Generalized calculation of magnetic coupling constants for Mott-Hubbard insulators: Application to ferromagnetic Cr compounds

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Using a Rayleigh-Schrödinger perturbation expansion of multi-band Hubbard models, we present analytic expressions for the super-exchange coupling constants between magnetic transition metal ions of arbitrary separation in Mott-Hubbard insulators. The only restrictions are i) all ligand ions are closed shell anions and ii) all contributing interaction paths are of equal length. For short paths, our results essentially confirm the Goodenough-Kanamori-Anderson rules, yet in general there does not exist any simple rule to predict the sign of the magnetic coupling constants. The most favorable situation for ferromagnetic coupling is found for ions with less than half filled d shells, the (relative) tendency to ferromagnetic coupling increases with increasing path length. As an application, the magnetic interactions of the Cr compounds Rb₂CrCl₄, CrCl₃, CrBr₃ and CrI₃ are investigated, all of which except CrCl₃ are ferromagnets.

1. INTRODUCTION

The understanding of the magnetic properties of the nonmetallic 3d-transition metal compounds is not satisfying though they have been investigated intensively experimentally and theoretically. In particular there exists only a qualitative understanding of magnitude and sign of the magnetic coupling on the basis of the so-called Goodenough-Kanamori-Anderson (GKA) rules. In this paper we present a more systematic way of calculating the magnetic coupling constants of these materials based on the concept of super-exchange. We also test our methods by applying them to a sub-class of the rare class of ferromagnetic 3d insulators, i.e. to Cr compounds, where the GKA rules apparently do not apply.

In nonmetallic, magnetic 3d-transition metal oxides and halides the spins are localized in the incompletely filled 3d shells of the transition metal sites, hence-forward called magnetic sites. This is a consequence of large correlation effects. They are Mott-Hubbard insulators and are thus described by a Hubbard-type model of the form

\[ H = \sum_{\alpha,\sigma} \epsilon^\alpha \hat{n}_{\alpha\sigma}(i) + \sum_{l,\sigma} \epsilon^l \hat{n}_{\tau\sigma}(l) \]

\[ + \sum_{\alpha,\sigma,\tau} \left[ t^\alpha_{\alpha\tau} \hat{c}^\dagger_{\alpha\sigma}(i) \hat{c}_{\tau\sigma}(l) + h.c. \right] \]

\[ + \sum_{\tau,\tau',\sigma} \left[ t^\tau_{\tau\tau'} \hat{c}^\dagger_{\tau\sigma}(l) \hat{c}_{\tau'\sigma}(l') + h.c. \right] \]

\[ + \frac{1}{2} \sum_{\alpha,\beta} U_{\alpha\beta} \hat{c}^\dagger_{\alpha\sigma}(i) \hat{c}^\dagger_{\beta\sigma'}(i) \hat{c}_{\beta\sigma'}(i) \hat{c}_{\alpha\sigma}(i) \]

\[ - \frac{1}{2} \sum_{\alpha,\beta} I_{\alpha\beta} \hat{c}^\dagger_{\alpha\sigma}(i) \hat{c}^\dagger_{\beta\sigma'}(i) \hat{c}_{\alpha\sigma'}(i) \hat{c}_{\beta\sigma}(i). \]  

Here \( \epsilon^\alpha \) is the energy of a d orbital \( \alpha \) at the magnetic site \( i \), \( \epsilon^l \) that of an orbital \( \tau \) at the ligand site \( l \). \( t^\alpha_{\alpha\tau} \) represents the hopping from the orbital \( \alpha \) to \( \tau \), \( t^\tau_{\tau\tau'} \) that from \( \tau \) to \( \tau' \). \( U_{\alpha\beta} \) and \( I_{\alpha\beta} \) are Coulomb and exchange interactions at the magnetic sites, respectively. In the atomic limit, \( I_{\alpha\beta} < 0 \) leads to the first Hund’s rule (maximum spin) and \( U_{\alpha\alpha} > U_{\alpha\beta} \) to the second Hund’s rule (maximum orbital momentum). \( I_{\alpha\beta} = I_{\alpha\beta} \hat{c}^\dagger_{\alpha\sigma}(i) \hat{c}^\dagger_{\beta\sigma'}(i) \hat{c}_{\beta\sigma'}(i) \hat{c}_{\alpha\sigma}(i) \) will be called Hund interaction in the following. Its effect is an exchange of spins between orbitals \( \alpha \) and \( \beta \). The application of \( I \) to symmetric (anti-symmetric) spin-states therefore has the effect of a multiplication with \(+(-)I_{\alpha\beta}\). In Eq. (1) we neglect the Coulomb interaction at the ligand ions and between different sites. We will also use the approximation \( U_{\alpha\alpha} = U_{\alpha\beta} = U \) and \( I_{\alpha\beta} = J_H \). These restrictions could be loosened but we do not expect qualitatively different results. We note that the atomic part of the Hamiltonian (\( J \)) has been used very satisfactorily in ligand field theory for, e.g. the interpretation of optical data of such compounds (\( J \))

Anderson has introduced the concept of super-exchange where the hopping of spins between the different sites leads to the coupling of the total spins \( \mathbf{S}_1 \) and \( \mathbf{S}_2 \) of the magnetic sites 1 and 2. As is known from experimental results the interaction is described very well by the Heisenberg Hamiltonian

\[ H_{\text{eff}} = J_{12} \mathbf{S}_1 \cdot \mathbf{S}_2. \]  

(2)

The interpretation of the interaction due to kinetic exchange (different from Coulomb exchange) is reflected in the formulation of the GKA rules. In a simplified version they read

A) If the hopping of a spin from a singly occupied \( \zeta_{1} \) of the ion \( M_1 \) to the singly occupied
orbital $\zeta_2$ of the ion $M_2$ is possible, the interaction between the spins in $\zeta_1$ and $\zeta_2$ is anti-ferromagnetic.

B) When a spin can hop from the singly occupied orbital $\zeta_1$ to an unoccupied orbital $\eta$ of $M_2$, a ferromagnetic contribution to the interaction results, which is weaker than the anti-ferromagnetic one from rule A.

With the use of these rules the sign of the coupling constant can be predicted in many cases. Especially, the GKA rules explain why most of the non-metallic 3d-transition-metal compounds do not show a macroscopic magnetic moment. This is related to the fact that orbital transition-metal compounds does not show a macroscopic magnetic moment. GKA rules explain why most of the non-metallic 3d- 

II. SUPER-EXCHANGE

In perturbation theory the coupling between the total spins $S_1$ and $S_2$ of two magnetic ions results from the exchange of the spins in the singly occupied orbitals. Since we do not consider spin-dependent interactions like spin-orbit coupling here, the spin Hamiltonian is isotropic and in the lowest order we get

$$H_{\text{eff}} = \sum_{\zeta_1 \zeta_2} J_{\zeta_1 \zeta_2} S_{\zeta_1} \cdot S_{\zeta_2}. \quad (3)$$

Here, $\zeta_1$ and $\zeta_2$ denote the half-filled orbitals at the sites 1 and 2. Assuming a strong Hund interaction, the ground-state has maximum spin and the replacement

$$S_{\zeta_i} = \frac{S_i}{2 < S_i >} \quad (4)$$

appears to be justified. Eq. (3) can then be written as

$$H_{\text{eff}} = \left( \sum_{\zeta_1 \zeta_2} J_{\zeta_1 \zeta_2} \right) \frac{S_1 \cdot S_2}{4 < S_1 > < S_2 >} \quad (5)$$

We begin with the coupling of spin-$\frac{1}{2}$ pairs. The generalization to pairs with larger total spins is possible with the help of Eq. (5).

We distinguish three cases:

A: Direct interaction of two singly occupied orbitals $\zeta_1$ and $\zeta_2$ without the involvement of another d orbital. In general, the resulting coupling will be anti-ferromagnetic, the coupling constant will therefore be called $J_{\zeta_1 \zeta_2}^A$.

FE: Indirect interaction of $\zeta_1$ and $\zeta_2$ via one ore more empty d orbitals $\eta$ involving the Hund interaction. The coupling constant is always negative and will be called $J_{\zeta_1 \zeta_2}^{FE}$.

