

## APPENDIX B: PERTURBATION EXPRESSION FOR SUPEREXCHANGE

We write the effective magnetic interaction between two TMIs as

$$\hat{H}_J = -2J_{dd} \hat{S}_A \hat{S}_B. \tag{B1}$$

In a superexchange calculation, the hopping term (A6) is considered as a perturbation to zeroth order Hamiltonian of isolated TMIs and ligands ions:

$$\hat{H}_0 = \sum_\alpha \hat{H}_{d,\alpha} + \sum_\beta \hat{H}_{p,\beta}. \tag{B2}$$

Then the isotropic superexchange may be calculated from the fourth-order formula [14,15,48]

$$\begin{aligned}
J_{dd} &= -\frac{1}{2\sqrt{S_A S_B}} \langle f | \hat{T} \hat{R}_1 \hat{T} \hat{R}_2 \hat{T} \hat{R}_3 \hat{T} | i \rangle \\
&= J_A + J_G,
\end{aligned} \tag{B3}$$

$$\begin{aligned}
\hat{R}_h &= (E_0 - \hat{H}_0)^{-1} \\
&= \sum_{I_h \in \text{CTE}} \frac{|I_h\rangle \langle I_h|}{(E_0 - E_{I_h})},
\end{aligned} \tag{B4}$$

where  $|i\rangle$  ( $|f\rangle$ ) denotes the initial (final) state, which is  $|S_A, S_B - 1\rangle$  ( $|S_A - 1, S_B\rangle$ ), here the notation  $|M_A, M_B\rangle$  means that the first TMI has the spin projection  $M_A$ , and the second  $M_B$ .  $J_A$  and  $J_G$  denote the Anderson [49] and Gertsma [50,51] contributions in the total exchange (see Appendix B 1 b). We consider the general case when TMIs may be different and have different  $d$ -shell filling. The sign  $I_h \in \text{CTE}$  means that the intermediate states are charge-transfer excitations, here the subscript  $h = 1, 2, 3$  indicates that only a specific subspace of the total Hilbert space gives nonzero contribution at every ‘‘hop’’ from the initial state  $|i\rangle$  to the final state  $|f\rangle$ . These subspaces will be considered below in detail. The product of matrix elements of the perturbation operator  $\hat{T}$  [Eq. (A6)] and the resolvent operator  $\hat{R}$  may be schematically depicted in diagram forms (cf. Fig. 3 of Ref. [48], or Fig. 1 of Ref. [15]), where every contributions in the sum [Eq. (B3)] corresponds to a four-step path from initial to final state.

### 1. Intermediate states

It is convenient to introduce the state  $|G\rangle \equiv |S_A, S_B\rangle$  (all hole spin projections on both TMI are  $\uparrow$ ), then

$$|i\rangle = \frac{1}{\sqrt{2S_B}} \hat{S}_B^- |G\rangle, \quad |f\rangle = \frac{1}{\sqrt{2S_A}} \hat{S}_A^- |G\rangle.$$

Note that for  $N_\alpha \leq 5$ ,  $N_\alpha = 2S_\alpha$ , which will be used below.

#### a. First hop, $d^{N_A} p^0 d^{N_B} \rightarrow d^{N_A-1} p^1 d^{N_B}, d^{N_A} p^1 d^{N_B-1}$

The first action of the  $\hat{T}$  [Eq. (A6)] on the initial state leads to a hole transfer from a TMI and ligand. Only a hole with spin projection  $\uparrow$  may hop from the first TMI ( $d^{N_A} p^0 d^{N_B} \rightarrow d^{N_A-1} p^1 d^{N_B}$ ), and only the hole with spin  $\downarrow$  may hop from the second TMI ( $d^{N_A} p^0 d^{N_B} \rightarrow d^{N_A} p^1 d^{N_B-1}$ ). The latter statement is not obvious but we should keep in mind that we should arrive to final state (where all holes on the

second TMI are  $\uparrow$ ) via four steps. So the intermediate states after the first step have the two forms

$$|I_{31}\rangle = p_{\beta,n_1,\uparrow}^\dagger d_{A,m_1,\uparrow} \hat{S}_B^- |G\rangle, \quad (\text{B5})$$

$$|I_{32}\rangle = p_{\beta,n_1,\downarrow}^\dagger d_{B,m_1,\uparrow} |G\rangle. \quad (\text{B6})$$

We can write

$$\hat{R}\hat{T}|i\rangle = |G_{31}\rangle + |G_{32}\rangle, \quad (\text{B7})$$

$$|G_{31}\rangle = - \sum_{n_1,m_1,\beta} \frac{t_{A,m_1,\beta,n_1}}{\Delta_{A,\beta} \sqrt{2S_B}} p_{\beta,n_1,\uparrow}^\dagger d_{A,m_1,\uparrow} \hat{S}_B^- |G\rangle, \quad (\text{B8})$$

$$|G_{32}\rangle = - \sum_{n_1,m_1,\beta} \frac{t_{B,m_1,\beta,n_1}}{\Delta_{B,\beta} \sqrt{2S_B}} p_{\beta,n_1,\downarrow}^\dagger d_{B,m_1,\uparrow} |G\rangle, \quad (\text{B9})$$

where

$$\Delta_{\alpha\beta} \equiv \epsilon_{p\beta} - \epsilon_{d\alpha} - (U_{d\alpha} - 3J_{H\alpha})(N_\alpha - 1). \quad (\text{B10})$$

These energy denominators  $\Delta_{\alpha,\beta} = E_I - E_0$  are simply obtained by remarking that the initial and intermediate  $|I_{31}\rangle$ ,  $|I_{32}\rangle$  states do not contain any doubly occupied orbitals so that last term of Eq. (1) can be ignored and the unperturbed Hamiltonian is diagonal.

