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# A DFT based ligand field model for magnetic exchange coupling in transition metal dimer complexes: (ii) application to magnetic systems with more than one unpaired electron per site

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## Abstract

The DFT based ligand field model for magnetic exchange coupling proposed recently, has been extended to systems containing more than one unpaired electron per site. The guidelines for this extension are described using a model example – the complex  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$ . The exchange Hamiltonian,  $H_{\text{ex}} = -J_{12}\mathbf{S}_1\mathbf{S}_2$  has been simplified using symmetry principles, i.e. utilizing the  $D_{3h}(C_{3v})$   $\text{Cr}^{\text{III}}$  – dimer(site) symmetry. Both antiferro- and ferromagnetic exchange coupling constants are found to yield important contributions to the value of the (negative, antiferromagnetic) exchange coupling constant in good agreement with experiment.

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## 1. Introduction

Exchange coupling in transition metal (TM) dimers has been and still is of great challenge for both experimentalists and theoreticians [1]. Theoretical work has been mainly based on two approaches; semi-empirical models focus on chemically meaningful parameterizations of the exchange Hamiltonian  $H_{\text{ex}} = -J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2$ . Their

drawback lies in the high number of model parameters, to necessitate frequently assumptions which are sometimes not justified. Thus, within Andersons' theory of superexchange [2], ferromagnetic couplings are neglected [3], focus being placed on the kinetic (antiferromagnetic) contributions to the exchange coupling constant  $J_{12}$ . Ab initio work [4–8] and DFT calculations (broken symmetry approach [9–11]) on the other hand are free from such shortcomings. However, resulting theoretical values of  $J_{12}$  cannot be analyzed to provide a bridge between basic theory and chemical intuition. In addition theoretically, excited state exchange coupling is not easily accessible by

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this methodology, studies being focussed mainly on non-degenerate ground states.

In our first work of this series [12], a DFT based ligand field model for magnetic exchange coupling in TM dimer complexes has been proposed. Basic principles have been formulated using TM dimers with a single unpaired electron per site. In this letter, we extend the approach to more involved situations which include more than one electron per site. Instead of developing a general formalism, we pragmatically take a simple model example, that of a  $\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}$  dimer. Detailed information from experiment on such systems [13] provide a stringent test of the theory. The method allows to both calculate and analyze the exchange integral  $J_{12}$ . A comparison with earlier theoretical treatments will be included to check the existing concepts and approximations made. Finally, outlooks for applications including excited states and problems encountered in the case of orbital degeneracy will be briefly discussed.

## 2. Computational details

DFT calculations have been performed using the ADF program package, version 2002.02 [14–16]. The approximate SCF KS one-electron equations are solved by employing an expansion of the molecular orbitals in a basis set of Slater-type orbitals (STO). All atoms were described through triple- $\zeta$  STO basis sets given in the program database (TZP basis) and the core-orbitals up to 3 p for the TM ('large core') and up to 1 s (for O, C, N) were kept frozen. Exchange-correlation potential and energies have been computed according to the Vosko, Wilk, and Nusair's (VWN) [17] parameterization of the electron gas data and gradient corrections (GGA) have been included. For the generalised gradient approximation (GGA) we used the functional of Perdew et al. [18], which uses gradient correction to the local expression both of the exchange and the correlation energies. Exchange parameters in this study are calculated using energies of single Slater determinants (SD) as a data base. SD energies have been obtained using spin-unrestricted non-SCF DFT calculations based on average-of-configuration electron density. This

is routinely accomplished in ADF code making use of 'SLATERDETERMINANTS' keyword followed by occupation numbers defining each SD. SD energies have been used in a second step in a least square MATLAB program to fit model parameters of the exchange Hamiltonian in the basis of local (magnetic) orbitals to yield  $J_{12}$  and various contributions to it.