FD: Indirect coupling of $\zeta_1$ and $\zeta_2$ via one ore more doubly occupied d orbitals $\mu$ involving the Hund interaction. The coupling constant is negative, in general, and will be called $J_{\zeta_1 \zeta_2}^{FD}$.

A. super-exchange via one ligand

We first consider the direct coupling of two equivalent magnetic ions 1,2 with singly occupied orbitals $\zeta_1$, $\zeta_2$ via one ligand with an empty hole orbital, see Fig. 1a. Fourth order perturbation theory is the lowest contributing order. There exist six possibilities of exchanging the
spins which differ in the sequence of spin exchange. In the following these sequences will be called channels. For each channel three intermediate states \( m \) exist. Two of them contain only singly occupied sites (one spin at the ligand and the other at one of the magnetic ions). In the third state the two spins occupy the same ion. The excitation energy of the singly occupied states is the charge transfer energy \( \Delta \) when the magnetic ion 1 (2) is singly occupied. We have \( \Delta_i = e^i - e^j \), when the ligand is empty, which is the usual case in the hole picture. Note, that when transforming to the electron picture, the numerical value of \( \Delta \) remains unchanged, but the orbital energies \( e \) have to be renormalized. If one of the magnetic ions is doubly occupied, the excitation energy is \( U \pm (\Delta_i - \Delta_{j}) \), if it is the ligand we have \( \Delta_i + \Delta_{j} \).

The matrix elements between the states are the hopping integrals given by (1) and each channel yields the same factor \((t_{\xi j})^2 (t_{\eta j})^2\). Note that the energy denominators \((E_0 - E_m)^{-1}\) are negative, but an additional minus sign occurs because of the exchange of the spins.

The total contribution of the six channels is

\[
J_{i \xi j \eta j}^{A,1} = \left( \frac{1}{U} \right) \frac{1}{U - \omega_{i \xi j \eta j}} + \left( \frac{1}{U} \right) \frac{1}{U + \omega_{i \xi j \eta j}}
\]

with \( \omega_{i \xi j \eta j} = \Delta_{i \xi j} - \Delta_{j \xi j} \), \( t_{\xi j} \) is the hopping integral between orbitals \( \xi \) (\( \eta \)) and the ligand. Assuming \( \Delta_{i \xi j} = \Delta_{j \xi j} = \Delta_L \) in Eq. (4), we obtain the well known expression

\[
J_{i \xi j \eta j}^{A,1} = 2 \frac{t_{\xi j}^2 (t_{\eta j})^2}{U} \left( \frac{1}{U} + \frac{1}{\Delta_L} \right).
\]

With the replacements

\[
2 \left( \frac{1}{U} + \frac{1}{\Delta_L} \right) = A_1
\]

\[
\frac{t_{\xi j} t_{\eta j}}{\Delta_L} = \tilde{t}_{i \xi j \eta j}
\]

this leads to

\[
J_{i \xi j \eta j}^{A,1} = A_1 \left( \tilde{t}_{i \xi j \eta j} \right)^2.
\]

\( \tilde{t} \) represents the effective hopping from one to the other magnetic ion via the ligand. \( J^A \) is always non-negative and leads, because of the Pauli principle, to an anti-parallel ordering of \( S_1 \) and \( S_2 \).

For the indirect coupling of the spins at the magnetic sites, an intermediate state with a total spin larger than that of the ground state has to be generated at one of the magnetic ions. Thus, there has to exist at least one spin-free orbital (empty or doubly occupied) at this ion, which is the case for most 3d ions except those in high spin \( d^5 \) configuration. Then an inter-orbital on-site exchange can take place, leading to a negative coupling constant.

The intermediate high spin state can occur in two ways.\( FE \): If the spin-free orbital at the magnetic ion, where the direct exchange takes place, is empty, the spin from the half-filled orbital of the other magnetic ion can hop into it.\( FD \): If the spin-free orbital is doubly occupied, one of the spins can hop to the empty ligand, energetically preferred is the one anti-parallel to the ground state spin. Both cases lead to a polarization of the ligand which is parallel to the spin of the magnetic ion in case \( FE \) and anti-parallel to it in the case \( FD \). We will begin with the investigation of \( FE \).

We assume a system of two magnetic ions\( M_1 \) and \( M_2 \) with only one singly occupied orbital \( \zeta \) and one empty orbital \( \eta \) each. Also, the intermediate ligand is empty, see Fig. 1 b).

There exist only two possibilities for exchanging the spins. For each, the spin from the half filled orbital \( \zeta \) of one magnetic ion has to migrate to the empty orbital \( \eta \) of the other ion, where the on-site exchange of the spins takes place, leading to the preference of the ferromagnetic state. Simplifying \( \Delta_{i \xi j} = \Delta_{j \xi j} = \Delta_L \) and \( \Delta_{i \eta j} = \Delta_{j \eta j} = \Delta_L \) the coupling constant is given by

\[
J_{i \xi j \eta j}^{FE,1} = \frac{J_H}{U} \frac{J_H}{U - (\Delta_L - \Delta_L)^2 (\Delta_L)^2} \frac{[t_{\xi j} t_{\eta j}^2 + (t_{\eta j} t_{\xi j})]^2}{\Delta_L}.
\]

\( t_{\xi j} (t_{\eta j}) \) represents the hopping-integral from the orbital \( \xi (\eta) \) to the ligand. We note that \( J^{FE} \) is proportional to \( J_H \).

Using the simplification \( \Delta_L = \Delta_L = \Delta_L \) we have

\[
J_{i \xi j \eta j}^{FE,1} = \frac{1}{U} \frac{J_H}{U} \frac{J_H}{U} \frac{[t_{\xi j} t_{\eta j}^2 + (t_{\eta j} t_{\xi j})]^2}{\Delta_L}.
\]

With the substitutions

\[
FE_1 = \frac{J_H}{U^2}
\]

\[
(t_{\xi j} (t_{\eta j}))^2 = \frac{t_{\xi j}^2 t_{\eta j}^2}{\Delta_L}
\]

this expression can be written as

\[
J_{i \xi j \eta j}^{FE,1} = J_{i \xi j \eta j}^{FE,1} + J_{i \xi j \eta j}^{FE,1} = FE_1 \frac{(\tilde{t}_{i \xi j \eta j})^2 + (\tilde{t}_{i \xi j \eta j})^2}{\Delta_L}.
\]

\( J^{FE} \) contains two different hopping contributions, each of which is independent of the orbital \( \zeta \) of that site where the Hund interaction takes place. \( J^{FE} \) is non-positive and leads to a parallel orientation of the spins \( S_1 \) and \( S_2 \). This mechanism has been proposed by GKA to explain the occurrence of ferromagnetic coupling in non-metallic
compounds. Yet, since $|FE_1| \ll A_1$, it is necessary that $\tilde{t}_{\zeta,\zeta_2}^1$ of Eq. 3 disappears or is very small at least.

For case $FD$ we consider a system of two equivalent magnetic ions $M_1$ and $M_2$ with one singly occupied orbital $\zeta$ and one doubly occupied orbital $\mu$ each, see Fig. 1 c). As above, the ligand is empty.