$$\begin{aligned} \text{b. Second hop, } d^{N_A-1} p^1 d^{N_B} &\rightarrow d^{N_A-1} p^2 d^{N_B-1}, \\ d^{N_A-1} p^1 d^{N_B} &\rightarrow d^{N_A-1} p^0 d^{N_B+1}, \text{ etc.} \end{aligned}$$

Now our task is to find the intermediate states  $|I_2\rangle$ , which arise after the action of the  $\hat{T}$  [Eq. (A6)] on  $|I_3\rangle$ . They are of two qualitatively different kinds: one having two holes on ligand  $d^{N_A-1} p^1 d^{N_B} \rightarrow d^{N_A-1} p^2 d^{N_B-1}$  (Gertsma process [50,51]), and the second corresponds to the transfer of the hole from ligand to the second TMI  $d^{N_A-1} p^1 d^{N_B} \rightarrow d^{N_A-1} p^0 d^{N_B+1}$  (Anderson process [49]).

The former ones cannot contain doubly occupied orbitals since the TMI holes number has just decreased. As a consequence, the unperturbed Hamiltonian is still diagonal in this kind of intermediate states and no particular difficulties are then encountered. The resulting contribution of these processes are directly given in Appendix B 3.

Regarding the second kind of intermediate states, we see that the hole number is increased by one from the initial configuration on one TMI, thus opening the possibility for having doubly occupied orbitals. Then, the off-diagonal part of  $\hat{W}$  cannot be ignored anymore, leading to ferromagnetic contribution in the Anderson process. In the following, we consider this in detail.

$\hat{T}|I_{31}\rangle$  gives the functions of the form  $d_{A,m_1,\uparrow}^\dagger d_{B,m_3,\uparrow}^\dagger \hat{S}_B^- |G\rangle$ , which are not eigenfunctions of  $\hat{H}_0$  in the general case. We introduce two auxiliary states

$$|F_1\rangle \equiv d_{B,m_3,\downarrow}^\dagger \hat{n}_{B,m_3,\uparrow} |G\rangle, \quad (\text{B11})$$

$$|F_2\rangle \equiv \frac{1}{\sqrt{2S_B}} d_{B,m_3,\uparrow}^\dagger \hat{S}_B^- (1 - \hat{n}_{B,m_3,\uparrow}) |G\rangle, \quad (\text{B12})$$

that correspond to the cases when an additional hole comes to the orbital  $m_3$  occupied in  $|G\rangle$  [Eq. (B11)] or empty:

$$\langle F_1|F_1\rangle = b_{01}^2 = \langle G|\hat{n}_{B,m_3,\uparrow}|G\rangle \equiv n_{B,m_3,\uparrow}, \quad (\text{B13})$$

$$\langle F_2|F_2\rangle = b_{02}^2 = 1 - n_{B,m_3,\uparrow}. \quad (\text{B14})$$

Using the commutation

$$\begin{aligned} [\hat{W}, d_{\alpha,m,s}^\dagger] &= ([d_{\alpha,m,s}, \hat{W}])^\dagger = \left( U_{d,\alpha} - \frac{5}{2} J_{H,\alpha} \right) d_{\alpha,m,s}^\dagger \hat{N}_{d,\alpha} \\ &\quad - J_{H,\alpha} (s d_{\alpha,m,s}^\dagger \hat{S}_\alpha^z + \delta_{s,\uparrow} d_{\alpha,m,\downarrow}^\dagger \hat{S}_\alpha^+ \\ &\quad + \delta_{s,\downarrow} d_{\alpha,m,\uparrow}^\dagger \hat{S}_\alpha^-) + J_{H,\alpha} (\delta_{s,\uparrow} d_{\alpha,m,\downarrow} \\ &\quad - \delta_{s,\downarrow} d_{\alpha,m,\uparrow}) \hat{P}_\alpha^\dagger + J_{H,\alpha} d_{\alpha,m,s}^\dagger, \\ \hat{W} &\equiv \hat{W}_A + \hat{W}_B, \end{aligned} \quad (\text{B15})$$

and general properties of spin operators

$$S^+ S^- = S(S+1) + S^z - (S^z)^2, \quad (\text{B16})$$

$$S^- S^+ = S(S+1) - S^z - (S^z)^2, \quad (\text{B17})$$

we obtain

$$\begin{aligned} \hat{W}|F_1\rangle &= E_0|F_1\rangle + \left( U_{dB} - \frac{5J_{H,B}}{2} \right) N_B |F_1\rangle \\ &\quad - J_{H,B} [d_{B,m_3,\downarrow}^\dagger \hat{S}_B^z + d_{B,m_3,\uparrow}^\dagger \hat{S}_B^- + d_{B,m_3,\uparrow} \hat{P}_B^\dagger \\ &\quad - d_{B,m_3,\downarrow}^\dagger] \hat{S}_B^- \hat{n}_{B,m_3,\uparrow} |G\rangle \\ &= [E_0 + (U_{dB} - 2J_{H,B})N_B + 2J_{H,B}] |F_1\rangle \\ &\quad + J_{H,B} \sqrt{5 - N_B} |f_1\rangle, \end{aligned} \quad (\text{B18})$$

where

$$|f_1\rangle \equiv - \frac{1}{\sqrt{5 - N_B}} d_{B,m_3,\uparrow} \hat{P}_B^\dagger \hat{n}_{B,m_3,\uparrow} |G\rangle.$$