## 3. Results

The  $(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3^{3+}$  model complex (Fig. 1) approximates the coordination geometry of a series of compounds with the same bridging geometry containing cyclic amines as terminal ligands [19]. The octahedral  $t_{2g}$  orbitals of  $\text{Cr}^{\text{III}}$  are split by the local ligand field of  $C_{3v}$  symmetry and give rise to one  $a_1(a)$  and two  $e(x,y)$  magnetic orbitals, whose energies and eigenvectors (d-contributions only) are listed in Table 1. They have predominantly d-character as expected. Neglecting in a first and rough analysis the overlap between the two metal centres ( $t_{12}$ , transfer, hopping integral equals to zero) we can characterize the intra-atomic (Hund) coupling between the singly occupied  $t_{2g}$  orbitals by the parameters  $k_{ae}$  and  $k_{ee}$  (Table 2). In a cubic ligand field approach, the value of these integrals equals  $3B+C$  which lead to the  $^4A_2$  ground state and an  $^2E$  excited state,

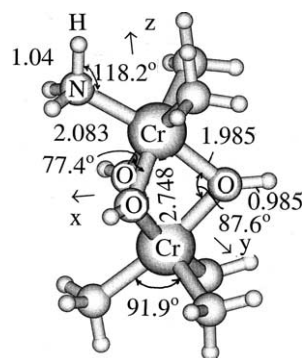


Fig. 1. The DFT optimized geometry (spin-restricted DFT geometry optimization), adopted for the calculation of the exchange coupling constant in the  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$  model complex.

Table 1

Kohn–Sham orbitals and energies of magnetic d-orbitals on centers  $M_1$  and  $M_2$  (above) and their combinations to dimer  $M_1$ – $M_2$  orbitals (below) hosting the magnetic electrons in the  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$  model complex

Localized ( $\text{C}_{3v}$ ) orbitals					
Notation	Symmetry	Linear combination	Energy		
$ x_1\rangle$	$e(x)$ [E1:1]	$0.783d_{x^2y}(1)d_{x^2-y^2}(1)-0.515d_{xz}(1)+\dots$	−14.500		
$ x_2\rangle$	$e(x)$ [E1:1]	$0.783d_{x^2-y^2}(2)+0.515d_{xz}(2)+\dots$	−14.500		
$ y_1\rangle$	$e(y)$ [E1:2]	$0.783d_{xy}(1)+0.515d_{yz}(1)+\dots$	−14.500		
$ y_2\rangle$	$e(y)$ [E1:2]	$0.783d_{xy}(2)-0.515d_{yz}(2)+\dots$	−14.500		
$ a_1\rangle$	$a_1$ A1	$0.956d_{z^2}(1)+\dots$	−14.765		
$ a_2\rangle$	$a_1$ A1	$0.956d_{z^2}(2)+\dots$	−14.765		
Dimmer ( $\text{D}_{3h}$ ) orbitals					
Notation	Symmetry	MO	Energy	%d.	$M_1$ – $M_2$ Bonding type
$ 1\rangle$	$a_1'$ (AA1)	$(a_1+a_2)/\sqrt{2}$	−15.196	89	(b)
$ 2\rangle$	$e''\xi$ (EEE1:1)	$(y_1-y_2)/\sqrt{2}$	−14.759	95	(b)
$ 3\rangle$	$e''\eta$ (EEE1:1)	$(x_1-x_2)/\sqrt{2}$	−14.759	95	(b)
$ 4\rangle$	$a_2''$ (AAA2)	$(a_1-a_2)/\sqrt{2}$	−14.335	94	(a)
$ 5\rangle$	$e'\varepsilon$ (EE1:1)	$(x_1+x_2)/\sqrt{2}$	−14.240	81	(a)
$ 6\rangle$	$e'\varsigma$ (EE1:2)	$(-y_1-y_2)/\sqrt{2}$	−14.240	81	(a)

Symmetries according to the irreducible representations of the monomer  $\text{C}_{3v}$  and the dimer  $\text{D}_{3h}$  point groups, and their notations in the ADF program package (in square brackets), along with the d-electron percentage and the type of  $M$ – $M$  overlap (bonding – b, antibonding – a) are also included. Only d-orbital contribution to a given localized MO are listed.

Table 2

Symmetry independent intra- and inter-atomic exchange integrals  $[dl_i dl_j | dl_i dl_j]$  in the basis of the magnetic  $t_{2g}(\text{O}_h) \rightarrow a_1(a) + e(x,y)$  ( $\text{C}_{3v}$ ) orbitals localized on each center, as well as charge-transfer ( $U_{ii}$ ) and hopping ( $t_{ii}$ ) energy parameters ( $i = a, e$ ) in a homo nuclear dimer complex with face-shared octahedra ( $\text{D}_{3h}$ -symmetry)