In contrast to case $FE$ there are now 22 (= 2 · 11) channels, instead of two, all leading to a ferromagnetic coupling. The main difference between the channels is whether the spin of $\zeta$ or one of the spins of $\mu$ first hops to the ligand. Putting $\Delta_{\zeta} = \Delta_{\zeta}^1$ and $\Delta_{\mu} = \Delta_{\mu}^1$ we have

$$J_{\zeta,\zeta_2}^{FD,1} = J_H \left[ \frac{2}{\Delta_{\zeta}^1} \left( \frac{1}{\Delta_{\zeta}^1} + \frac{1}{\Delta_{\mu}^1} \right) + \frac{1}{(\Delta_{\mu}^1)(\Delta_{\zeta}^1 + \Delta_{\mu}^1)} \left( \frac{2}{\Delta_{\mu}^1} + \frac{1}{\Delta_{\zeta}^1 + \Delta_{\mu}^1} \right) \right] (14)$$

$$+ \frac{1}{(\Delta_{\mu}^1)^2(U + \Delta_{\zeta}^1 - \Delta_{\mu}^1)} \left( \frac{2}{\Delta_{\mu}^1} + U + \Delta_{\zeta}^1 - \Delta_{\mu}^1 \right)$$

$$+ \frac{1}{(\Delta_{\zeta}^1)^2(\Delta_{\zeta}^1 + \Delta_{\mu}^1)^2} \left[ \langle t_{\zeta_1 \mu_2} \rangle^2 + \langle t_{\zeta_2 \mu_1} \rangle^2 \right].$$

A further simplification is obtained when we put $\Delta_{\zeta} = \Delta_{\mu} = \Delta_L$. Then

$$J_{\zeta,\zeta_2}^{FD,1} = J_H \left[ \frac{2}{\Delta_L^2} \left( \frac{3}{\Delta_L^2} + \frac{2}{U} \right) + \frac{1}{\Delta_L^2(U+2)} \right] \left[ \langle t_{\zeta_1 \mu_2} \rangle^2 + \langle t_{\zeta_2 \mu_1} \rangle^2 \right]$$

$$= J_{\zeta_2,\zeta_2}^{FD,1} + J_{\zeta_1,\mu_1}^{FD,1}$$

$$= \tilde{J}_{\zeta_1 \mu_1}^{FD,1} \left[ \langle \tilde{t}_{\zeta_1 \mu_2} \rangle^2 + \langle \tilde{t}_{\zeta_2 \mu_1} \rangle^2 \right].$$

Here, we have put

$$FD_1 = \tilde{J}_{\zeta_1 \mu_1}^{FD,1} = \frac{J_H}{U} \left( \frac{1}{U} + \frac{2}{\Delta_L} \right)$$

$$= \frac{t_{\zeta_1 \mu_2}^2 + t_{\zeta_2 \mu_1}^2}{\Delta_L^2}. \quad (16b)$$

$J_{\zeta_1 \mu_1}^{FD,1}$ is non-positive and therefore leads to a parallel orientation of the spins. The expression is quadratic in the effective hopping-integrals $t$ and the factor $FD_1$ is positive ($U, \Delta_L > 0$). The coupling constants $J_{\zeta_1 \mu_2}$ are independent of the orbital $\zeta$ of the Hund interaction site. We note that $FD_1 > FE_1$. As a consequence, the ferromagnetic interaction should be more favorable for cases of a doubly occupied d orbital than for those of empty ones. This has already been pointed out by Anderson.

B. super-exchange via $N$ ligands

In the following we consider the interaction via $N$ unoccupied ligands with one orbital each. We will assume hopping only between nearest neighbors along the chain of $N + 2$ atoms and we investigate again the cases $A$, $FE$ and $FD$.

Case $A$ requires a perturbation expansion up to order $2(N + 1)$. There are $\binom{2(N+1)}{N+1}$ possibilities (channels) to exchange the spins. To take account of all channels we use a simple method to generate them. For this purpose each channel will be written as a sequence of numbers

$$(p_1, p_2, \ldots, p_N, \ldots, p_{N+2} | p_{N+3}, \ldots, p_{2(N+1)} | p_{2(N+1)+2}) \quad (17)$$

which represents the order of the hopping. Here $p_1$ stands for the hopping from $M_1$ to the first ligand, $p_2$ for the hopping from the first to the second ligand, $p_{N+1}$ for the hopping from the last ligand to $M_2$, $p_{N+2}$ for the hopping back from $M_2$ to the $N$th ligand, see Fig. 2. The arrangement of the numbers in this sequence has to fulfill the restriction that the left as well as the right half must contain numbers of increasing magnitude. In the case of an expression of sixth order the numbers 1 to 6 have to be distributed. Therefore a possible sequence is

$$(124356). \quad (18)$$

First a spin from $M_1$ hops to the first ligand (1) and from there to $l_2$ (2). Then the spin from $M_2$ hops to $l_2$ (3) such that the two spins meet at $l_2$. Next $M_2$ becomes singly occupied again (4). The last two processes are the hopping from $l_2$ to $l_1$ (5) and then back to $M_1$ (6). Not possible is the sequence

$$(356214), \quad (19)$$

since the ligands are empty and thus the hopping from $l_2$ to $l_1$ cannot occur first.

With the simplification $\Delta_{l_1} = \Delta_{l_2}$ we find

$$J_{l_1, l_2}^{A,N} = A_N \langle \tilde{t}_{l_1, l_2}^N \rangle^2. \quad (19b)$$

Here

$$A_N = 2 \left( \frac{1}{U} + \sum_{k=1}^{N} \frac{1}{\Delta_{l_k}} \right) \quad (21a)$$

$$(\langle \tilde{t}_{l_1, l_2}^N \rangle^2) \left( \prod_{k=1}^{N} \frac{1}{\Delta_{l_k}} \right)^2.$$

The structure of Eq. 21 is the same as that of Eq. 3 for ligand. Again, $J_{l_1, l_2}^{A,N}$ is the product of a non-negative hopping-term and a positive energy factor $A_N$. Thus we have anti-ferromagnetic coupling. Comparing $A_N$ with $A_1$ indicates that $J_{l_1, l_2}^{A,N}$ is reduced as compared to $J_{l_1, l_2}^{A,1}$, because $\tilde{t}_{l_1, l_2}^N \ll \tilde{t}_{l_1, l_2}^1$. For large $N$ this is partly compensated by $A_N \gg A_1$.

Case $FE$ involving an empty $M$ orbital, can be handled in the same way. Nevertheless the structure of the sequences is somewhat different since the Hund interaction has to be taken into account. The sequences contain $2N + 3$ numbers which are ordered as follows
\[(p_1 p_2 \ldots p_{N+1} p_{N+2} p_{N+3} \ldots p_{2N+3}). \tag{22}\]

The central number indicates when the Hund interaction at a specific magnetic ion (either \(M_1\) or \(M_2\), takes place, see Fig. 3. There is an additional restriction for the ordering of the \(p_i\). Both the series \(p_1 \ldots p_{N+1}\) and \(p_{N+3} \ldots p_{2N+3}\) as well as the triple \(p_{N+1} p_{N+2} p_{N+3}\) have to contain numbers of increasing size. For this reason there is only one channel left. When two ligands are present this is

\[(1 2 3 | 4 5 6 7). \tag{23}\]

Then, the interaction constant is given by

\[J_{\zeta_1 \zeta_2}^{FE,N} = J_{\zeta_1 \zeta_2, \eta_2}^{FE,N} + J_{\zeta_1 \zeta_2, \eta_1}^{FE,N} = FE_N \left( (\tilde{t}_{\zeta_1 \eta_2})^2 + (\tilde{t}_{\zeta_1 \eta_1})^2 \right). \tag{24}\]

With \(\Delta_\zeta \approx \Delta_\eta\) we have

\[FE_N = FE_1 = \frac{J_H}{U^2} \] (25a)

\[\tilde{t}_{\zeta_1 \eta_1}^{N} = \frac{t_{\zeta_1 \eta_1} \prod_{k=1}^{(N-1)} t_{\eta_k \eta_{k+1}} t_{\zeta_k \eta_1}}{\prod_{k=1}^{N} \Delta_k}. \tag{25b}\]

\[J_{\zeta_1 \zeta_2, \eta_1}^{FE,N}\] is non-positive and, because of \(FE_N = FE_1\), it is much smaller than \(J_{\zeta_1 \zeta_2, \eta_2}^{FE,1}\) for large \(N\), since \(\tilde{t}^N << t^1\). There is no compensation from an increasing number of channels.

Case \(FD\): Here we find a rapidly growing number of channels. In sixth order these are 142. For this reason we restrict our investigation to the case of equivalent (\(\Delta_k = \Delta \forall k\)) ligands in the chain.

The sequences introduced in Eq. 24 can also be used here. Yet the restrictions are modified. The series \(p_1 \ldots p_{N+1}\) and \(p_{N+3} \ldots p_{2N+3}\) now contain numbers of increasing magnitude, while the center triple \(p_{N+1} p_{N+2} p_{N+3}\) now contains numbers of descending size.