We see that  $|F_1\rangle$  is coupled by Hund interaction with another state when  $N_B < 5$ :

$$\langle f_1|f_1\rangle = \frac{\langle G|\hat{P}_B \hat{n}_{B,m_3,\uparrow} \hat{P}_B^\dagger |G\rangle}{5 - N_B} = n_{B,m_3,\uparrow}, \quad (\text{B19})$$

$$\langle F_1|f_1\rangle = 0. \quad (\text{B20})$$

Projecting the function (B18) onto  $|F_1\rangle$  we have

$$\begin{aligned} a_{01} &\equiv \frac{1}{b_{01}^2} \langle F_1|\hat{W}|F_1\rangle \\ &= E_0 + (U_{dB} - 2J_{H,B})N_B + 2J_{H,B}, \end{aligned} \quad (\text{B21})$$

$$E_0 = \langle G|\hat{W}|G\rangle = \sum_{\alpha} (U_{d\alpha} - 3J_{H,\alpha}) \frac{N_\alpha(N_\alpha - 1)}{2}. \quad (\text{B22})$$

The next action of ion Hamiltonian gives

$$\begin{aligned} \hat{W}|f_1\rangle &= - \frac{n_{B,m_3,\uparrow}}{\sqrt{5 - N_B}} \{ d_{B,m_3,\uparrow} \hat{P}_B^\dagger \hat{W} \\ &\quad + [\hat{W}, d_{B,m_3,\uparrow}] \hat{P}_B^\dagger + d_{B,m_3,\uparrow} [\hat{W}, \hat{P}_B^\dagger] \} |G\rangle \\ &= \{ E_0 + U_{dB} N_B - 3J_{H,B} (N_B - 2) \} |f_1\rangle \\ &\quad + J_{H,B} \sqrt{5 - N_B} |F_1\rangle, \end{aligned} \quad (\text{B23})$$

so, in the subspace spanned by  $|f_1\rangle$  and  $|F_1\rangle$  (when  $n_{B,m_3,\uparrow} = 1$ ), the Coulomb Hamiltonian has the form

$$W = \begin{pmatrix} a_{01} & b_{11} \\ b_{11} & a_{11} \end{pmatrix}, \quad (\text{B24})$$

where

$$a_{11} = E_0 + U_{dB}N_B - 3J_{H,B}(N_B - 2), \quad (\text{B25})$$

$$b_{11} = J_{H,B}\sqrt{5 - N_B}. \quad (\text{B26})$$

The eigenvalues are

$$W_{1\nu} = \epsilon_1 + \nu R_1, \quad \nu = \pm 1, \quad (\text{B27})$$

$$\epsilon_1 \equiv \frac{a_{01} + a_{11}}{2}, \quad (\text{B28})$$

$$D_1 \equiv a_{01} - a_{11} = J_{H,B}(N_B - 4), \quad (\text{B29})$$

$$R_1 \equiv \sqrt{\frac{D_1^2}{4} + b_{11}^2} = \frac{J_{H,B}}{2}(6 - N_B), \quad (\text{B30})$$

and the eigenfunctions are given by

$$\begin{aligned} |\psi_{1\nu}\rangle &= u_{1\nu}|F_1\rangle + v_{1\nu}|f_1\rangle \\ &= \left( u_{1\nu}d_{B,m_3,\downarrow}^\dagger - \frac{v_{1\nu}}{\sqrt{5 - N_B}}d_{B,m_3,\uparrow}\hat{P}^\dagger \right) \hat{n}_{B,m_3,\uparrow}|G\rangle, \end{aligned} \quad (\text{B31})$$

where

$$u_{1\nu} \equiv \frac{1}{\sqrt{2}}\sqrt{1 + \frac{\nu D_1}{2R_1}}, \quad v_{1\nu} = \frac{\nu}{\sqrt{2}}\sqrt{1 - \frac{\nu D_1}{2R_1}}. \quad (\text{B32})$$

Now we proceed with the state (B12)

$$\begin{aligned} \hat{W}|F_2\rangle &= E_0|F_2\rangle + \left( U_{dB} - \frac{5J_{H,B}}{2} \right) N_B|F_2\rangle \\ &\quad - \frac{J_{H,B}}{\sqrt{2}\mathcal{S}_B} [d_{B,m_3,\uparrow}^\dagger \hat{S}_B^z + d_{B,m_3,\downarrow}^\dagger \hat{S}_B^+ \\ &\quad - d_{B,m_3,\downarrow} \hat{P}^\dagger - d_{B,m_3,\uparrow}^\dagger] \hat{S}_B^- (1 - \hat{n}_{B,m_3,\uparrow})|G\rangle \\ &= [E_0 + U_{dB}N_B - J_{H,B}(3N_B - 1)]|F_2\rangle \\ &\quad + J_{H,B}\sqrt{N_B}|f_2\rangle, \end{aligned} \quad (\text{B33})$$

where

$$|f_2\rangle \equiv -d_{B,m_3,\downarrow}^\dagger (1 - \hat{n}_{B,m_3,\uparrow})|G\rangle. \quad (\text{B34})$$

We see that  $|f_2\rangle$  vanishes only for  $N_2 = 5$ . For other fillings we have to find the eigenfunctions, which will be the superpositions of  $|F_2\rangle$  and  $|f_2\rangle$ .