$dl_i dl_j \rightarrow$ $\downarrow$	$a_1$	$x_1$	$y_1$	$a_2$	$x_2$	$y_2$
$a_1$	–	$k_{ae}$	$k_{ae}$	$K_{aa}$	$K_{ae}$	$K_{ae}$
$x_1$	$k_{ae}$	–	$k_{ee}$	$K_{ae}$	$K_{ee}$	$K'_{ee}$
$y_1$	$k_{ae}$	$k_{ee}$	–	$K_{ae}$	$K'_{ee}$	$K_{ee}$
$a_2$	$K_{aa}$	$K_{ae}$	$K_{ae}$	–	$k_{ae}$	$k_{ae}$
$x_2$	$K_{ae}$	$K_{ee}$	$K'_{ee}$	$k_{ae}$	–	$k_{ee}$
$y_2$	$K_{ae}$	$K'_{ee}$	$K_{ee}$	$k_{ae}$	$k_{ee}$	–

$$a_1 \leftrightarrow a_2 \ U_{aa}, t_{aa}; x_1 \leftrightarrow x_2 \ U_{ee}, t_{ee}; y_1 \leftrightarrow y_2 \ U_{ee}, t_{ee}.$$

separated by  $3 \cdot (3B+C)$ . This gives rise to six states in the dimer, obtained when combining products of  $^4A_2(M_s = 3/2)$  and  $^4A_2(M_s = 1/2)$  and  $^4A_2(M_s = 3/2)$  and  $^2E(M_s = 1/2)$  for sites 1 and 2. Including inter atomic exchange coupling we have four more independent parameters,  $K_{aa}$ ,  $K_{ee}$ ,  $K_{ae}$

and  $K'_{ee}$  (Table 2) which are analogous to the exchange integral  $K_{ij} = \int \int \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_1) (1/r_{12}) \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$  (with  $\phi_i$  and  $\phi_j$  – the magnetic orbitals) described previously [12]. A list of the SD's ( $\phi_1$ – $\phi_6$ ), connected with the flip of one spin starting from the  $S = 3$  state, which we take as energy reference is listed in Table 3. Here we also include functions for a transfer of one electron from  $M_1$  to  $M_2$  or vice versa ( $\phi_7$ – $\phi_9$ ). The latter mix via the hopping integrals  $t_{aa}$  (for species  $a_1$ ) and  $t_{ee}$  {for species  $e(x, y)$ } with the corresponding  $\phi_1$  to  $\phi_6$  functions to lead to a lowering of  $S = 2$  ( $M_s = 2$ ) spin states with respect to the  $S = 3$  ( $M_s = 2$ ) one. The matrix of the Hamiltonian (Table 4) contains in addition the charge transfer energies  $U_{aa}$  and  $U_{ee}$ , corresponding to the transfer of one electron from (to) the singly occupied orbitals  $a_1$  and  $e$  on center 1(2) and vice versa. These quantities are differences between 'on-site' and 'intersite' Coulomb repulsion terms, screened by electrons, not directly involved in the exchange mechanism. In Table 4 additional electron repulsion parameters appear in the sub-matrix,

Table 3

SD constructed from localized magnetic spin-orbitals accounting for spin-flip and charge-transfer transitions imposed on the  $S = 3$  reference state, of relevance for the ground state exchange coupling in a  $\text{Cr}^{\text{III}}$  dimer complex of  $D_{3h}$  symmetry

Spin-flip	Charge-transfer
$\phi_1 =  a_1^- x_1^+ y_1^+ a_2^+ x_2^+ y_2^+ $	$\phi_7 = (1/\sqrt{2}) [ a_1^+ a_1^- x_1^+ y_1^+ x_2^+ y_2^+  +  x_1^+ y_1^+ a_2^+ a_2^- x_2^+ y_2^+ ]$
$\phi_2 =  a_1^+ x_1^- y_1^+ a_2^+ x_2^+ y_2^+ $	
$\phi_3 =  a_1^+ x_1^+ y_1^- a_2^+ x_2^+ y_2^+ $	$\phi_8 = (1/\sqrt{2}) [ a_1^+ x_1^+ x_1^- y_1^+ a_2^+ y_2^+  +  x_1^+ y_1^+ a_2^+ x_2^+ x_2^- y_2^+ ]$
$\phi_4 =  a_1^+ x_1^+ y_1^+ a_2^- x_2^+ y_2^+ $	
$\phi_5 =  a_1^+ x_1^+ y_1^+ a_2^+ x_2^- y_2^+ $	$\phi_9 = (1/\sqrt{2}) [ a_1^+ x_1^+ y_1^+ y_1^- a_2^+ x_2^+  +  a_1^+ x_1^+ a_2^+ x_2^+ y_2^+ y_2^- ]$
$\phi_6 =  a_1^+ x_1^+ y_1^+ a_2^+ x_2^+ y_2^- $	

