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"Channel decomposition" of superexchange interactions in the valence-bond method

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A valence-bond (VB) study is made of the channel structure of indirect-exchange interactions between paramagnetic transition-metal cations via diamagnetic ligands. The Introduction briefly surveys the literature regarding the channel concept in molecular-orbital (MO), VB, and hybrid MO-VB treatments. A computationally convenient expression, well known in direct-exchange formalism, for the exchange-coupling constant J is extended with corrections due to biquadratic terms in the effective spin Hamiltonian. We present a decomposition of J into a sum of contributions from unpaired-electron pairs (channel sum). The validity of this decomposition is numerically confirmed.

I. INTRODUCTION

The aim of the present paper is to analyze the possibility, in the framework of the valence-bond (VB) method, to decompose the indirect-exchange interaction between two paramagnetic transition-metal cations via an intervening diamagnetic anion, in a sum of electron-pair contributions from so-called "channels." In each channel, only one unpaired electron per cation is "active" in the exchange interaction, whereas the other electrons at the cations are "passive," except for some averaged potential. The channel concept was first introduced in the theory of direct-exchange interactions (see, e.g., Van Vleck[1]). Later on, channels were broached by Goodenough[2] in the qualitative description of indirect-exchange interactions and their dependence on geometry and chemical composition. Three types of approaches to the channel concept can be distinguished: the molecular-orbital (MO),[3] the VB,[4,5] and the mixed MO-VB[6,7] treatments. In the following, we briefly indicate, in examples with orbitally nondegenerate cations, on what premises the channel concept rests.

A. MO treatments

In the MO treatments, one first applies a self-consistent-field (SCF) procedure in the system considered, which yields delocalized molecular orbitals. Subsequently, the unpaired electron orbitals are unitarily transformed into orbitals localized at the cations, which are used for the orbital description of the ground configuration. Then, in increasing order of approximation, contributions to the exchange coupling are formulated.[8,9] The first-order spin-dependent energy correction, usually called the "potential exchange,"[3] is a sum of direct-exchange terms between pairs of electrons, one at each cation, and thus shows an exact channel structure. In the second order of approximation, different spin-dependent corrections arise. Depending on the type of excitation considered, one speaks of "kinetic" exchange (cation-cation charge transfer), "correlation," and "polarization" exchange (ligand-cation transfer and excitations to unoccupied orbitals). An examination of these second-order terms[9] reveals that, in good approximation, per cation, at most one of the singly occupied orbitals in the ground configuration enters the formal expressions, leading again to a channel summation. The electrons in the remaining orbitals give rise to additional one-electron potentials in the expression for the kinetic exchange. Since in numerical applications of the MO treatment, the kinetic exchange is often found to be dominant, the influence of these potentials is expected to be important and has to be considered with great care.

B. VB approaches

In the VB approaches, the ground-state spin multiplets are expressed, in zeroth order of approximation, as linear combinations of antisymmetrized products of, generally nonorthogonal, ion ground-state wave functions. In this type of description, a formulation of the indirect-exchange interaction between cations with more than one unpaired electron in terms of channel contributions has, as far as we know, to date not been deduced. In the papers of Keffer and Oguchi,[4] and Huang and Orbach,[5] the validity of the channel property is adopted from the beginning. Their analyses deal with three-center, four-electron systems representing channels which, from orbital-overlap considerations, are assumed to be dominant. In this paper we deal in particular with the validity of the channel property in the VB type of approach.