We have

$$\langle f_2|f_2\rangle = 1 - n_{B,m_3,\uparrow}, \quad \langle F_2|f_2\rangle = 0. \quad (\text{B35})$$

Projecting the function (B33) onto  $|F_2\rangle$ , we have

$$\begin{aligned} a_{02} &\equiv \langle F_2|\hat{W}|F_2\rangle / \langle F_2|F_2\rangle \\ &= E_0 + U_{dB}N_B - J_{H,B}(3N_B - 1), \end{aligned} \quad (\text{B36})$$

we now may calculate

$$\hat{W}|f_2\rangle = [E_0 + (U_{dB} - 2J_{H,B})N_B]|f_2\rangle + J_{H,B}\sqrt{N_B}|F_2\rangle, \quad (\text{B37})$$

and see that  $|F_2\rangle$  and  $|f_2\rangle$  form an invariant subspace of  $\hat{W}$ . Then

$$a_{12} = \langle f_2|\hat{W}|f_2\rangle / \langle f_2|f_2\rangle = E_0 + (U_{dB} - 2J_{H,B})N_B \quad (\text{B38})$$

and the  $\hat{W}$  matrix has the form analogous to (B24). Then the eigenvalues and eigenfunctions will have the form analogous to Eqs. (B27) and (B31), respectively, and the eigenfunctions may be immediately written as

$$\begin{aligned} |\psi_{2\nu}\rangle &= u_{2\nu}|F_2\rangle + v_{2\nu}|f_2\rangle \\ &= \left( \frac{u_{2\nu}}{\sqrt{N_B}}d_{B,m_3,\uparrow}^\dagger \hat{S}_B^- - v_{2\nu}d_{B,m_3,\downarrow}^\dagger \right) (1 - \hat{n}_{B,m_3,\uparrow})|G\rangle, \end{aligned} \quad (\text{B39})$$

where  $u_{2\nu}, v_{2\nu}$  has the form similar to (B32) with obvious change of indices, and  $b_{12} = J_H\sqrt{N_2}$ ,

$$D_2 = -J_{H,B}(N_B - 1), \quad (\text{B40})$$

$$R_2 = \frac{J_{H,B}}{2}(N_B + 1). \quad (\text{B41})$$

The action of  $\hat{T}$  on  $|I_{32}\rangle$  generates the functions of the form  $d_{B,m_1,\uparrow}d_{A,m_3,\downarrow}^\dagger|G\rangle = d_{B,m_1,\uparrow}d_{A,m_3,\downarrow}^\dagger(\hat{n}_{A,m_3,\uparrow} + 1 - \hat{n}_{A,m_3,\uparrow})|G\rangle$ .

In analogy with the considered cases, we may introduce

$$|\tilde{F}_1\rangle \equiv d_{A,m_3,\downarrow}^\dagger \hat{n}_{A,m_3,\uparrow}|G\rangle, \quad (\text{B42})$$

$$|\tilde{F}_2\rangle \equiv \frac{1}{\sqrt{N_A}}d_{A,m_3,\uparrow}^\dagger \hat{S}_A^- (1 - \hat{n}_{A,m_3,\uparrow})|G\rangle, \quad (\text{B43})$$

$$|\tilde{f}_1\rangle \equiv -\frac{1}{\sqrt{5 - N_A}}d_{A,m_3,\uparrow} \hat{P}^\dagger \hat{n}_{A,m_3,\uparrow}|G\rangle, \quad (\text{B44})$$

$$|\tilde{f}_2\rangle \equiv -d_{A,m_3,\downarrow}^\dagger (1 - \hat{n}_{A,m_3,\uparrow})|G\rangle, \quad (\text{B45})$$

and diagonalize the  $\hat{W}$  matrix, thus we obtain

$$\begin{aligned} |\psi_{3\nu}\rangle &= u_{3\nu}|\tilde{F}_1\rangle + v_{3\nu}|\tilde{f}_1\rangle = \left( u_{3\nu}d_{A,m_3,\downarrow}^\dagger \right. \\ &\quad \left. - \frac{v_{3\nu}}{\sqrt{5 - N_A}}d_{A,m_3,\uparrow} \hat{P}^\dagger \right) \hat{n}_{A,m_3,\uparrow}|G_1\rangle, \end{aligned} \quad (\text{B46})$$

$$\begin{aligned} |\psi_{4\nu}\rangle &= u_{4\nu}|\tilde{f}_2\rangle + v_{4\nu}|\tilde{F}_2\rangle = \left( -u_{4\nu}d_{A,m_3,\downarrow}^\dagger \right. \\ &\quad \left. + \frac{v_{4\nu}}{\sqrt{N_A}}d_{A,m_3,\uparrow}^\dagger \hat{S}_A^- \right) (1 - \hat{n}_{A,m_3,\uparrow})|G_1\rangle, \end{aligned} \quad (\text{B47})$$

where again  $u_{i\nu}, v_{i\nu}$  has the form similar to (B32) with the parameters  $D_3 = J_{H,A}(N_A - 4)$ ,  $R_3$  calculated similar to Eqs. (B29) and (B28)  $R_3 = J_{H,A}(6 - N_A)/2$ .

For the calculations of the  $D_4$ ,  $R_4$ , we should analogously calculate  $\tilde{a}_{02}$ ,  $\tilde{b}_{12}$ ,  $\tilde{a}_{12}$ , but to put  $D_4 \equiv \tilde{a}_{11} - \tilde{a}_{01} = J_{H,A}(N_A - 1)$ , we have  $R_4 = J_{H,A}(N_A + 1)/2$ .