In this situation the coupling constant is (using \(\Delta_\zeta \approx \Delta_\mu \approx \Delta\))

\[J_{\zeta_1 \zeta_2}^{FD,N} = J_{\zeta_1 \zeta_2, \mu_2}^{FD,N} + J_{\zeta_1 \zeta_2, \mu_1}^{FD,N} = FD_N \left( (\tilde{t}_{\zeta_1 \mu_2})^2 + (\tilde{t}_{\zeta_1 \mu_1})^2 \right). \tag{26}\]

Here

\[FD_N = \frac{J_H}{U} \left[ \frac{1}{U} + 2N \frac{1}{\Delta} + N(2N + 1) \frac{U}{\Delta^2} \right] \tag{27a}\]

\[\tilde{t}_{\zeta_1 \mu_1}^{N} = \frac{t_{\zeta_1 \mu_1} \prod_{k=1}^{(N-1)} t_{\mu_k \mu_{k+1}} t_{\zeta_1 \mu_j}}{\prod_{k=1}^{N} \Delta_N}. \tag{27b}\]

\(J_{\zeta_1 \zeta_2}^{FD,N}\) is non-positive as is \(J_{\zeta_1 \zeta_2}^{FD,1}\). As it contains terms of order \(N^2\) it will compensate the decreasing magnitude of the hopping terms \(\tilde{t}^N\), even more than for the case \(A\).

The structure of \(FD_N\) can be made plausible by comparison with \(A_N\). The perturbation series that was needed to calculate \(J^A\) has the order \(2N + 2\), when \(N\) ligands are present, i.e. it contains products of \(2N + 2\) factors. The corresponding ferromagnetic interaction additionally includes the Hund interaction in first order. This factor can be introduced at \(2N + 1\) positions into the product of \((2N + 2)\) factors. In case of a \(U\)-channel in \(A_N\), i.e. when the spins meet at a magnetic ion, there is only one term of order \(U\Delta^{-1}\). Then there are \(N\) ligand channels, here each of the \(2N + 1\) terms give the same contribution of order \(\Delta^{-2}\).

We have restricted the discussion of the coupling via more than one ligand to the case of ligands of the same type, i.e. they are either all anions or all cations. The generalization to the case of mixed-type ligands remains work to be done.

C. super-exchange via various paths

So far we have discussed the super-exchange via one path. But clearly several paths of the same order can exist along which the spins can be exchanged. A schematic view of this situation is shown in Fig. 3.

We distinguish between equivalent and non-equivalent paths. Paths \(p\) and \(p'\) are called equivalent when \(Q^p = Q^{p'}\) holds, with \(Q^p = A_N^p, FE_N^p\) or \(FD_N^p\). The additional paths can arise by introducing further ligand orbitals or by adding further ligand atoms.

The interaction constant for a multi-path system is calculated by combining the contributions of the individual paths. The exchange takes place in two different ways. The first one is the use of only one path, forth and back, as before. The second one is a ring exchange using two different paths forth and back.

Again we consider the direct coupling of two half filled orbitals for the cases \(A, FE\) and \(FD\). Altogether we find the following expressions

\[J_{\zeta_1 \zeta_2}^{A,N}(P) = \frac{1}{2} \sum_{p,p'} (A_N^p + A_N^{p'}) \tilde{t}_{\zeta_1 \zeta_2}^{N,p} \tilde{t}_{\zeta_1 \zeta_2}^{N,p'} \] (28a)

\[J_{\zeta_1 \zeta_2}^{FE,N}(P) = \frac{1}{2} \sum_{p,p'} (FE_N^p + FE_N^{p'}) \tilde{t}_{\zeta_1 \zeta_2}^{N,p} \tilde{t}_{\zeta_1 \zeta_2}^{N,p'} \] (28b)

\[J_{\zeta_1 \zeta_2}^{FD,N}(P) = \frac{1}{2} \sum_{p,p'} (FD_N^p + FD_N^{p'}) \tilde{t}_{\zeta_1 \zeta_2}^{N,p} \tilde{t}_{\zeta_1 \zeta_2}^{N,p'} \] (28c)
$P$ denotes the number of paths.

If $Q^p = Q \forall p$ the corresponding expressions for $J_Q$ are quadratic in the effective hopping-integrals.

$$J_{\zeta_1\zeta_2}^{A,N}(P) = A_N \left( \sum_{p=1}^{P} t_{\zeta_1\zeta_2}^{N,p} \right)^2$$  \hspace{1cm} (29a)

$$J_{\zeta_1\zeta_2}^{FE,N}(P) = F_{E,N} \left[ \left( \sum_{p=1}^{P} t_{\zeta_1\zeta_2}^{N,p} \right)^2 + \left( \sum_{p=1}^{P} \sum_{\eta_{1,2}} t_{\zeta_1\zeta_2}^{N,p,\eta} \right)^2 \right]$$  \hspace{1cm} (29b)

$$J_{\zeta_1\zeta_2}^{FD,N}(P) = F_{D,N} \left[ \left( \sum_{p=1}^{P} \sum_{\eta_{1,2}} t_{\zeta_1\zeta_2}^{N,p,\eta} \right)^2 + \left( \sum_{p=1}^{P} \sum_{\eta_{1,2}} \sum_{\mu_{1,2}} t_{\zeta_1\zeta_2}^{N,p,\eta,\mu} \right)^2 \right]$$  \hspace{1cm} (29c)

In all above cases the existence of several equivalent paths only leads to a new effective hopping $T_{\alpha\beta}^{P,N} = \sum_{p=1}^{P} t_{\alpha\beta}^{N,p}$. In particular the sign of the coupling constant remains unchanged, though the effective hopping $T_{\alpha\beta}$ and thus the coupling may vanish when an appropriate set of parameters is chosen.

In case where the different paths are inequivalent this can lead to a ferromagnetic coupling resulting from direct super-exchange as has been discussed in a previous paper.\[1\]

D. total interaction

The total interaction $J$ of two magnetic ions with total spins $S_1$ and $S_2$ is obtained from Eq. (29) as the sum of the interaction of the half-filled orbitals

$$J = \sum_{\zeta_1\zeta_2} J_{\zeta_1\zeta_2},$$  \hspace{1cm} (30)

where

$$J_{\zeta_1\zeta_2} = J_{\zeta_1\zeta_2}^{A} + J_{\zeta_1\zeta_2}^{FE,\eta_1} + J_{\zeta_1\zeta_2}^{FE,\eta_2} + J_{\zeta_1\zeta_2}^{FD,\mu_1} + J_{\zeta_1\zeta_2}^{FD,\mu_2}.$$  \hspace{1cm} (31)

Here $\sum_{\eta_1}$ runs over all relevant unoccupied orbitals of $M_i$, $\sum_{\eta_2}$ over the doubly occupied respectively. Then it follows

$$J = \sum_{\zeta_1\zeta_2} \left[ J_{\zeta_1\zeta_2}^{A} + J_{\zeta_1\zeta_2}^{FE,\eta_1} + J_{\zeta_1\zeta_2}^{FE,\eta_2} + J_{\zeta_1\zeta_2}^{FD,\mu_1} + J_{\zeta_1\zeta_2}^{FD,\mu_2} \right]$$  \hspace{1cm} (32)

$$+ \sum_{\mu_1} J_{\zeta_1\zeta_2}^{FD,\mu_1} + \sum_{\mu_2} J_{\zeta_1\zeta_2}^{FD,\mu_2}.$$  \hspace{1cm} (33)

The factors $N_{\zeta_1}$, denoting the number of singly occupied orbitals at $M_i$, result from the assumption of an orbital-independent on-site exchange.

We will use equation (32) to calculate the coupling constants of two magnetic ions with arbitrary (integral) occupation which are coupled via unoccupied ligands in the frame of a Hubbard-model. We note that we are restricted to the case that all contributing paths are of the same order.

III. FERROMAGNETIC COMPOUNDS

In this section we apply our theory to selected insulating ferromagnets, i.e. to Rb$_2$CrCl$_4$ and the Cr tri-halides CrCl$_3$, CrBr$_3$ and CrI$_3$. In none of these cases an obvious argument along the GKA rules can be found for the occurrence of ferromagnetism.

