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Numerical comparison between the "channel model" and the "effective-electron model" descriptions of linear superexchange interactions in ionic solids

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Two current models for the description of superexchange interactions—i.e., the "channel model" of Eremin and Rakitin and the "effective-electron model" of Jansen *et al.*—are numerically compared. Although quite different in the basic assumptions, the two models are each successfully applied. The comparison of the models is carried out for the predictions of exchange-coupling constants in linear units of two $3d$ cations separated by a halide anion. A striking mutual consistency in the results is found and qualitatively discussed.

I. INTRODUCTION

The accurate description of weak-interaction phenomena in molecules, complexes, and solids represents one of the most challenging, and most difficult, tasks of applied quantum theory. To this category belong indirect-exchange interactions in ionic solids between paramagnetic $3d$ cations, mediated by one or more diamagnetic ligands. Such interactions are responsible for the observed (antiferromagnetic) ordering of unpaired electron spins at low temperatures. They are very weak ($\approx 10^{-4}$—10^{-3} hartree, i.e., ≈ 60—600 cal/mol) compared to "conventional" chemical bonding (≈ 30—100 kcal/mol).

The theoretical possibility of indirect-exchange coupling was already recognized fifty years ago.[1,2] During the 1950s, when accurate experimental results on a wide variety of solids became available, attempts were initiated towards a quantitative explanation of the phenomena observed. These formulations ranged from crude semiempirical analyses to large-scale *ab initio* variational (-perturbational) methods utilizing extensive sets of basis functions. About ten years ago, first-principle analyses for magnetic solids were largely abandoned when it appeared that the weakness of the interactions generally puts too excessive demands on their accuracy.[3] In the process of computation one was forced to make uncertain, and often nontransparent, approximations. Present-day, high-speed computations, while greatly increasing the range of manageable basis sets, have not eliminated methodological problems in the millihartree range or below (e.g., persistent basis-set deficiencies, superposition errors, slow convergence of electron-correlation contributions), even for simple systems such as the hydrogen molecule[4] and the HF dimer.[5] An accurate, generally applicable, theory of very weak interactions along these lines in solids is an even more remote possibility.

Instead of adopting such extended schemes one also *a priori* defines simple theoretical models which afford an accurate quantitative evaluation, while retaining assumedly relevant quantum-mechanical characteristics. It is then hoped that at least the experimentally observed *trends* are reproduced. Such model approaches show the advantage of covering exchange coupling in *series* of chemically, and structurally, related compounds, whereas *ab initio* methods generally deal with one compound only.[6,7] In this context we mention the observed dependence of the exchange coupling on the chemical constituents and the interionic distances in a linear cation-ligand-cation unit (so-called "180° superexchange"). Questions concerning these trends are still not satisfactorily resolved. For instance, the dependence on the type of $3d$ cation is generally described qualitatively using orbital-symmetry arguments.[8–10] Further, the reasoning[10] that bonds involving ligands with decreasing electronegativity become more "covalent" and thus should cause a stronger indirect exchange is in conflict with the observation that in a number of $3d$ compounds the exchange coupling increases in the order Br^-, Cl^-.

In the present paper we consider two current models which appear capable of predicting quantitatively exchange couplings in series of linear superexchange units. In view of the quite different presuppositions in their definitions, it is of interest to analyze in a comparison whether *all* their predictions are mutually consistent. The first is the channel model as formulated by Eremin and Rakitin;[11(a)–11(c)] the second is the effective-electron model introduced by Jansen and co-workers.[12(a),12(b)] The channel model is based on a many-electron description of the system, introducing nonlocal exchange parameters, whereas in the effective-electron model the number of electrons is drastically reduced and a description in terms of ionic parameters is employed.

In the next section we first briefly describe the two models and indicate their capability of correctly reproducing observed trends in the data. Section III deals with a comparative analysis of the two models. In Sec. IV the results obtained are further discussed.