Now we may write expressions for various states  $|I_2\rangle$  for Anderson processes

$$|I_{2i\nu}\rangle \equiv d_{A,m_1,\uparrow}|\psi_{i\nu}\rangle, \quad i = 1,2, \quad (\text{B48})$$

$$|I_{2j\nu}\rangle \equiv d_{B,m_1,\uparrow}|\psi_{j\nu}\rangle, \quad j = 3,4. \quad (\text{B49})$$

Those energies are

$$\begin{aligned} E_{21\nu} &= E_0 + \epsilon_{d,B} - \epsilon_{d,A} - (U_{dA} - 3J_{H,A})(N_A - 1) \\ &\quad + U_{dB}N_B - J_{H,B}\left(\frac{5}{2}N_B - 4\right) + \nu R_1, \\ E_{22\nu} &= E_0 + \epsilon_{d,B} - \epsilon_{d,A} - (U_{dA} - 3J_{H,A})(N_A - 1) \\ &\quad + U_{dB}N_B - J_{H,B}\left(\frac{5}{2}N_B - \frac{1}{2}\right) + \nu R_2, \\ E_{23\nu} &= E_0 + \epsilon_{d,A} - \epsilon_{d,B} - (U_{dB} - 3J_{H,B})(N_B - 1) \\ &\quad + U_{dA}N_A - J_{H,A}\left(\frac{5}{2}N_A - 4\right) + \nu R_3, \\ E_{24\nu} &= E_0 + \epsilon_{d,A} - \epsilon_{d,B} - (U_{dB} - 3J_{H,B})(N_B - 1) \\ &\quad + U_{dA}N_A - J_{H,A}\left(\frac{5}{2}N_A - \frac{1}{2}\right) + \nu R_4. \end{aligned} \quad (\text{B50})$$

Now we are ready for the calculation of matrix elements and energy differences for the Anderson processes contribution in Eq. (B3):

$$\begin{aligned} \langle I_{21\nu}|\hat{T}|I_{31}\rangle &= r t_{B,m_3,\beta,n_1} \frac{u_{1\nu}}{\sqrt{N_B}} n_{A,m_1,\uparrow} n_{B,m_3,\uparrow}, \\ \langle I_{22\nu}|\hat{T}|I_{31}\rangle &= -r t_{B,m_3,\beta,n_1} u_{2\nu} n_{A,m_1,\uparrow} (1 - n_{B,m_3,\uparrow}), \\ \langle I_{23\nu}|\hat{T}|I_{32}\rangle &= -r t_{A,m_3,\beta,n_1} u_{3\nu} n_{B,m_1,\uparrow} n_{A,m_3,\uparrow}, \\ \langle I_{24\nu}|\hat{T}|I_{32}\rangle &= r t_{A,m_3,\beta,n_1} u_{4\nu} n_{B,m_1,\uparrow} (1 - n_{A,m_3,\uparrow}), \end{aligned} \quad (\text{B51})$$

the factor  $r$  [see Eq. (6)] allows for the transfer integrals dependence on the  $d$ -shell filling of the TMI. The matrix elements (B51) involves the transfer integrals between configurations  $d^{N+1}$  and  $d^N p^1$ , which are smaller by the factor  $r$  than the integrals between  $d^N$  and  $d^{N-1} p^1$ .

Now we may write the states  $|I_1\rangle$ , which looks like  $|I_3\rangle$  [Eqs. (B5) and (B6)] with the interchange of  $d$ -operators indices  $A \leftrightarrow B$ :

$$|I_{11}\rangle = \frac{1}{\sqrt{N_A}} p_{\beta_4,n_4,\uparrow}^\dagger d_{B,m_4,\uparrow} \hat{S}_A^- |G\rangle, \quad (\text{B52})$$

$$|I_{12}\rangle = p_{\beta_4,n_4,\downarrow}^\dagger d_{A,m_4,\uparrow} |G\rangle. \quad (\text{B53})$$

The action of  $\hat{T}$  gives

$$\begin{aligned} \hat{T}|I_{11}\rangle &= \frac{1}{\sqrt{N_A}} \left[ \sum_m t_{A,m,\beta_4,n_4} d_{A,m,\uparrow}^\dagger d_{B,m_4,\uparrow} \hat{S}_A^- |G\rangle \right. \\ &\quad \left. + \sum_{m,\beta,n} t_{A,m,\beta,n} p_{\beta,n,\downarrow}^\dagger d_{A,m,\downarrow} p_{\beta_4,n_4,\uparrow}^\dagger d_{B,m_4,\uparrow} \hat{S}_A^- |G\rangle \right], \end{aligned} \quad (\text{B54})$$

$$\begin{aligned} \hat{T}|I_{12}\rangle &= \frac{1}{\sqrt{N_A}} \left[ \sum_m t_{B,m,\beta_4,n_4} d_{B,m,\downarrow}^\dagger d_{A,m_4,\uparrow} |G\rangle \right. \\ &\quad \left. + \sum_{m,\beta,n} t_{B,m,\beta,n} p_{\beta,n,\uparrow}^\dagger d_{B,m,\uparrow} p_{\beta_4,n_4,\downarrow}^\dagger d_{A,m_4,\uparrow} |G\rangle \right], \end{aligned} \quad (\text{B55})$$

this gives (here the factor  $r$  appears again)

$$\begin{aligned} \langle I_{12}|\hat{T}|I_{21\nu}\rangle &= -r t_{B,m_3,\beta_4,n_4} u_{1\nu} \delta_{m_1,m_4} n_{A,m_1,\uparrow} n_{B,m_3,\uparrow}, \\ \langle I_{12}|\hat{T}|I_{22\nu}\rangle &= r t_{B,m_3,\beta_4,n_4} v_{2\nu} \delta_{m_1,m_4} n_{A,m_1,\uparrow} (1 - n_{B,m_3,\uparrow}), \\ \langle I_{11}|\hat{T}|I_{23\nu}\rangle &= \frac{r}{\sqrt{N_A}} t_{A,m_3,\beta_4,n_4} u_{3\nu} \delta_{m_1,m_4} n_{B,m_1,\uparrow} n_{A,m_3,\uparrow}, \\ \langle I_{11}|\hat{T}|I_{24\nu}\rangle &= -r t_{A,m_3,\beta_4,n_4} v_{4\nu} \delta_{m_1,m_4} n_{B,m_1,\uparrow} (1 - n_{A,m_3,\uparrow}), \end{aligned}$$