C. MO-VB methods

In the hybrid MO-VB methods, one first constructs "magnetic" orbitals for the unpaired electrons in clusters each containing *one* cation and its ligands by, e.g., applying a SCF procedure.[10] The magnetic orbitals thus obtained for the two cations are generally nonorthogonal. In the second step, the indirect-exchange interaction between the cations is formulated as a direct-exchange coupling of the electrons occupying these nonorthogonal magnetic orbitals. The role of the ligands in this coupling is differently accounted for in the various papers.[6,7,10] A principal problem is to define proper wave functions for bridging ligands shared by the clusters.[10] Channel formulations of the MO-VB method are given by Kahn and Briat,[6] and by Eremin and Rakitin.[7] An examination of the analysis of Kahn and Briat shows that cubic and higher-order powers of the intercluster overlap are neglected. Consequently, the exchange splittings only arise from single intercluster permutations and simply become, in this order of approximation, a sum of channel contributions. Each channel represents a direct-exchange coupling between two unpaired electrons, assuming some one-electron potential as a substitute for all electron repulsions. In the papers by Eremin and Rakitin, the channel concept rests again on the restriction that only single intercluster permutations in the total antisymmetrizer are considered. In a formal analysis of the channel contributions, the authors take into account, in some way, the role of the ligand electrons.

In the following, we analyze the channel concept for the indirect-exchange interaction in the VB method. Usually, the bilinear Heisenberg—Dirac—Van Vleck (HDVV) spin Hamiltonian is adopted as a description of the spin-multiplet energies and the exchange-coupling constant (ECC) is expressed in terms of the difference between the energies of two specific spin states. We note, however, that VB treatments yield, already in the ground configuration, biquadratic and even higher-order terms in the effective spin Hamiltonian which are due to multiple intercation permutations and the spin dependence of normalization factors. We will examine the influence of these additional effects. Subsequently, we will show the possibility of decomposing the ECC in terms of channel contributions associated with similar sets of permutations. In the example of a linear Mn^{2+}—F^{-}—Mn^{2+}-like system, numerical values of the channel sums, as obtained at different levels of approximation, are compared with the energy difference of the two specific spin states. We further comment on the neglect of biquadratic terms and, in addition, on the feasibility of a "transferable" channel model in a VB type of description.

II. FORMALISM

A. Total-spin energies

If the total-spin multiplet energies of two coupled identical open-shell ions A and B with spin quantum numbers S_A and S_B, respectively, are correctly described by the energy spectrum of the HDVV Hamiltonian,

$$c-2J\mathcal{S}_A\cdot\mathcal{S}_B=C-J\mathcal{S}\cdot\mathcal{S}\ ,$$

(c, $C=c+J[S_A(S_A+1)+S_B(S_B+1)]$, and J are scalars; $\mathcal{S}_A$, $\mathcal{S}_B$, and $\mathcal{S}$ are spin operators of A,B, and the total system, respectively), the exchange-coupling constant J can obviously be determined from two total-spin state energies. In the following, we recapitulate the derivation of the well-known and computationally convenient expression for the ECC in terms of energies corresponding with a specific "mixed-spin" state (M) and the state with highest total-spin value (H) of the form[11]

$$J=(E_M-E_H)/4S_AS_B\ . \tag{1}$$

In a simple orbital description of the electrons, these two spin states are in an orbitally nondegenerate ground configuration associated with single Slater determinants, which renders the computational effort relatively small. Dealing with a three-center superexchange unit A-C-B, where A and B are the paramagnetic centers and C an intervening closed-shell anion, the total VB spin-orbital wave functions are of the form

$$\Psi_f=N_f^{-1/2}\mathcal{A}\Phi\sigma_f\ ,$$

with $\Phi=\phi_A\phi_B\phi_C$, the product of the many-electron orbital functions of the ions; $\mathcal{A}$, the antisymmetrizer with respect to all electrons; σ_f, a spin function; and N_f, the normalization constant which, due to the nonorthogonality between the ion orbital functions, is dependent on the choice of σ_f. The interionic interactions are considered to be small compared to the intraionic coupling energies, so that S_A and S_B remain good quantum numbers. Consequently, σ_f can be expanded in the tensorial product of the ion spin functions. The ion orbital functions are assumed to be the ground-state eigenfunctions of the Hamiltonians for the ions, $\mathcal{H}_X$ ($X=A,B,C$), i.e., they obey the eigenvalue equations

$$\mathcal{H}_X\phi_X=\epsilon_X\phi_X\ .$$

Selecting from the highest-spin multiplet the function (in the usual notation)