II. DESCRIPTION OF THE TWO MODELS

A. The channel model of Eremin and Rakitin

In the framework of an intermediate crystal-field scheme a many-electron type of semiempirical model for

(180° super-) exchange interactions in $3d$-ionic solids was developed by Eremin and Rakitin in a series of papers.[11] In their approach, the weak exchange interactions are first-order perturbation corrections to a zeroth-order orbital description of the superexchange unit consisting of two subunits, each containing one cation and its ligands. The role of the ligands is, at least in principle, accounted for by adapting the magnetic orbitals on the cations, and by one-electron operators in the effective Hamiltonian for the unpaired electrons. The model contains a more quantitative formulation of the well-known qualitative rules of Goodenough[8] and Kanamori[9] as applied to 180° superexchange.

For nonorbitally degenerate cations, the exchange-coupling constant (ECC) appears to be a sum of contributions from individual "exchange channels" (i.e., pairs of interacting half-filled orbitals), divided by the number of channels. Further, it is argued that in series of isostructural compounds, containing different magnetic cations of the same period, the contribution from each exchange channel depends only insignificantly on the total number of electrons in the open-shell system. Consequently, channel contributions are considered to be transferable in the *$3d$ series*. Somewhat later the model was extended to orbitally degenerate cations by introducing orbitals with noninteger occupation numbers.[11(c)] We will not analyze the derivation of the model and consider only its application to exchange coupling between octahedrally coordinated ions. The ligand-field splitting in the $3d$ shell of the cation gives rise to three (transferable) channel sums, i.e., J_{tt}, J_{ee}, and J_{te}, representing the contributions of all exchange channels between the t_{2g}-t_{2g}, e_g-e_g, and t_{2g}-e_g subshell orbitals, respectively. For a particular electron occupation of the $3d$-cation orbitals with n_t and n_e unpaired electrons in the t_{2g} and e_g subshells, respectively, these rules lead straightforwardly to an ECC J (in the expression $-2J\mathbf{S}_A\cdot\mathbf{S}_B$), given by

$$n^2J=\left[\frac{n_t}{3}\right]^2 J_{tt}+\left[\frac{n_e}{2}\right]^2 J_{ee}+2\left[\frac{n_t}{3}\right]\left[\frac{n_e}{2}\right]J_{te}\,, \qquad (1)$$

with $n=n_t+n_e$. The factors $n_t/3$ and $n_e/2$ are the average unpaired-electron occupation numbers of the orbitals in the two subshells.

In a numerical application of the model, one first determines the quantities J_{tt}, J_{ee}, and J_{te} by Eq. (1) from three *experimental* ECC's and uses the obtained values for predicting the ECC's in other, isostructural, compounds. We note that in the model the channel sums implicitly depend on the type of ligand considered. As an example, we list in Table I the model results reported by Eremin and Rakitin[11(b),11(c)] for the coupling constants in a number of solids with perovskite structure. The numbers n_t and n_e in Eq. (1) follow from the ground configurations with maximum spin multiplicity. The experimental values for the V, Mn, and Ni compounds were taken to determine the three channel-sum parameters.

If one disregards the Jahn-Teller distortion in $KCuF_3$, the value -45 K is predicted for this compound, which lies far from the observed value -190 K. The distortion, however, removes the degeneracy in the e_g shell and leads[11(b),13] to a singly occupied d_σ orbital. Since the channel d_σ-d_σ is expected, in Ref. 11(b), to constitute the only important part of J_{ee}, this effect is simply accounted for by removing in Eq. (1) the degeneracy factor of e_g. Aside from the reasonable values predicted for the ECC in $KCoF_3$ and $KFeF_3$, now also a correct value for $KCuF_3$ is obtained. For further applications of the model we refer to the original papers.[11]

TABLE I. Channel-model results reported by Eremin and Rakitin for the ECC's in 180° superexchange interactions in a number of solids with the perovskite structure. For the experimental data, see Refs. 11(b), 11(c), and 14. The numbers within parentheses denote the uncertainties in the last digit(s). The second value (45 K), predicted for $KCuF_3$, is found if the Jahn-Teller distortion is disregarded. The experimental ECC's of the first three compounds were used to determine the channel-sum parameters J_{tt} (-29 K), J_{ee} (-180 K), and J_{te} (63 K).