and we may write

$$\begin{aligned} &\sum_{I_2, I_3 \in \text{CTE}} \frac{|I_2\rangle \langle I_2| \hat{T} |I_3\rangle \langle I_3| \hat{T} \hat{S}_2^- |G\rangle}{(E_0 - E_{I_2})(E_0 - E_{I_3})} \\ &= -r \sum_{n_1, \beta, \nu} \sum_{m_1} \left\{ \left[ \sum_{m_3}^{\text{occ.}} |I_{21\nu}\rangle \frac{t_{B,m_3,\beta,n_1} u_{1\nu}}{\sqrt{N_B} (E_0 - E_{21\nu})} \right. \right. \\ &\quad \left. \left. - \sum_{m_3}^{\text{unocc.}} |I_{22\nu}\rangle \frac{t_{B,m_3,\beta,n_1} u_{2\nu}}{(E_0 - E_{22\nu})} \right] \frac{t_{A,m_1,\beta,n_1}}{\Delta_{A\beta}} \right. \\ &\quad \left. + \left[ - \sum_{m_3}^{\text{occ.}} |I_{23\nu}\rangle \frac{t_{A,m_3,\beta,n_1} u_{3\nu}}{(E_0 - E_{23\nu})} \right. \right. \\ &\quad \left. \left. + \sum_{m_3}^{\text{unocc.}} |I_{24\nu}\rangle \frac{t_{A,m_3,\beta,n_1} u_{4\nu}}{(E_0 - E_{24\nu})} \right] \frac{t_{B,m_1,\beta,n_1}}{\Delta_{B\beta} \sqrt{N_B}} \right\}. \end{aligned} \quad (\text{B56})$$

In the first member of Eq. (B56), second intermediate states  $I_2$  concern only Anderson processes.

## 2. Anderson contribution to superexchange, $N_\alpha < 5$

From the above intermediate states we have the Anderson contribution as

$$\begin{aligned} J_A &= -\frac{r^2}{2\sqrt{S_A S_B}} \sum_{\beta, \beta', n, n', \nu} \sum_{m_1}^{\text{occ.}} \left\{ \frac{t_{A,m_1,\beta,n}}{\sqrt{N_A} \Delta_{A\beta}} \left[ \sum_{m_3}^{\text{occ.}} \frac{t_{B,m_3,\beta,n} t_{B,m_3,\beta',n'} u_{1\nu}^2}{\sqrt{N_B} (E_{21\nu} - E_0)} + \sum_{m_3}^{\text{unocc.}} \frac{t_{B,m_3,\beta,n} t_{B,m_3,\beta',n'} v_{2\nu} u_{2\nu}}{(E_{22\nu} - E_0)} \right] \frac{t_{A,m_1,\beta',n'}}{\Delta_{A\beta'}} \right. \\ &\quad \left. + \frac{t_{B,m_1,\beta,n}}{\Delta_{B\beta}} \left[ \sum_{m_3}^{\text{occ.}} \frac{t_{A,m_3,\beta,n} t_{A,m_3,\beta',n'} u_{3\nu}^2}{\sqrt{N_A} (E_{23\nu} - E_0)} + \sum_{m_3}^{\text{unocc.}} \frac{t_{A,m_3,\beta,n} t_{A,m_3,\beta',n'} v_{4\nu} u_{4\nu}}{(E_{24\nu} - E_0)} \right] \frac{t_{B,m_1,\beta',n'}}{\sqrt{N_B} \Delta_{B\beta}} \right\}. \end{aligned} \quad (\text{B57})$$

Let us note that in our approximations  $E_{2i,v,u_{i\nu},v_{i\nu}}$  does not depend on the orbital  $m_3$ , so we may calculate for every  $i$

$$\sum_{\nu} \frac{u_{i\nu}^2}{\Delta_{2i} + \nu R_i} = \frac{\Delta_{2i} - D_i/2}{\Delta_{2i}^2 - R_i^2}, \quad i = 1, 3, \quad (\text{B58})$$

$$\sum_{\nu} \frac{u_{2\nu}v_{2\nu}}{\Delta_{22} + \nu R_2} = -\frac{|b_{12}|}{\Delta_{22}^2 - R_2^2}, \quad (\text{B59})$$

here we have denoted  $E_{2i\nu} - E_0 \equiv \Delta_{2i} + \nu R_i$ . The expression for  $i = 4$  has the same form as Eq. (B59), but with  $\tilde{b}_{12} = J_{H,A}\sqrt{N_A}$  in the numerator. We see that the contribution that comes from the sum over unoccupied  $m_3$  gives ferromagnetic contribution.

If we consider two TMIs having the same number of holes (but not necessarily identic, e.g.,  $\text{Mn}^{2+}\text{-Fe}^{3+}$ ),  $N_A = N_B = N = 5$ , all orbitals of both TMI in  $|G\rangle$  are occupied by holes with spin up and sums over unoccupied orbitals of Eq. (B57) disappear. Then  $b_{11} = 0 = b_{31}$ , also  $|F_2\rangle = |f_2\rangle = |\tilde{f}_2\rangle = |\tilde{F}_2\rangle = 0$ , as  $n_{\alpha,m_3,\uparrow} = 1$ . This means that  $R_i(N = 5) = D_i/2$ ,  $u_{11} = 1$ , and  $u_{1-1} = 0$  so that only  $\nu = 1$  has to be retained in the sum over  $\nu$  for occupied orbitals. We then denote the energy of intermediate states  $|I_2\rangle = d_{A,m_1,\uparrow}|F_1\rangle, d_{B,m_1,\uparrow}|\tilde{F}_1\rangle$  by  $E_{2i,\uparrow}(N = 5) \equiv E_{21}(N = 5)$ , which reads

$$E_{21}(N = 5) = E_0 + 5U_{dB} - 8J_{H,B} - 4U_{dA} + 12J_{H,A} \quad (\text{B60})$$

and  $E_{23}(N = 5)$  is obtained by an exchange of indices  $\alpha = A \leftrightarrow B$ . These values should be substituted in the denominators of the sums over occupied states in Eq. (B57).