$$\sigma_H=|S_A,S_A\rangle\,|S_B,S_B\rangle\,|S_C=0,M_C=0\rangle\ ,$$

and defining the mixed-spin function by

$$\sigma_M=|S_A,S_A\rangle\,|S_B,-S_B\rangle\,|S_C=0,M_C=0\rangle\ ,$$

the spin-orbital functions Ψ_H and Ψ_M become single determinants. The function σ_M can be expanded in terms of the pure total-spin states σ_S, according to

$$\sigma_M=\sum_{S=0}^{S_{\max}}c_S\sigma_S\ ,$$

with c_S the vector-coupling coefficients and $S_{\max}=S_A+S_B$. Using the commutation property of the total Hamiltonian and the antisymmetrizer, and substituting the eigenvalue equations for the ions, one finds that the spin-multiplet energies are given by

$$E_S=E^0+N_S^{-1}\langle\Phi\sigma_S,\mathcal{V}\mathcal{A}\Phi\sigma_S\rangle\ ,$$

with $E^0=\epsilon_A+\epsilon_B+\epsilon_C$ and $\mathcal{V}$ the interionic interaction operator. The energy of the mixed-spin state can be written as

$$E_M=N_M^{-1}\sum_{S=0}^{S_{\max}}c_S^2E_SN_S\quad\text{with }N_M=\sum_{S=0}^{S_{\max}}c_S^2N_S\ . \tag{2}$$

In the evaluation of E_S, the nonorthogonality of the ion-orbital functions leads to nonvanishing contributions of multiple intercation permutations in the antisymmetrizer and a spin dependence of the normalization constants.[12,13] As a consequence, in representing E_S as the expectation value of an effective spin Hamiltonian, also quadratic and higher-order terms in the scalar product $\mathcal{S}\cdot\mathcal{S}$ arise in the operator.[12,13] To analyze the effect of the (relatively small) additional terms, we extend the effective spin operators for the energy E_S and norm N_S with a biquadratic term, leading to

$$E_S = j_0 - j_1 S(S+1) + j_2[S(S+1)]^2 , \tag{3a}$$

$$N_S = n_0 + n_1 S(S+1) + n_2[S(S+1)]^2 . \tag{3b}$$

It should be realized that the spin dependence of the norms N_S is incorporated in the coefficients j_1 and j_2 of the expression (3a) for E_S. After substitution of these quadratic forms in the expressions for the energies of the mixed- and highest-spin states, expansion of N_M^{-1} and summation[14] over S in (2), one can verify that, up to and including biquadratic terms $(\mathcal{S}\cdot\mathcal{S})^2$, the energy difference between the two states becomes

$$\frac{E_M - E_H}{4S_A S_B} = j_1 + \left\{ -j_1 \frac{n_1}{n_0} + j_2[4-(2S_A+1)^2 - (2S_B+1)^2]/2 \right\} . \tag{4}$$

The expression in parentheses is a correction to Eq. (1) and results from taking into account the biquadratic terms in E_H and the expansion of E_M.

One may optimally approximate the *biquadratic* spectrum of E_S, given in Eq. (3a), with a *bilinear* HDVV spectrum by a least-squares fit on the splittings. In that case, it is found that

$$J = j_1 + j_2[7 - 12(S_A + S_B + \tfrac{1}{2})^2]/10 . \tag{5}$$

The values of the coefficients of j_2 in Eqs. (4) and (5) differ by, at most, 5%, whereas the quotient n_1/n_0 is generally found in the applications to be of the order 10^{-3}. Hence, expression (4) is a good approximation to the optimal exchange-coupling constant according to Eq. (5).

B. Channel summation

We now concentrate on the possibility of decomposing expression (1), discussed in the preceding subsection, for the ECC in terms of a channel summation. Obviously, if the one-electron orbitals for the description of the ionic ground states are assumed to be mutually orthogonal, the ECC in the ground configuration of the coupled system can indeed be simply written as a sum of channel contributions. In that case, each channel is associated with a single intercation transposition of electron labels and yields (a weak) exchange coupling of ferromagnetic sign. However, there is a fundamental nonorthogonality between the ion orbital functions. Consequently, higher-order permutations in the total antisymmetrizer of indirect-exchange type then contribute as well to the spin-dependent part of the interaction energy. These contributions can be of either ferromagnetic or antiferromagnetic sign. In the following, we demonstrate that, taking into account this nonorthogonality, the channel property of expression (1) remains approximately valid.