A. Rb$_2$CrCl$_4$

This compound is a quasi-two-dimensional ferromagnet with a Curie temperature $T_C = 52.4$ K. Values of $J_\parallel = -1.04 \times 10^{-2}$ eV and $J_\perp = 3 \times 10^{-4}$ are reported.\[2\]

The moments lie in the CrCl$_2$-planes and are almost parallel\[3\].

The crystal structure is analogous to that of K$_2$CuF$_4$. The parent structure is of K$_2$NiF$_4$-type, a body centered tetragonal lattice with $a = b = 5.086$ Å and $c = 15.72$ Å.\[4\] The Cl$^-$ ligands form an almost perfect octahedron around the Cr$^{2+}$ ions; yet, because of the $d^3$ configuration, a strong Jahn-Teller distortion takes place in order to remove the degeneracy of the $e_g$-orbitals, singly occupied in Cr$^{2+}$. The distortion leads to elongation of the ligand cage along the $y$ and $x$ axes, respectively, and corresponding to contractions in the $zz$ and $zy$ planes, respectively\[1\].

The same distortions are found in K$_2$CuF$_4$,\[5\] yet there is one important difference. While for K$_2$CuF$_4$ ($d^9$ configuration of Cu$^{2+}$) with its occupied $d$ holes of alternatingly $z^2 - y^2$ and $x^2 - y^2$ type, the GKA rules can be applied in an obvious manner (the hopping between those orbitals is identical zero by symmetry; and ferromagnetism results), no such rules apply for the occupied $e_g$-orbitals of the Cr$^{2+}$ ions which are of $3y^2 - r^2$ and $3x^2 - r^2$ type, respectively. This orbital order has been established by neutron measurements.\[6\]

Consequently, $\alpha$-type hopping is possible between neighboring orbitals. In addition, there exists $\pi$-type hopping between the singly occupied $t_{2g}$-orbitals. All these hopping processes favor an anti-ferromagnetic coupling. Nevertheless, the planar coupling is ferromagnetic. We
note that K$_2$CuF$_4$ and Rb$_2$CrCl$_4$ also show ferromagnetic coupling along the c-direction.

In the hole picture for Cr$^{2+}$, one of the $e_g$-orbitals is doubly occupied. The other one is singly occupied (as are the $t_{2g}$-orbitals) and alternates due to the orbital ordering. When we define the hole state by

$$g(\theta) = \cos \theta |x^2 - y^2 > + \sin \theta |3z^2 - r^2 >,$$

we have values of $\theta_{1,2} = \pm \frac{\pi}{2}$. Then we find for the anti-ferromagnetic and the ferromagnetic contributions to the intra-planar coupling

$$J^A_{\parallel} = \sum_{\zeta_{1,2}} J^A_{\zeta_{1,2}}$$

$$= \frac{1}{\Delta_{CI}} A_1 (CI) \left( 2 (pd\pi)^4 + \frac{1}{16} (pd\sigma)^4 \right)$$

Here, $\zeta$ denotes the singly occupied d-orbitals $xy, yz, zx$ and $g(\theta_{1,2})$. For simplicity we have put $\Delta_c = \Delta$, i.e. we have ignored the level splitting of the $t_{2g}$ and $e_g$ orbitals. The total coupling is given by

$$J^A_{\parallel} = \frac{1}{\Delta_{CI}} \left[ \frac{4}{U} \left( \frac{1}{U} + \frac{1}{\Delta_{CI}} \right) (pd\pi)^4 + \frac{1}{8} \left( \frac{1}{U} + \frac{1}{\Delta_{CI}} \right) (pd\sigma)^4 + \frac{3}{2} \frac{J_H}{U} \left( \frac{2}{U} + \frac{2}{\Delta_{CI}} + \frac{3}{U} \right) (pd\sigma)^4 \right].$$

The first two terms represent $J^A$, where the first one, containing the factor $(pd\pi)^4$, represents the coupling due to the $t_{2g}$ orbitals. When we assume the ‘canonical’ ratio $pd\pi/pd\sigma \approx -0.4$, the $t_{2g}$ orbitals contribute less than 1/3 to $J^A$. Note that any mixed terms $(pd\pi)^2(pd\pi)^2$ etc. do not exist, since the $e_g$ and $t_{2g}$ orbitals are decoupled by symmetry. The third term represents $J^F$, which contains a factor $J_H/U \approx -0.1$. Yet, on the other hand, the geometry of the $\sigma$-hopping provides a factor 3/2 (compared to 1/8 in term 2). In addition, the large number of channels in $FD_2$ leads to a reduction of the effective energy denominator by approximately a factor of 2.

As a consequence, a net ferromagnetic coupling is obtained. This result is rather stable, when energy and hopping parameters are varied within reasonable limits. We note that this situation may change, when further octahedral distortions occur which mix the $t_{2g}$ and $e_g$ orbitals. Probably, there exists an easy axis single ion anisotropy, favoring spin alignments either along the $y$ or the $z$ axis. The ferromagnetic nearest neighbor coupling will then produce the almost complete alignment of spins.

For the related case of KCrF$_3$, with the same structure of Cr planes as in Rb$_2$CrCl$_4$ suggesting the same orbital structure of the Cr ions, the puzzle of ferromagnetic intra-planar coupling has been studied previously by other researchers. They have assumed direct hopping between the magnetic sites and have suggested that values of $\theta \approx \frac{\pi}{4}$ should occur, in contrast to the findings in Rb$_2$CrCl$_4$, which yield $\theta = \frac{\pi}{2}$. Note that the neglect of ligand orbitals strongly reduces the number of ferromagnetic channels - there is only one left as $FD_0 = FE_0$. The coupling $J^A$, which vanishes only for $\theta = \frac{\pi}{4}$, is relatively large for $\theta \approx \frac{\pi}{4}$ and wins over $FD_0$. A further, even more questionable consequence is the fact that, neglecting the ligands, the energy change due to the octahedral distortion is of the same order as the magnetic interaction. When the ligands are included, the energy gain due to the Jahn-Teller distortion dominates over any magnetic energies. An analogous d$^4$ system with planar ferromagnetic coupling is LaMnO$_3$. Again we think that simplified coupling estimates neglecting the ligands are not appropriate.

An analysis of the inter-planar coupling has not been performed. On the one hand our formalism is not applicable to the situation with occupied and unoccupied ligands. On the other hand the number of spins is large (16 in the hole picture) such that a numerical calculation is very extensive. But we expect a similar behavior as in K$_2$CuF$_4$, where a reduction of $J^A$ due to destructive interference with a possible sign change and a more or less unmodified $J^F$ was obtained. Furthermore, for Rb$_2$CrCl$_4$ the spin-free orbital is doubly occupied and therefore the case $FD_0$ holds, which always leads to larger ferromagnetic coupling than the case $FE$.

B. CrHa$_3$ (Ha = Cl, Br, I)

The Cr tri-halides with rhombohedral symmetry (R3) contain two formula units per trigonal unit cell. The two Cr atoms occupy equivalent positions, so do all six halide atoms. They form triple layers Ha-Cr-Ha which are stacked along the c-axis. In the central Cr layer, the Cr atoms form a honeycomb lattice like a single layer of graphite. It is helpful to view this plane as a closed packed triangular arrangement of two Cr atoms (I and II) and of a vacancy V in the center of the honeycomb. Both the Cr atoms and the vacancy are surrounded by edge sharing octahedra of halide atoms. As a result, the two halide planes above and below are closed packed triangular layers with a stacking sequence A-B (see Fig. 3). The triple layers are now repeated along c in such a way that the vacancies V successively shift by $\frac{1}{4}(a - b + c)$, where a and b are the basal plane lattice vectors $(a = b, a \cdot b = -\frac{1}{2})$ and c is the c axis vector of the corresponding hexagonal unit cell. The motion of V from positions A to B to C to A (see Figs. 3 and 4) leads to a packing of
the halide planes along c of the form A-(Cr)-B-(empty)-A-(Cr)-B-(empty)-A-(Cr)-B etc. As a consequence, the interlayer space B-(empty)-A also consists of halide octahedra. One can define a perfect octahedral closed packed halide lattice by requiring that all octahedra are regular (rhombohedral angle \( \alpha = 60^\circ \)). This would lead to the same separation of A and B planes whether or not a Cr layer is intercalated. It is clear however that the interplanar distances are quite different, see Tab. I. The lattice parameters of the Cr tri-halides are given in Tab. I. some relevant atomic separations are listed in Tab. II. Note that for our calculations of magnetic coupling constants it was advantageous to start from an ‘ideal’ rhombohedral lattice by assuming regular octahedra around the Cr atoms. In the real lattice, there exists a compression of the octahedra enclosing the Cr plane. As a result, the octahedra surrounding the empty layer are considerably elongated along the c direction. There are two further types of distortion allowed by the R3m symmetry, which, however, appear to be of minor effect.