If in addition the two TMIs are identic, so are the Hubbard and Hund constants for both. Then,  $E_{21}(N = 5) = E_0 + U_d + 4J_H = E_0 + U + 56J_H/9$  and we obtain the first term of Eq. (9) of Ref. [20] for the  $\text{Mn}^{2+}\text{-Mn}^{2+}$  superexchange.

### 3. Gertsma contribution

The Gertsma contribution to superexchange arise from the intermediate configuration (after the second hop)  $d^{N_A-1}p^2d^{N_B-1}$ , with no doubly occupied orbital, in which the Coulomb operator  $\hat{W}$  is diagonal. The calculation is then straightforward, and the total contribution reads

$$J_G = -\frac{1}{4S_A S_B} \sum_{\beta,\beta',n,n'} \sum_{m_1,m_3}^{\text{occ.}} \frac{1}{\Delta_{A,\beta} + \Delta_{B,\beta'}} \left( \frac{1}{\Delta_{A,\beta}} + \frac{1}{\Delta_{B,\beta'}} \right) \times \left( \frac{1}{\Delta_{A,\beta'}} + \frac{1}{\Delta_{B,\beta}} \right) t_{A,m_1,\beta,n} t_{B,m_3,\beta,n} t_{A,m_1,\beta',n'} t_{B,m_3,\beta',n'}. \quad (\text{B61})$$

In any case, this contribution involves only sums over occupied  $d$  orbitals of TMIs.

### 4. Interaction between two identical ions

In the case when two TMI have the same kind, i.e.,  $N_{\alpha} = N_{\alpha'}$ ,  $U_{d\alpha} = U_{d\alpha'}$ ,  $J_{H,\alpha} = J_{H,\alpha'}$ , Eq. (B3) reduces to

$$J_{dd} = -\frac{1}{2S^2} \left( r^2 \frac{\Delta_{21} - D_1/2}{\Delta_{21}^2 - R_1^2} + \frac{1}{\Delta_{\text{eff}}} \right) \sum_{m_A, m_B}^{\text{occ.}} \mathcal{R}_{m_A m_B} + \frac{r^2}{2S} \frac{J_H}{\Delta_{22}^2 - R_2^2} \sum_{m_A}^{\text{occ.}} \sum_{m_B}^{\text{unocc.}} (\mathcal{R}_{m_A m_B} + \mathcal{R}_{m_B m_A}), \quad (\text{B62})$$

where  $\mathcal{R}_{m_A m_B}$  and  $\Delta_{\text{eff}}$  are defined in Eqs. (3) and (7), respectively:

$$\Delta_{21} = U_d + J_H \left( \frac{N}{2} + 1 \right), \quad (\text{B63})$$

$$\Delta_{22} = U_d + J_H \left( \frac{N-5}{2} \right), \quad (\text{B64})$$

$$R_1 = \frac{J_H}{2}(6-N), \quad R_2 = \frac{J_H}{2}(N+1), \quad (\text{B65})$$

$$D_1 = J_H(N-4), \quad (\text{B66})$$

$$D_2 = -D_4 = J_H(N-1). \quad (\text{B67})$$

Equation (B62) is equivalent to Eq. (2). We may see that the antiferromagnetic contribution has the order of magnitude  $J_{\text{AFM}} \sim \mathcal{T}^2/U_d$ , whereas the ferromagnetic contribution is  $J_{\text{FM}} \sim J_H \mathcal{T}^2/U_d^2 \sim J_{\text{AFM}} J_H/U_d$ . The effective hopping between TMI  $\mathcal{T}_{mm'}$  depends on the geometry of metal-ligand-metal bonds.

### APPENDIX C: CALCULATION OF HOPPINGS

According to the Harrison model [33], the hopping  $t_{\alpha,p,\beta,q}$  between the  $p$ th  $d$  function of metal ion  $\alpha = A, B$  and the  $q$ th  $p$  function of ligand  $\beta = 1, 2$  is expressed via direction cosines  $l, m, n$  of the direction of the vector  $\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}$ , and two Slater-Koster [32] parameters  $V_{pd\sigma}(R), V_{pd\pi}(R)$ , which depend on sorts of metal ion and on the distance  $R = |\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|$ . Starting from the Slater-Koster paper, the hopping matrix elements are denoted as  $t_{\alpha,p,\beta,q} \equiv E_{q,p}(l, m, n)$ . We use the following symmetry relations:

$$\begin{aligned} E_{y,xy}(l, m, n) &= -E_{x,xy}(m, -l, n), \\ E_{y,zx}(l, m, n) &= -E_{x,yz}(m, -l, n), \\ E_{y,yz}(l, m, n) &= E_{x,zx}(m, -l, n), \\ E_{z,xy}(l, m, n) &= -E_{x,yz}(n, m, -l), \\ E_{z,zx}(l, m, n) &= -E_{x,zx}(n, m, -l), \\ E_{z,yz}(l, m, n) &= -E_{x,xy}(n, m, -l), \end{aligned} \quad (\text{C1})$$

in order to obtain all hoppings that are given in Table III. In this table the cubic harmonics are used for the  $d$  functions,