Applying the technique of a symmetric double-coset (SDC) decomposition[15,16] of the permutation group G of all electron labels with respect to the subgroup $G_A \times G_B \times G_C$, i.e., the direct product of the permutation groups associated with the n_X $(X = A,B,C)$ electrons on the ions, it is straightforwardly found that

$$\mathcal{A} = \mathcal{A}_C(\mathcal{A}_A\mathcal{A}_B\mathcal{Q}\mathcal{A}_A\mathcal{A}_B)\mathcal{A}_C ,$$

where the projector $\mathcal{Q}$ is a linear combination of interionic permutations $\mathscr{q}$ (SDC generators). The SDC generators can be chosen as permutations with a disjoint cycle structure, each cycle containing at most one electron label per ion. In this analysis, we confine ourselves to permutation operators involving only the valence-shell electrons of the ions. Calculations have shown[17] that contributions from SDC generators to exchange splittings rapidly decrease with the number of electron labels involved. Even when large interionic overlap integrals occur, the limitation to generators with five labels or less resulted in errors of only 1–2 %. To attain the channel decomposition of the ECC, we adopt here this truncation in $\mathcal{Q}$ and list in Table I the SDC generators grouped in conveniently chosen subsets Q_i, $i = 0$–5. Q_0 is the unity operator, and Q_1 and Q_2 are the sets of single and double cation-ligand transpositions, respectively. Q_3 comprises the simplest permutations which yield spin-dependent terms in the numerator and denominator (norm) of the energy expressions. Avoiding shared labels, Q_2 and Q_4 can be expressed as the products of Q_1Q_1 and Q_3Q_1, respectively. Q_5 is the set of permutations responsible for a biquadratic term in the effective spin Hamiltonian, and will therefore be neglected. The operator product $\mathcal{R} = \mathcal{A}_A\mathcal{A}_B\mathcal{Q}\mathcal{A}_A\mathcal{A}_B$, obviously sym-

TABLE I. SDC generators $\mathscr{q}$ with five or less electron labels for the permutation group G with respect to the subgroup $G_A \times G_B \times G_C$, grouped in the sets Q_i, $i = 0$–5. The factors $f_{\mathscr{p}}$ are the weight factors of permutations $\mathscr{p}$ in the projector $\mathcal{R}$, which is obtained from a symmetrization of $\mathcal{Q}$ as described in the text. x,x' $(x = a,\ b,$ and $c)$ in the permutations $\mathscr{q}$ denote different electron labels on the ion X, with $X = A$, B, or C, respectively. n_C is the number of valence electrons at the ligand.

Q_i	$\mathscr{q}$	$f_{\mathscr{p}}$
Q_0	$(\,)$	1
Q_1	(ac) (bc)	$-n_C$ $-n_C$
Q_2	$(ac)(a'c')$ $(bc)(b'c')$	$n_C(n_C-1)$ $n_C(n_C-1)$
Q_3	(ab) (abc) (acb) $(ac)(bc')$	-1 n_C n_C $n_C(n_C-1)$
Q_4	$(ab)(a'c)$ $(ab)(b'c)$ $(ac)(a'bc')$ $(ac)(a'c'b)$ $(bc)(ab'c')$ $(bc)(ac'b')$	n_C n_C $-n_C(n_C-1)$ $-n_C(n_C-1)$ $-n_C(n_C-1)$ $-n_C(n_C-1)$
Q_5	$(ab)(a'b')$ $(ab)(a'b'c)$ $(ab)(a'cb')$	1 $-n_C$ $-n_C$