	$-J/k$ (K)	
	Experiment	Channel model
$KMgF_3$:V^{2+}	3.2(7)	3.2
$KMnF_3$	3.1, 3.6, 3.65(10)	3.3
$KNiF_3$	45(1), 44(3), 50.8(6)	45
$KFeF_3$	6.0	6.8
$KCoF_3$	9.6, 11.8, 19.2(10)	15.7
$KCuF_3$	190	180, 45

B. The effective-electron model of Jansen *et al.*

A quite differently defined model for the description of 180° superexchange interaction in $3d$-ionic solids was developed by Jansen and co-workers in a series of papers.[12(a),12(b)] In this approach the weak exchange interactions are again first-order perturbation corrections, but now on a zeroth-order description with free-ion wave functions. In order to arrive at the effective-electron model (EEM), the following assumptions were adopted. First, the permutation symmetry of the Hamiltonian determines the characteristics of the weak exchange interaction, whereas the local spatial symmetries around the cations are considered to be of minor importance. Since exchange interactions are of short range, the superexchange unit is restricted to the linear three-center cation-anion-cation system. Secondly, it is argued from experimental data that the exchange interactions depend only implicitly on the number of unpaired electrons per cation. To render this argument concrete, the unpaired electrons on each cation are, in the model, replaced by one electron in an "effective" orbital. In the same vein, the electrons of the closed-shell anions are replaced by two, spin-paired electrons in an effective orbital. The effective orbitals are described by $1s$-Slater functions, $\exp(-\lambda r)$, of which the "size" increases with the number of valence electrons in a well-defined manner. Further, the individual centers are supposed to have a zero net charge. These simplifications together lead to the well-known three-center, four-electron model system.[2] Because of the obvious nonorthogonality of the three effective orbitals, an indirect-exchange effect already occurs in a first-order exchange perturbation cal-

TABLE II. Effective-electron model results for the ECC's in 180° superexchange interactions in a number of solids with perovskite structure or of the composition X_2MF_4. For the experimental data of the ECC's and cation-cation distances R, see Refs. 11(b), 11(c), 12(b), 14, and 15. The numbers within parentheses denote the uncertainties in the last digit(s).

		$-J/k$ (K)	
	R (a.u.)	Experiment	Effective-electron model
$KMnF_3$	7.922	3.1, 3.6, 3.65(10)	3.7
Rb_2FeF_4	7.966	6.5(15)	6.1
$KCoF_3$	7.671	9.6, 11.8, 19.2(10)	17.6
K_2NiF_4	7.546	48(3), 49(4), 55.4(15), 51.8(3), 51.4(4)	50.0
$KCuF_3$	7.43	190	233
Rb_2MnCl_4	9.537	6.2(2)	6.1
$(C_3H_7NH_3)MnBr_4$	10.51	4.2(1)	3.7

culation. The ECC is given by (in the expression $-2J\mathbf{S}_A \cdot \mathbf{S}_B$, where $\mathbf{S}_A, \mathbf{S}_B$ are the actual *total*-spin operators of the cations),

$$n^2 J = J_{\mathrm{EEM}} = (E_S - E_T)/2 , \qquad (2)$$

where E_S and E_T are the first-order energy corrections for the singlet and triplet state, respectively, and n is the number of unpaired electrons on the actual cation.

In numerical applications of the effective-electron model the interionic distances are taken from experiment. The orbital parameters λ, measuring the extension of the effective orbitals, are essential parameters in the model. Their ratios are determined by demanding the expectation values $\langle r^2 \rangle$ of the effective orbitals to be proportional to the diamagnetic susceptibilities of the valence shells of the ions considered. By a fit of the model prediction for the ECC in only one compound to experiment,[14] definite values are simultaneously assigned to all effective-orbital parameters for the various cations and anions. As an example we have collected in Table II a few model results[12,14,15] for the 180° superexchange-coupling constants in solids of two well-known series of antiferromagnetic compounds.

It can be concluded that the model yields ECC's which are all in good agreement with the experimental data. Furthermore, it is found that the model correctly predicts the observed power-law dependence of the ECC on intercation distances R of the form $\sim R^{-p}$, with $p \approx 12$.[14] For this reason, the number of compounds listed in Table II is restricted to only one example for each kind of chemical composition in the superexchange unit.