TABLE III.  $p$ - $d$  hoppings expressed via direction cosines  $l, m, n$  of the vector radii pointing from the ligand to the  $d$  ion.

|   |
|---|
| $E_{x,xy} = \sqrt{3}l^2mV_{pd\sigma} + m(1-2l^2)V_{pd\pi}$                      |
| $E_{x,yz} = lmn(\sqrt{3}V_{pd\sigma} - 2V_{pd\pi})$                             |
| $E_{x,zx} = n[\sqrt{3}l^2V_{pd\sigma} + (1-2l^2)V_{pd\pi}]$                     |
| $E_{x,x^2-y^2} = \sqrt{3}l(l^2-m^2)V_{pd\sigma}/2 + l(1-l^2+m^2)V_{pd\pi}$      |
| $E_{x,3z^2-r^2} = l[n^2-(l^2+m^2)/2]V_{pd\sigma} - \sqrt{3}ln^2V_{pd\pi}$       |
| $E_{y,xy} = -[\sqrt{3}m^2(-l)V_{pd\sigma} - l(1-2m^2)V_{pd\pi}]$                |
| $E_{y,yz} = n[\sqrt{3}m^2V_{pd\sigma} + (1-2m^2)V_{pd\pi}]$                     |
| $E_{y,zx} = lmn(\sqrt{3}V_{pd\sigma} - 2V_{pd\pi})$                             |
| $E_{y,x^2-y^2} = \sqrt{3}m(l^2-m^2)V_{pd\sigma}/2 - m(1+l^2-m^2)V_{pd\pi}$      |
| $E_{y,3z^2-r^2} = m[n^2-(l^2+m^2)/2]V_{pd\sigma} - \sqrt{3}mn^2V_{pd\pi}$       |
| $E_{z,xy} = lmn(\sqrt{3}V_{pd\sigma} - 2V_{pd\pi})$                             |
| $E_{z,yz} = \sqrt{3}n^2mV_{pd\sigma} + m(1-2n^2)V_{pd\pi}$                      |
| $E_{z,zx} = l[\sqrt{3}n^2V_{pd\sigma} + (1-2n^2)V_{pd\pi}]$                     |
| $E_{z,x^2-y^2} = \sqrt{3}n(l^2-m^2)V_{pd\sigma}/2 - n(l^2-m^2)V_{pd\pi}$        |
| $E_{z,3z^2-r^2} = n[n^2-(l^2+m^2)/2]V_{pd\sigma} + \sqrt{3}n(l^2+m^2)V_{pd\pi}$ |

which should be expressed via our basis function using Eq. (A5).

The coordinate systems for metal ions A and B may have different axes directions because they are fixed by local crystal field, i.e., by the geometry of local surrounding. In the W structure, the  $Z$  axis is directed along the  $c$  crystal axis for all ions, and the  $X, Y$  axes direction may differ. The hoppings entering Eq. (B3) should be written in the same ‘‘global’’ coordinate system which have their origin in the ligand  $\beta$  site. Let us denote the angle between local  $X$  axis of the metal ion and the global  $X$  axis as  $\phi$ . The cubic harmonic in the global system is related to the harmonic in the local system by the expression

$$\mathbf{d}'_c = \mathbf{D}_\phi \mathbf{d}_c, \quad (\text{C2})$$

where the transition matrix is

$$\mathbf{D}_\phi = \begin{pmatrix} \cos 2\phi & 0 & 0 & -\sin 2\phi & 0 \\ 0 & \cos \phi & -\sin \phi & 0 & 0 \\ 0 & \sin \phi & \cos \phi & 0 & 0 \\ \sin 2\phi & 0 & 0 & \cos 2\phi & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}. \quad (\text{C3})$$

Now for the hopping matrix we may write

$$\mathbf{T}_{\beta\alpha} = \mathbf{E} \mathbf{D}_\phi \mathbf{B}^{-1} \quad (\text{C4})$$

or

$$t_{\alpha,p,\beta,q} = t_{\beta,q,\alpha,p} = \sum_{k,l} E_{qk} D_{kl} (\mathbf{B}^{-1})_{lp}, \quad (\text{C5})$$

where the  $\mathbf{B}$  matrix is defined in Eqs. (A4) and (A5). The sum over  $l$  goes over the cubic harmonics in the local coordinate system of ion  $\alpha$ , and the sum over  $k$  goes over the cubic harmonics in the global coordinate system, index  $p$  refers to a  $d$  function in the local trigonal basis, and index  $q$  refers to a  $p$  function in the global coordinate system.

We give in the following the coordinates of each TMI in W structure with respect to the ligand of interest, as function of  $a, c$ , and  $u$  parameters:

$$\begin{aligned} \vec{R}_{5A} &= \begin{pmatrix} a/2\sqrt{3} \\ -a/2 \\ c(1/2-u) \end{pmatrix}, & \vec{R}_{5B} &= \begin{pmatrix} a/2\sqrt{3} \\ a/2 \\ c(1/2-u) \end{pmatrix}, \\ \vec{R}_{1A} &= \begin{pmatrix} 0 \\ 0 \\ -cu \end{pmatrix}, & \vec{R}_{5C} &= \begin{pmatrix} 0 \\ 0 \\ c(1-u) \end{pmatrix}. \end{aligned} \quad (\text{C6})$$

We have omitted the  $\mathbf{R}_{1C}$  bond because it is just  $\mathbf{R}_{5A}$  with the  $x$  and  $y$  signs changed. Direction cosines to enter in Slater-Koster matrix are defined by  $l = x_{\beta,\alpha}/R_{\beta,\alpha}$ ,  $m = y_{\beta,\alpha}/R_{\beta,\alpha}$ , and  $n = z_{\beta,\alpha}/R_{\beta,\alpha}$ .

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