metric in the labels of the electrons on each cation, is nothing but the projector arising from a SDC decomposition of $\mathscr{A}$ with respect to G_C. In this projector we consider only the permutations $\wp$ of the same cycle type as those in the sets Q_i, thus neglecting permutations with more than one electron label per cation in a cycle. In passing, we note that SDC generators with pure intracation transpositions do not contribute to the interaction energy, if the ion orbital functions are assumed to be exact solutions of their eigenvalue equations. The factors $f_\wp$ in the truncated projector $\mathscr{R}$, straightforwardly obtained in the SDC formalism, are also given in Table I. Defining projectors $\mathscr{D}_i$ by summations in the sets Q_i, weighted with coefficients $f_\wp$, the subprojectors $\mathscr{R}_i$ of $\mathscr{R}$, containing the Q_i-like permutations, are obtained by a symmetrization of $\mathscr{D}_i$ with respect to the electron labels on the cations. The subprojectors $\mathscr{R}_3$ and $\mathscr{R}_4$ take the form

$$\mathscr{R}_3=\sum_a\sum_b \mathscr{D}_3(a,b,c)\ ,$$

$$\mathscr{R}_4=\sum_a\sum_b\sum_{a'\,(\neq a)}\sum_{b'\,(\neq b)} \mathscr{D}_4(a,a',b,b',c,c')\ ,$$

where the summations run over the electron labels on each cation. The projector $\mathscr{R}_4$ can be rewritten as

$$\mathscr{R}_4=\sum_a\sum_b \mathscr{D}'_3(a,b,c)\sum_{a'\,(\neq a)}\sum_{b'\,(\neq b)} \mathscr{D}_1(a',b',c') \qquad \text{with } c\neq c'\ ,$$

where $\mathscr{D}'_3$ is similar to $\mathscr{D}_3$ but with slightly different weight factors. We note that if one approximates $n_C(n_C-1)$ by n_C^2, the projectors $\mathscr{D}'_3$ and $\mathscr{D}_3$ become identical.

A significant expression for the *spin* dependence of the interaction energy,

$$E_f-E^0=N_f^{-1}\langle \Phi\sigma_f,\mathscr{V}\mathscr{A}\Phi\sigma_f\rangle\ ,$$

is obtained by means of a series expansion of E_f-E^0, in terms of the subprojectors $\mathscr{R}_3$ and $\mathscr{R}_4$. The first term in this expansion, denoted E^1, is the energy expression in which the permutations in $\mathscr{R}$ responsible for the spin dependence do not occur. Up to and including terms of the same order as those arising from $\mathscr{R}_4$, the expansion straightforwardly yields

$$\begin{aligned}E_f=E^0+E^1&+(\langle\mathscr{V}\mathscr{R}_3\rangle_f-\langle\mathscr{V}\rangle\langle\mathscr{R}_3\rangle_f)(1-\langle\mathscr{R}_1\rangle)\\&-(\langle\mathscr{V}\mathscr{R}_1\rangle-\langle\mathscr{R}_1\rangle\langle\mathscr{V}\rangle)\langle\mathscr{R}_3\rangle_f\\&+(\langle\mathscr{V}\mathscr{R}_4\rangle_f-\langle\mathscr{R}_4\rangle_f\langle\mathscr{V}\rangle)\ ,\end{aligned}\tag{6}$$

where $\Phi\sigma$ and $\mathscr{A}_C$ are omitted in the notation, and $\langle\ \rangle$ denotes the expectation value in the product space spanned by the antisymmetrized ligand function and the occupied cation spin orbitals. Further, note that $\mathscr{R}_2$ vanishes, in this order of approximation, in the spin-dependent energy corrections.

A channel decomposition of the spin-dependent part of E_f is simply obtained by substituting in Eq. (6) the sum expressions for $\mathscr{R}_3$ and $\mathscr{R}_4$, obtained above. This leads to the channel expression

$$\begin{aligned}E_f=E^0+E^1+\sum_{a,b}[&(\langle\mathscr{V}\mathscr{D}_3\rangle_f-\langle\mathscr{D}_3\rangle_f\langle\mathscr{V}\rangle)(1-\langle\mathscr{D}_1\rangle)\\&-(\langle\mathscr{V}\mathscr{D}_1\rangle-\langle\mathscr{D}_1\rangle\langle\mathscr{V}\rangle)\langle\mathscr{D}_3\rangle_f\\&+T(a,b)]\ ,\end{aligned}\tag{7a}$$