Four-body contributions to the exchange interaction are generally expected to be small relative to that of the three-center superexchange unit, and are implicitly absorbed in the parameters by the fitting procedure. However, it has been shown[12(b)] that the four-body terms are, in contrast to the three-center term, very sensitive to small Jahn-Teller distortions and yield a ferromagnetic shift. The (relatively small) deviation of the predicted ECC for $KCuF_3$ from its experimental value can thus be understood. Referring back to the preceding section, it has to be noted that the role of the Jahn-Teller distortion in the effective-electron model is only of minor importance compared with the role of the distortion in the channel model where a crucial factor of 4 in the value of the ECC resulted from lifting the e_g degeneracy.

Other successful applications of the model on indirect-exchange coupling[12(c)] and, as well, on quite different phenomena such as hydrogen bonding,[12(d)] rotational barriers,[12(e)] and long-range superexchange,[12(f)] can be found in the papers mentioned and references therein.

III. A COMPARISON OF THE TWO MODELS

As outlined in the preceding section, the application of the model of Eremin and Rakitin (ERRAM) demands for *each* type of anion the knowledge of *three* ECC's in order to determine the three channel-sum parameters. On the other hand, the effective-electron model (EEM) demands only *one* experimental ECC and predicts, for each type of ligand and at any value of the interionic distances, the ECC's in the $3d$ series. Therefore, a comparison between the predictions of the two models, without invoking experimental values for ECC's, is only possible by taking EEM results as "experimental" data for the determination of the ERRAM parameters J_{tt}, J_{ee}, and J_{te}.

The problem arises at which values of ionic distances the model predictions are to be compared. In the ERRAM, the channel sums are considered as transferable parameters irrespective of the ionic separations. However, experimental findings show that, aside from changes in the size of the superexchange unit caused by altering the type of $3d$ cation, even variations within the same unit occur due to differences in chemical constitution or geometrical structure of the solid (e.g., $KMnF_3$ versus Rb_2MnF_4). By relating the latter variations with observed ECC's in compounds of compositions XMF_3 and X_2MF_4 with X=K, Rb, and Tl, and M=Mn, Co, and Ni, de Jongh and Block[14] were able to study the variations of indirect-exchange coupling with the type of magnetic ion at equal interionic distances. In their analyses, the EEM was found to describe the results correctly. Therefore, we will first compare the model predictions at a *fixed* value

TABLE III. EEM predictions for the ECC's in the unit *MXM*, with *M* ranging from Sc^{2+} to Cu^{2+}, and $X=F^-$, Cl^-, and Br^-, at fixed anion-characteristic, cation-cation distances of 7.70, 9.54, and 10.50 a.u., respectively. The values for λ are orbital parameters as used in the EEM. The ERRAM data are calculated from the EEM results, as described in the text.

		$-J/k$ (K)					
		F		Cl		Br	
		EEM	ERRAM	EEM	ERRAM	EEM	ERRAM
	λ (a.u.$^{-1}$)	1.11		0.70		0.62	
Sc	1.77	8.0	8.0	8.6	8.1	5.1	4.8
Ti	1.38	9.9	8.0	9.6	8.1	5.6	4.8
V	1.22	8.5	8.0	8.8	8.1	5.1	4.8
Cr	1.13	6.7	7.9	7.6	9.2	4.5	5.5
Mn	1.08	5.1	5.1	6.2	5.9	3.7	3.5
Fe	1.04	9.1	7.9	11.7	10.2	7.2	6.2
Co	1.02	17.2	15.8	22.9	21.5	14.1	13.3
Ni	1.00	40.9	43.3	56.8	60.2	35.3	37.5
Cu	0.99	167.7	173.3	238.4	240.9	149.1	150.1
$-J_{tt}/k$ (K)			72.4		73.3		42.9
$-J_{ee}/k$ (K)			173.3		240.9		150.1
$-J_{te}/k$ (K)			-59.3		-83.3		-52.1

for the ionic separations.