1) The Cr planes buckle, i.e., the Cr(I) and Cr(II) atoms lie respectively above and below the plane, as defined by the vacancy positions (deviation from 1/3 of the lattice parameter u, see Tab. I).

2) There are some minor shifts in the halide positions (lattice parameters x deviating from 1/3 or 2/3 values and y deviating from zero). These shifts result partly from a relaxation of the octahedra around the vacancy V and partly from the Cr buckling. Note that a slight rotation of the V octahedra follows, which should lead to optical activity along the c axis.

Of the three compounds, the lattice structure of CrBr\(_3\) has been investigated most extensively. Here, the internal lattice parameters x,y,z,u are known, while for CrCl\(_3\) these quantities have not been determined. For CrCl\(_3\), Morosin and Narath report a low temperature transition from an orthorhombic to the R3m near \( T = 225 \) K and give values for x,y,z,u. The difference of the two structures are different stacking arrangements of the Cr tri-halide planes. To our knowledge, the CrCl\(_3\) structural phase transition has not been confirmed by other groups. There is evidence that CrCl\(_3\) remains orthorhombic to low temperature into the anti-ferromagnetic phase.

All three compounds exhibit strong intra-planar ferromagnetic coupling. This feature is to be expected from the GKA rules, as the Cr-Ha-Cr angle for the nearest neighbor (fourth order) super-exchange paths (leading to the coupling constant \( J_1 \)) is rather close to 90\(^\circ\) - it is 94\(^\circ\) for CrCl\(_3\) and 93\(^\circ\) for CrBr\(_3\).

The inter-planar coupling is anti-ferromagnetic for CrCl\(_3\), while it is ferromagnetic for the other two materials. The critical temperatures are \( T_{\text{C}1}^\text{Cl} = 16.8 \) K, \( T_{\text{C}1}^\text{Br} = 32.5 \) K, and \( T_{\text{C}}^\text{I} = 68 \) K. Note that an easy plane anisotropy is reported for CrCl\(_3\), while easy axis anisotropies occur in CrBr\(_3\) and CrI\(_3\).

From analyses of magnetic susceptibility data intra-planar coupling constants \( J_{\parallel} \) have been obtained. The values reported in Ref. I are \( J_{\parallel}^\text{Cl} = -4.1 \) meV, \( J_{\parallel}^\text{Br} = -6.4 \) meV and \( J_{\parallel} = -10.5 \) meV. On the other hand, Samuelsen et al. have carried out neutron measurements of spin wave dispersion curves for CrBr\(_3\). They have been able to extract several near neighbor coupling constants, in particular for the inter-planar coupling. For the intra-planar coupling, they report \( J_1 = -7.6 \) meV and \( J_3 = 0.13 \) meV (next nearest neighbor, sixth order super-exchange). Note that \( |J_{\parallel}^\text{Br}| < |J_1 + 2 J_3| \). Since the \( J_1 \) value of Ref. I probably is the most reliable experimental quantity available, we have used the relation \( J_1 = 1.2 J_{\parallel}^\text{Br} \) to scale \( J_{\parallel}^\text{Cl} \) and \( J_{\parallel} \) accordingly and have assumed \( J_{\parallel}^\text{Cl} = -4.8 \) meV and \( J_{\parallel} = -12.4 \) meV. Note that we use the definition of J of Eq. I leading to a multiplication by a factor of nine of the values originally given by Refs. I and II.

There exist three different inter-planar coupling constants of sixth order super-exchange, labeled \( J_2 \), \( J_4 \) and \( J_5 \) by Samuelsen et al. \( J_2 \) is the vertical Cr(I)-Cr(II) coupling constant, \( J_4 \) represents another I-II coupling, while \( J_5 \) stands for I-I or II-II couplings (see Fig. I). The values given by Ref. I are \( J_2 = 0.22 \) meV, \( J_4 = -0.06 \) meV and \( J_5 = -0.12 \) meV.

In the following we present results of calculations for the coupling constants \( J_1 \), \( J_2 \), \( J_4 \) and \( J_5 \) using the theory of Section II. We have not included \( J_3 \), as we mainly focussed on the question of inter-planar coupling.

The electronic structure of the Cr ions depends on the ligand position. Because of almost perfect octahedra the three singly occupied states are almost \( e_g \) character, as can be found from diagonalizing the d-states in the ligand field. Note that Cr\(^{3+}\) is not a Jahn-Teller ion. The three empty p-states of the halides are treated as degenerate.

The intra-planar coupling of two nearest Cr ions takes place via two ligand ions, see Fig. I. From Eq. (35) the exchange interaction is given by

\[
J_1 = A_1(\text{Ha}) \sum_{\zeta \zeta'} (T^1_{\zeta \zeta'})^2 + 6F(D_1(\text{Ha}) \sum_{\zeta \zeta'} (T^1_{\zeta \zeta'})^2 \tag{36}
\]

with the effective hoppings \( T^1_{\zeta \zeta'} \) and \( T^1_{\zeta \zeta'} \) and the energy factors \( A_1 \) and \( F(D_1) \), Tabs. V, VI. The effective hoppings are calculated corresponding to their definition in Eq. (35). For the energy denominators, we have neglected the energy difference between \( e_g \) and \( t_{2g} \) like states.

The hopping parameters from Tab. II are found by a fitting process, where the charge-transfer energy \( \Delta \) was determined by adjusting \( H_{\text{Ha}} \) to the experimental values as given above, while \( U \) and \( J_H \) were kept fixed. We note that the order of magnitude and tendency of the \( \Delta \) according to those given by Zaanen. These values are also consistent with those found for Rb\(_2\)CrCl\(_4\).

The calculation of the inter-planar coupling is very complicated. On the one hand up to six ligands with three orbitals each are involved in lowest order exchange. On the other hand there are three occupied ground state orbitals.
For the calculation of $J_2$, $J_4$ and $J_5$ we need the direct (here anti-ferromagnetic) and the indirect (ferromagnetic) coupling constant in sixth order. Each of these couplings is mediated via several paths. Nevertheless, because we have assumed that all ligand orbitals are equivalent, this only leads to the introduction of an effective coupling as was discussed above.

The vertical inter-planar coupling $J_2$ is mediated via six halide ions with three orbitals each. The halide ions form an (empty) octahedron elongated along the $c$ axes, see Fig. 3. Three halide ions are ligands of the lower Cr ion and the other three those of the upper one. The couplings $J_4$(II-II) and $J_5$(I-II-II) are mediated via four halide ions where to each Cr belong two ligands, see Fig. 4.

For the coupling constants we get from equations (29) and (32)

$$J = A_2(Ha) \sum_{\zeta_1, \zeta_2} (T_{\zeta_1, \zeta_2}^2)^2 + 6 FD_2(Ha) \sum_{\zeta_1} (T_{\zeta_1, \mu}^2)^2. \quad (37)$$

Thus we have to determine the effective hopping integrals $T_{\zeta_1, \zeta_2}^2$, $T_{\zeta_1, \mu_2}^2$ and $T_{\mu_1, \zeta_2}^2$ and the energy factors $A_2(Ha)$ and $FD_2(Ha)$ (independent of the path).