where $\mathscr{D}_1=\mathscr{D}_1(a,b,c)$ and $\mathscr{D}_3=\mathscr{D}_3(a,b,c)$. The term $T(a,b)$ is a correction which, in the approximation $\mathscr{D}'_3=\mathscr{D}_3$, mentioned before, is of the form

$$T(a,b)=\frac{1}{(n_A-1)(n_B-1)}\sum_{a'\,(\neq a)}\sum_{b'\,(\neq b)}(\langle g\mathscr{D}_3\mathscr{D}_1\rangle_f-\langle g\mathscr{D}_3\rangle_f\langle\mathscr{D}_1\rangle-\langle g\mathscr{D}_1\rangle\langle\mathscr{D}_3\rangle_f+\langle g\rangle\langle\mathscr{D}_1\rangle\langle\mathscr{D}_3\rangle_f)\ ,\tag{7b}$$

where now $\mathscr{D}_1=\mathscr{D}_1(a',b',c')$ and $\mathscr{D}_3=\mathscr{D}_3(a,b,c)$. Dependent on the pair of permutations from $\mathscr{D}_3$ and $\mathscr{D}_1$, g denotes the sum of all interionic electron-repulsion operators involving one label in each of these permutations. Omitting the correction term in expression (7a), E_f becomes the sum of the spin-dependent energies of the channel systems (aCb), expressed in the same order of approximation. In this case, the remaining electrons $a'\neq a$ and $b'\neq b$ are accounted for by their Coulomb potentials. Since the contributions of spin-paired valence electrons at the cations to the exchange interaction cancel, the summation can be limited to the unpaired-electron labels. The corrections (7b) all involve two permutations, each with a different electron label on one cation. We note that these terms are left after an extensive cancellation between contributions from $\mathscr{R}_4$ in the numerator and crossterms occurring after expansion of the norm. For this reason, a neglect of the corrections is *not* simply equivalent with an elimination of $\mathscr{R}_4$ in $\mathscr{R}$ from the beginning.

The main approximations adopted to obtain the channel decomposition of the ECC, Eq. (7a), can be summarized as follows:

(a) Biquadratic and higher-order terms in the effective spin Hamiltonian are neglected. The ECC of the remaining bilinear spin Hamiltonian can then be expressed by Eq. (1), as outlined in Sec. II A.

(b) Only SDC generators with five electron labels or less, without intracation permutations, are considered.

As an additional approximation, we assume that the correction term, Eq. (7b), is small.

III. NUMERICAL COMPARISON AND DISCUSSION

In this section, we compare the two values of an ECC as obtained from Eq. (1) by, first, performing a *complete* calculation of the energies E_M and E_H, and, second, by using the channel approximation Eq. (7a) for these energies, omitting the correction term $T(a,b)$. If the two values are quite different, one can conclude that at least one of the approximations summarized above is incorrect. On the other hand, if the results agree, the premises in the decomposition are, apart from accidental cancellation of errors, apparently fulfilled and the channel property is confirmed. The comparison is made in a linear model system representing the unit Mn^{2+}—F^{-}—Mn^{2+}, the ligand in the middle of the two cations, with ionic separations according to experiment. To establish the reliability of the result, the calculations are carried out using different orbital sets obtained by changing the parameters of the $2s$ and $2p$, and $3d$ Slater orbitals in the description of the valence shells of the ligand and cations, respectively. The core electrons are contracted at their nuclei, thus leaving a $3d^5(2s^2 2p^6)3d^5$ configuration.