An alternative choice of the ionic distances in the comparison is prompted if one assumes that the *decrease* of the experimental separations in compounds along the $3d$ series is an *implicit* requirement for the transferability of the channel sums. For this reason, we carry out a second comparison of the two models, but now with EEM results at separations according to ionic radii.[16] Table III presents the EEM predictions for the ECC in the unit *MXM* with $M=Sc^{2+},\ldots,Cu^{2+}$ and $X=F^-$, Cl^-, and Br^-, at a fixed, anion-characteristic, separation of the cations. The analogous results with decreasing cation distances are listed in Table IV. We note in passing that the tables also comprise results for superexchange units for which no experimental data are available.

Generally, in solving ERRAM parameters from three experimental ECC's, one finds the channel sums sensitively depending on the $3d$ cations selected. In the comparisons we therefore determine the channel sums in Eq. (1) from a least-squares fit to the EEM results for n^2J, using *all* $3d$-cation data. In addition, the Jahn-Teller splitting of the e_g level in Cr^{2+} ($c/a>1$) and Cu^{2+} ($c/a<1$) (Ref. 13) is accounted for in this procedure. The optimal values of J_{tt}, J_{ee}, and J_{te} thus found in the two comparisons are also listed in Tables III and IV.

In order to analyze the correspondence in the two model comparisons we have plotted the values for the quantity n^2J as obtained from EEM versus those from the ERRAM, for the three types of anion. As an example we present in Figs. 1 and 2 the two plots for Cl^-. If the models were equivalent, all points in these plots obviously would lie on the bisector of the axes. Actually, they are somewhat scattered about this line, but in all six analyses the linear regression lines coincide almost exactly with the

TABLE IV. EEM predictions for the ECC's in the unit *MXM*, with *M* ranging from Sc^{2+} to Cu^{2+}, and $X=F^-$, Cl^-, and Br^-, at cation-cation distances determined from the ionic radii *r* taken from Ref. 16. The ERRAM data are calculated from the EEM results, as described in the text.

		$-J/k$ (K)					
		F		Cl		Br	
		EEM	ERRAM	EEM	ERRAM	EEM	ERRAM
	r (a.u.)	2.53		3.41		3.69	
Sc	1.74	1.5	2.6	3.1	3.8	3.3	3.8
Ti	1.70	2.6	2.6	4.0	3.8	4.0	3.8
V	1.66	2.8	2.6	4.2	3.8	4.1	3.8
Cr	1.59	3.0	4.0	4.4	5.9	4.2	5.7
Mn	1.51	2.9	2.6	4.3	3.8	4.1	3.6
Fe	1.44	6.5	5.7	9.7	8.7	9.2	8.2
Co	1.40	13.7	13.9	20.9	21.2	19.7	20.0
Ni	1.36	36.6	40.8	56.6	62.6	53.4	59.0
Cu	1.30	177.1	163.3	271.0	250.5	254.2	235.9
$-J_{tt}/k$ (K)			23.0		34.6		34.2
$-J_{ee}/k$ (K)			163.3		250.5		235.9
$-J_{te}/k$ (K)			-61.1		-95.5		-89.8

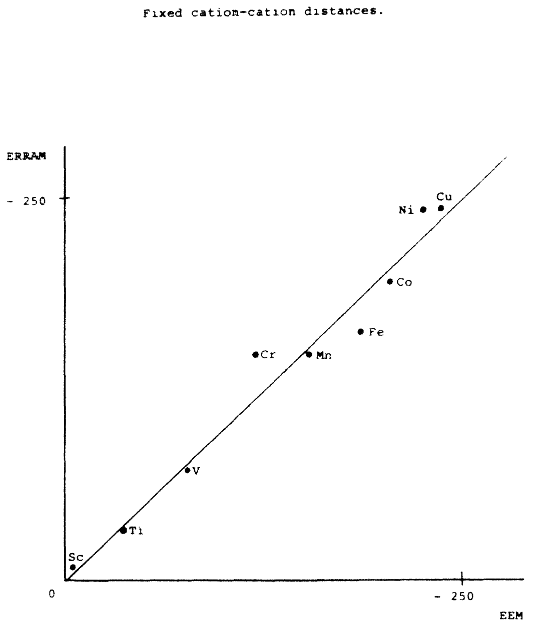

FIG. 1. Plot of EEM versus ERRAM results for n^2J/k (K) from Table III for the chlorides. The linear regression line is drawn.

bisector. The largest deviation in the slope tangent is only 3% and the intersections with the axes lie within 3 K from the origin. The correlation coefficients are larger than 0.98. The analysis shows a remarkable correspondence in the predictions of the two models. We note that this result is not a mathematical consequence of the least-squares fit for the channel sums, but arises from a common property of the two models, discussed in the next section.