The terms $T_{\zeta_1 \zeta_2}^2$ depend on the individual Cr-halide and halide-halide hopping integrals. In particular, the ratio $(pp\sigma)/(pp\pi)$ of the halide-halide hopping integrals may modify the relative magnitudes of the $J_2$, $J_4$ and $J_5$ couplings. The values for $T_{\zeta_1 \zeta_2}^2$ for the inter-planar couplings are shown in Tab. V and the resulting energy factors as well as the values of the $J_2$, $J_4$, $J_5$ coupling constants are given in Tab. VI. For CrBr$_3$ these numbers compare well with the neutron data of Ref. [3], though the ratio $J_4/J_5$ is not very good. Note that the ‘vertical’ $J_2$ always is relatively large and anti-ferromagnetic. In the case of CrBr$_3$ and CrI$_3$, this coupling is over-compensated by the ferromagnetic $J_4$ and $J_5$ couplings. This is also found for CrCl$_3$ unless the ratio $(pp\sigma)/(pp\pi)$ was shifted from the usual range of 3 - 5 to an extremely large value of $\approx 36$, such that $J_c = \sum_{\zeta_1=2,4,5} z_1 J_i > 0$. If so, the inter-planar coupling is probably anti-ferromagnetic for CrCl$_3$ with this set of parameters. (But note, that $J_c$ can not be identified with the inter-planar coupling $J_\perp$ in a model with two couplings $J_\parallel$ and $J_\perp$.)

Nevertheless, we think that $(pp\sigma)/(pp\pi) = 36$ is outside the range of physically meaningful parameters. Thus we suspect that there may indeed exist a difference in the low temperature structures of CrCl$_3$ and the other two materials. We finally note that the dominant magnetic coupling constant of these materials is the intra-planar $J_1$ (4th order super-exchange). As we pointed out in Sec. II A, the FD-type coupling should cause a minority spin polarization on the halide ligands, as observed in the neutron study of spin density distributions in CrBr$_3$ by Radhakrishna and Brown [4].

### IV. CONCLUSION

Nonmetallic transition-metal oxides and halides appear to be the most prominent members of the family of Mott-Hubbard insulators. In this paper we have generalized the expansion of extended Hubbard models by a Rayleigh-Schrödinger perturbation series into Heisenberg models, with the goal to determine general expressions for the super-exchange coupling constants. Each part of this series that corresponds to an exchange of the spins in the half-filled orbitals $\zeta_1$ and $\zeta_2$ of two magnetic ions $M_1$ and $M_2$ gives a contribution to the (isotropic) coupling constant $J = \sum_{\zeta_1, \zeta_2} J_{\zeta_1, \zeta_2}$ of the Heisenberg Hamiltonian

$$H = J \sum_i S_i \cdot S_j \quad \frac{1}{4} (S_1 \cdot S_2).$$

Here $S_i$ denotes the total spin at the magnetic site $M_i$. This form of the effective spin Hamiltonian follows from the assumption of a relatively strong Hund interaction at the magnetic sites such that $S_i = \sum_{\zeta} S_{\zeta}$.

The couplings $J_{\zeta_1, \zeta_2}$ are built from two different parts. Either the exchange takes place involving only the d orbitals $\zeta_1$ and $\zeta_2$. This ‘direct super-exchange’ interaction is anti-ferromagnetic (A) in general. Or ‘indirect super-exchange’ occurs, which involves an additional, empty (E) or doubly occupied (D), d orbital. In this case, because of the Hund interaction, the coupling is negative in general. These general results correspond to the Goodenough-Kanamori-Anderson (GKA) rules as stated in the introduction, yet quantitative results - and this may include the sign of the coupling constant - depend strongly on details of the involved exchange processes. The simplest cases are those when only one specific path via ligands occurs. Then, each hopping integral enters quadratically the expressions for the coupling constants $J_i$. Therefore, the sign of $J$ is given by kind of super-exchange, direct (+) or indirect (−). The magnitude of $J$ depends on i) an effective energy denominator $E_Q$ and ii) on an effective term $t$, such that $J^2 = t^2/E_Q$. Here $Q = A, FE, FD$ represents the different possibilities of super-exchange and $t = \prod_{k=1}^{N-1} t_k / \Delta^N$, where $N$ denotes the number of ligands involved in the exchange and the $t_k$ the corresponding hopping integrals. $\Delta$ is a characteristic energy of an excited state with $t_k/\Delta \ll 1$. Thus $t$ decreases rapidly with increasing path length $N$, $1/E_Q$, which we also call $Q_N$, is strongly influenced by the number of exchange channels. This number depends on the specific super-exchange A, FE, or FD, each of which exhibits a different dependence on $N$. $FE_N$ is independent of $N$, there are always only two channels. $A_N$ is of the form $A_N = 2(1/U + N/\Delta)$ and $FD_N$ includes in addition a term quadratic in $N$. For $N = 1$ one finds $FE_1 < FD_1 < A_1$, mainly because $FE$ and $FD$ contain an additional factor $J_{H}/U$. With growing number of ligands we may find cases $A_N < FD_N$. As a consequence, when $N > 1$, the interaction of ions with more than half-filled d-shells should exhibit a bigger tendency.
towards ferromagnetic coupling than those with less than half-filled d-shells (hole picture, empty ligands).

The exchange can also take place via several (P) interfering paths. The structure of a coupling constant resulting from P paths with N ligands each is \( J^Q(P) = \frac{1}{2} \sum_{p,p'=1}^P (Q_N^p + Q_N^{p'}) \delta_{pp'} \). Here \( p \) and \( p' \) indicate the various paths. The energy denominators \( Q_N^p \) are the same as in the case of \( P = 1 \), yet the hopping factors no longer enter quadratically into the expressions for the effective hopping integrals. In the presence of inequivalent paths \( (Q_N^p \neq Q_N^{p'}) \) this leads to the possibility of a ferromagnetic coupling of two spins by direct super-exchange as was discussed in Ref. 12. When all \( P \) paths are equivalent, the \( J^Q \) are again quadratic in the effective hopping, i.e. the sign is fixed, but the magnitude may be strongly influenced by interference. This behavior always occurs for case \( FE \), since \( FE_N \) is independent of \( N \).

From the above considerations we see that even the sign of the coupling cannot be guessed except in the simplest cases, even if the orbital order at the magnetic sites is known. For better quantitative estimates, a reasonable knowledge of hopping integrals, of charge transfer gaps and of \( U \) parameters is required. These numbers are accessible, in principle, via total energy calculations using constrained density functional theory, see e.g. Ref. 24.

Our present studies are based on such evaluations for \( \text{La}_2\text{CuO}_4 \).

In order to test the quality of our treatment, we have investigated some ferromagnetic Cr compound insulators, where the GKA rules cannot be applied in any simple fashion. In \( \text{Rh}_2\text{CrCl}_4 \), with the same structure as \( \text{K}_2\text{CuF}_4 \), orbital order of the Cr\(^{2+}\) ions occurs because of the Jahn-Teller effect. However, for the first nearest neighbor (1NN) intra-planar coupling, the direct super-exchange \( J_A \) does not vanish, in contrast to the case of \( \text{K}_2\text{CuF}_4 \). Nevertheless, we find \( |J_{DF}^1| > J_A^1 \) for various reasons as discussed above and in detail in chapter 3. Also the quantitative result agrees well with experiment. Concerning the inter-planar coupling, we believe that \( \text{Rh}_2\text{CrCl}_4 \) is rather similar to \( \text{K}_2\text{CuF}_4 \) which has been studied previously. We note that some of the \( N = 2 \) super-exchange paths involve both empty (Cl\(^-\)) and doubly occupied (Rh\(^+\)) ligands. Such cases, which may occur in ternary compounds, are not covered by our present theoretical treatment.