Concerning the choice of orbital parameters, it has to be noted that the Clementi values,[18] albeit optimal for the isolated-ion energies, fail in correctly describing the more remote overlap regions which are important for the interaction. This can be verified by considering the numerical Hartree-Fock solutions[19] which show a much slower decrease in the orbital tails. As a consequence, the Clementi parameters yield an overly small value for the ECC. For this reason, we use more extended orbitals in the comparisons which lead to ECC's in the experimental order of magnitude. In Table II, results of three calculations are presented in which the parameters for the $2s$ and $2p$ orbitals at F^- are considered equal, whereas the ratio of the cation and ligand parameters is determined from the ratio of the averaged r^2 expectation values of the Hartree-Fock solutions for the valence-shell orbitals. For each example the orbital parameters, the individual channel contributions, their sum, and the exact value for $(E_M - E_H)/25$ are listed in the table. An excellent agreement is found and the channel approximation is correct to within 3%. The "diagonal" channels $\sigma\sigma$, $\pi\pi$, and $\delta\delta$ yield antiferromagnetic contributions, while those from "off-diagonal" channels $\sigma\pi,\sigma\delta,\ldots$, are ferromagnetic. The difference in sign is a consequence of the nonorthogonality of orbitals in the diagonal channels, which leads to dominant antiferromagnetic contributions from the nuclear-attraction operators. The relative smallness of the contribution of the $\sigma\sigma$ channel compared with that from the $\pi\pi$ channel is rather surprising in view of the common assumption that, due to the angular properties of the $3d$ orbitals, the $d_\sigma p_\sigma^2 d_\sigma$ subchannel dominates its π equivalent. However, we note that after a Schmidt orthogonalization of the d_σ orbitals, with respect to the ligand orbitals in the subchannels $d_\sigma p_\sigma^2 d_\sigma$ and $d_\sigma p_\sigma^2 s^2 d_\sigma$, respectively, the overlap integral between the Schmidt orbitals has, in the latter subchannel, a considerably smaller value. Interpreting the indirect-exchange interaction as a direct coupling of the unpaired electrons in the Schmidt orbitals (accounting for the ligand by one-electron potentials) the reduction of the overlap integral due to the $2s$ electrons simply leads to the weaker antiferromagnetic coupling obtained.

TABLE II. Results in the linear superexchange unit $3d^5(2s^2 2p^6)3d^5$ for the channel contributions to the ECC J, their sum, and the value for J as obtained from a complete calculation of Eq. (1). The intercation distance is 7.7 a.u. The choice of the Slater-orbital parameters λ is discussed in the text. σ, π, and δ indicate the symmetry type of the $3d$ orbitals involved in the channels. m is the number of equivalent channels of the type indicated. All quantities are expressed in atomic units.

			J (10^{-6})		
		λ_{3d}	1.30	1.55	2.04
Channel	m	$\lambda_{2s}=\lambda_{2p}$	0.86	1.02	1.34
$\delta\delta$	2		-6	-1	-0.0
$\pi\pi$	2		-525	-285	-22.1
$\sigma\sigma$	1		-774	-100	-2.5
$\delta\pi$	8		22	8	0.5
$\delta\sigma$	4		1	0	0.5
$\pi\sigma$	4		19	7	1.6
$\pi\bar{\pi}$	2		16	7	0.5
$\delta\bar{\delta}$	2		0	0	0.0
channel sum			-1546	-569	-33.9
$(E_M - E_H)/25$			-1578	-587	-34.3

The electron potentials of passive electrons $a' \neq a$ and $b' \neq b$, occurring in the diagonal channels aCb, incompletely screen the nuclear charge. As a consequence, contraction of these electrons at the nucleus induces a ferromagnetic shift in the channel contribution. Since the indirect-exchange interaction mainly arises in the ligand region, the latter shift has, as we have verified, only a moderate effect on the ECC. A subsequent simplification in the calculation of the $d_\sigma C d_\sigma$ and the $d_\pi C d_\pi$ channels is to consider only the exchange contributions from the $d_\sigma p_\sigma^2 s^2 d_\sigma$ and $d_\pi p_\pi^2 d_\pi$ *sub*channels, respectively, representing the remaining ligand electrons by their Coulomb potentials. It is again found that the ECC is only moderately influenced. However, a contraction of the passive ligand electrons at the nucleus then causes a strong ferromagnetic shift. Further, we note that in view of the observed dependence of the ECC on the interionic separations,[20] it is by no means evident that the channel contributions are transferable[7,21] in the $3d$, transition-metal series.

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