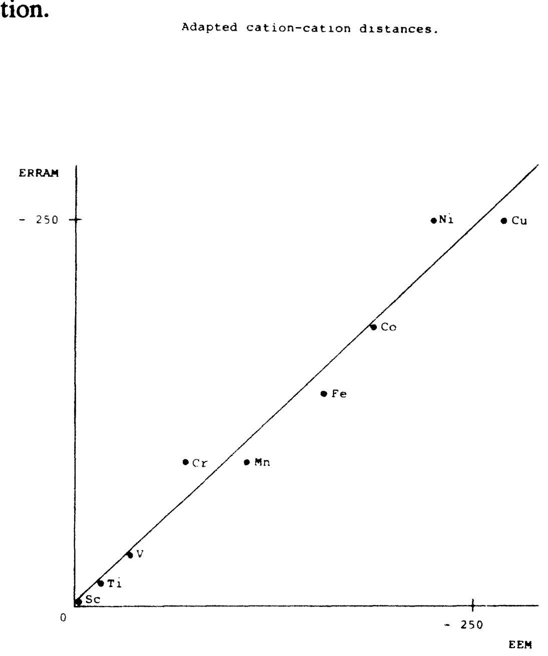

FIG. 2. Plot of EEM versus ERRAM results for n^2J/k (K) from Table IV for the chlorides. The linear regression line is drawn.

IV. DISCUSSION

Although the EEM and the ERRAM show a mutual consistency in all their predictions considered here, it seems rather impossible to relate their basic assumptions. The EEM disregards ligand-field effects, Jahn-Teller distortions, and angular dependence of the orbitals. The parameters for the effective orbitals are bound to "free" ions and quantum-mechanical calculations for ECC's are carried out in a three-center four-electron system. The ERRAM, on the other hand, explicitly removes orbital degeneracy by ligand-field splittings and Jahn-Teller distortions, leading to a definite filling scheme for the $3d$ orbitals. The ECC's are expressed as linear combinations of three nonlocal exchange parameters to be determined from experiment. It has to be noted that the removal of orbital degeneracy in the ERRAM is essential for its results since, otherwise, this model would yield equal ECC's, for all cations considered, of the form $J=(J_{tt}+J_{ee}+2J_{te})/25$.

From a theoretical point of view, the successes of the concepts of "effective orbitals" (EEM) and "transferable channels" (ERRAM) are still not understood from first principles. The correspondence is a result of the common property of the models that n^2J increases in going from Sc^{2+} to Cu^{2+}. The increase of the predicted n^2J values arises, however, from different origins. In the EEM the effective-orbital size grows with the number of $3d$ electrons, yielding larger values for n^2J. The expression (1) for n^2J in the ERRAM can be written as $n^2J=mJ_{ee}$, where m ranges from $J_{tt}/9J_{ee}$ (Sc^{2+}) to 1 (Cu^{2+}), representing an increase of the relative contribution from the dominant channel sum J_{ee}. As mentioned in Sec. II, this channel sum is practically determined by the channel d_σ-d_σ and, consequently, one obtains $n^2J=mJ_{\sigma\sigma}$. An extension of the ERRAM is attained if the power-law dependence on R of the ECC's is included in $J_{\sigma\sigma}$. The value of $J_{\sigma\sigma}$, for a given anion, then remains at all ionic distances almost equal to the corresponding EEM result for copper.

In view of the observed correspondence of the two models along the $3d$ series, it is apparently possible to "absorb" the increase of m into a decrease of the effective orbital parameter λ, resulting in the correspondence $mJ_{ee}\approx J_{\mathrm{EEM}}(\lambda)$, where λ varies inversely proportional with the diamagnetic susceptibility of the valence shells. Although the striking numerical correspondence of the two models can, qualitatively, be simply interpreted, the conceptual reconciliation of the two models is a far more intricate matter, beyond the scope of this paper.

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