The Cr\(^{3+}\) ions of the Cr tri-halides \( \text{CrCl}_3 \), \( \text{CrBr}_3 \) and \( \text{CrI}_3 \) are not Jahn-Teller ions and, thus, do not exhibit orbital ordering. The 1NN intra-planar coupling involves two equivalent \( N = 1 \) paths with Cr-Ha-Cr angles close to 90\(^\circ\). The \( FD \) coupling dominates the \( A \) coupling, both due to the 90\(^\circ\) angles and, also because of the very many \( FD \) channels. The inter-planar coupling takes place via three different \( N = 2 \) contributions, \( J_2 \), \( J_4 \) and \( J_5 \). Each of the couplings is mediated via a variety of paths. Using reasonable hopping parameters we get good agreement with the values \( J_2 \), \( J_4 \), \( J_5 \) as measured by neutron scattering in the case of \( \text{CrBr}_3 \). Further we obtain ferromagnetic coupling for both \( \text{CrBr}_3 \) and \( \text{CrI}_3 \). In the case of \( \text{CrCl}_3 \) we suspect that the low temperature structure is not \( R3 \).

We come to the conclusion that the perturbational calculation of the coupling constants in the non-metallic 3d-transition-metal compounds is an appropriate instrument, qualitatively as well as quantitatively. The qualitative agreement may appear somewhat surprising. It has been pointed out earlier that the higher order contributions of the perturbation series can have a similar magnitude as the lowest one. Under such circumstances we would expect that the coupling between next nearest neighbors becomes important. Experimentally, however, ratios \( J_2/J_1 \approx 10^{-2} \) are reported. An additional consequence should be that terms of the form \( \langle S_i \cdot S_j \rangle \langle S_k \cdot S_l \rangle \) can not be neglected. We are not aware of any experimental evidence for the importance of such 4-spin terms. The question remains how the good agreement between experimental value and the lowest order results can be understood.

**FIG. 1.** Spin interaction by super-exchange via one empty ligand with one orbital. a) anti-ferromagnetic case, b) and c) the ferromagnetic cases. The double arrow represents the direct exchange \( J_H \) that leads to the second Hund’s rule. b) and c) are differ by the occupation of the spin-free orbital at the magnetic ion. It is not possible to transform one into the other by a particle-hole transformation.

**FIG. 2.** a) Direct interaction on a linear chain between two half-filled orbitals \( \zeta_1 \) and \( \zeta_2 \) at the sites \( M_1 \) and \( M_2 \) via \( N \) unoccupied ligands with one orbital each. Only nearest neighbor hopping is considered. b) Indirect interaction between two half-filled orbitals \( \zeta_1 \) and \( \zeta_2 \) at the sites \( M_1 \) and \( M_2 \) involving one unoccupied orbital \( \eta \) via \( N \) unoccupied ligands with one orbital each which build a linear chain. Only the hopping between nearest neighbors is allowed.
FIG. 3. Super-exchange via three different paths with three ligands each.

FIG. 4. Projection of a Cr-plane with the corresponding ligands on the ab-plane. The small circles denote the Cr-ions, the large ones the halides. The darker ligand ions lie below the Cr-plane the lighter ones above. The Cr planes are stacked such that the Cr hexagon center successively lies at points A, B and C.

FIG. 5. Crystal structure of the tri-halides CrCl$_3$, CrBr$_3$ and CrI$_3$. The hexagonal unit cell contains four Cr-planes. Large circles denote the halide ions the smaller circles the Cr atoms. Clusters corresponding to the couplings $J_1$, $J_2$ and $J_4$, see Fig. 6, are indicated. Also shown are the position of a ligand octahedron and the corresponding local coordinate system of a Cr ion. The distances $d$, $l$ and $s$ are given in Tab. III.

FIG. 6. Near neighbor coupling constants $J_1$, $J_2$, $J_4$ and $J_6$ in CrHa$_3$. There exist three couplings $J_1$, one $J_2$, three $J_4$ and six $J_5$ per Cr.

TABLE I. Electronic parameters for Rb$_2$CrCl$_4$ (in eV).

| $(p\delta\sigma)$ | $(p\delta\pi)$ | $U$ | $J_H$ | $\Delta_{Cl}$ |
|-----------------|----------------|-----|--------|----------------|
| 1.0             | 0.4            | 4   | -0.52  | 4.15           |

TABLE II. Lattice parameters for CrCl$_3$ (Ref. 14), for CrBr$_3$ (Ref. 13) and for CrI$_3$ (Ref. 20). For CrI$_3$ the $x$, $y$, $z$ and $u$ values are approximated by the ‘ideal’ values, $2/3$, $0$, $z_i = a_0/2\sqrt{3}c_0$, and $1/3$, respectively.

|                | CrCl$_3$ | CrBr$_3$ | CrI$_3$ |
|----------------|----------|----------|---------|
| $a_0$          | 5.94Å    | 6.27Å    | 6.86Å   |
| $c_0$          | 17.33Å   | 18.21Å   | 19.88Å  |
| $x$            | 0.6507   | 0.6523   | 0.6666  |
| $y$            | -0.0075  | 0.0012   | 0.0     |
| $z$            | 0.0757   | 0.0786   | 0.0813  |
| $u$            | 0.3323   | 0.3339   | 0.3333  |
TABLE III. Relevant atomic separations for the CrHa₃ compounds (in Å, for definition, see Fig. 3). Because of the distortions $u \neq 1/3$, $y \neq 0$ etc. there exist two different distances $d$ (Cr-Ha) and $l$ (Ha-Ha). Also given are the separations of the Ha planes $r_1$ (Cr enclosed) and $r_2$ (empty site enclosed).

|       | CrCl₃ | CrBr₃ | CrI₃ |
|-------|-------|-------|------|
| $s$   | 3.43  | 3.62  | 3.96 |
| $d_1$ | 2.37  | 2.50  | 2.80 |
| $d_2$ | 2.33  | 2.50  | 2.80 |
| $l_1$ | 3.69  | 3.80  | 4.09 |
| $l_2$ | 3.80  | 3.87  | 4.09 |
| $r_1$ | 2.62  | 2.86  |      |
| $r_2$ | 3.15  | 3.21  |      |

TABLE IV. Electronic parameters (in eV) for CrHa₃. The hopping integrals are given for the ‘ideal’ structure. Distance variations are included via exponentials $e^{\beta(r_0-r)}$ with $\beta^d = 1.5$ eV/Å, $\beta^p = 2$ eV/Å, $\beta^{pd} = 2$ eV/Å and $\beta^{pp} = 2.5$ eV/Å, where $r_0$ denotes the distance in the ideal structure.

|       | CrCl₃ | CrBr₃ | CrI₃ |
|-------|-------|-------|------|
| $\Delta$ | 3.8   | 3.3   | 3.0  |
| $U$    | 3.5   | 3.5   | 3.5  |
| $4\mu$ | -0.1  | -0.1  | -0.1 |
| $(p\sigma)$ | -1.15 | -1.12 | -1.06 |
| $(p\pi)$ | 0.66  | 0.69  | 0.70 |
| $(pp\sigma)$ | 0.05  | 0.10  | 0.12 |
| $(pp\pi)$ | -0.0014 | -0.019 | -0.04 |

TABLE V. CrHa₃: Values of various effective hopping squares for the couplings $J_1$, $J_2$, $J_4$ and $J_5$ (in $10^{-4}$ eV²).

|       | CrCl₃ | CrBr₃ | CrI₃ |
|-------|-------|-------|------|
| $J_1$ | 9733  | 7670  | 4802 |
| $J_2$ | 12211 | 8862  | 5506 |
| $J_4$ | 84    | 359   | 444  |
| $J_5$ | 18    | 79    | 107  |

TABLE VI. CrHa₃: Effective energy denominators $A$ and $FD$ (in eV⁻¹) and coupling constants (in meV).

|       | CrCl₃ | CrBr₃ | CrI₃ |
|-------|-------|-------|------|
| $A_1$ | 1.10  | 1.18  | 1.24 |
| $A_2$ | 1.64  | 1.77  | 1.91 |
| $FD_1$ | -0.94 | -1.11 | -1.28 |
| $FD_2$ | -2.28 | -2.76 | -3.36 |
| $J_1$ | -4.8  | -7.6  | -12.4 |
| $J_2$ | 0.059 | 0.26  | 0.31  |
| $J_4$ | -0.007 | -0.08 | -0.33 |
| $J_5$ | -0.006 | -0.09 | -0.33 |
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