corresponding to the  $M_1 \leftrightarrow M_2$  charge transfer configurations ( $K_{11}^{22}$ ,  $K_{12}^{21}$ ,  $X_{12}^{21}$ ,  $X_{11}^{22}$ ). They are defined in the legend under Table 7 and shown to be negligible in a good approximation. In order to determine the model parameters we consider the MO's of the dimer with symmetries, energies and d-orbital populations listed in Table 1. We notice that  $a_1'$  and  $a_2''$ ;  $e''\xi$  and  $e'\zeta$ ;  $e''\eta$  and  $e'\varepsilon$  represent the plus and minus linear combinations of  $a_1$ ,  $e(y)$  and  $e(x)$  orbitals on centres 1 and 2, respectively. The number of exchange ( $K_{ab}$ ) and Coulomb integrals ( $J_{ab}$ ) between the dimer MOs are strongly reduced by symmetry. There are only 9 and 13 such symmetry independent parameters, respectively (Table 5). Using our DFT procedure we can calculate the  $K_{ab}$ -type parameters ( $g_1$ – $g_9$ ) from a fit to all 64 SDs resulting from the flip of 1, 2 and 3 spins starting from the  $S = 3$  ( $M_s = 3$ ) state, which we take again at zero energy. There is a remarkable consistency in this data reduction as evidenced by the small differences between DFT and calculated (using  $g_1$ – $g_9$  values, Table 7 and equations, Table 6) SD energies (standard deviations between two sets of data is less than 0.02 eV!). In Table 6 we include some of these SDs ( $\text{SD}_1$ – $\text{SD}_6$ ) along with the  $\text{SD}_7$ – $\text{SD}_{13}$  with doubly occupied MOs, their DFT energies and energy expressions in terms of symmetry independent Coulomb  $J_{ab}$ -type ( $f_1$ – $f_{13}$ ) and  $K_{ab}$ -type ( $g_1$ – $g_9$ ) parameters. In Table 7 we list the  $g_i$  ( $i = 1, \dots, 9$ ) parameters and their expressions in terms of quantities related to localized orbitals. As seen, the parameters  $g_2$  and  $g_7$  yield immediately  $U_{aa}$  and  $U_{ee}$ , respectively. We notice that the other parameters vary in a narrow range,  $g_{av} = 0.234 \pm 0.025$  eV, their values being dominated by the intra-atomic exchange integral  $k_{at} = 3B + C \cong k_{ae} \cong k_{ee} = 4g_{av}$ . As can

easily be derived using the expression in Table 7, the exchange parameters  $K_{aa}$  and  $K_{ee}$  and the hopping integrals  $t_{aa}$  and  $t_{ee}$  can be calculated by substituting the  $g_i$  and SD energies in Eqs. (1)–(4).

$$K_{aa} = (1/4)(f_1 + f_8 - 2f_3) \\ = (1/4)[E(\text{SD}_8) + E(\text{SD}_9) - 2g_1 - 2g_2 - 2g_3 - 2g_5 - 2g_8] \quad (1)$$

$$K_{ee} = (1/4)(f_5 + f_{12} - 2f_{10}) \\ = (1/4)[E(\text{SD}_{10}) + E(\text{SD}_{11}) - g_1 - g_3 - g_4 - g_5 - 2g_6 - 2g_7 - g_8 - g_9] \quad (2)$$

$$t_{aa} = (1/4)[E(\text{SD}_9) - E(\text{SD}_8)] \quad (3)$$

$$t_{ee} = (1/4)[E(\text{SD}_{11}) - E(\text{SD}_{10})] \quad (4)$$

Finally, the exchange integrals  $K_{ae}$ ,  $K'_{ee}$  which introduce ferromagnetic exchange between spins on orbitals of different local symmetry can be approximated using Eqs. (5) and (6). Here we utilise values of one-center  $k_{ae}$  and  $k_{ee}$  exchange integrals, derived in a separate DFT calculation in which a non-magnetic ion of about the same

$$K_{ae} \cong (1/2)(g_1 + g_3 + g_5 + g_8) - k_{ae} \quad (5)$$

$$K'_{ee} \cong 2g_6 - k_{ee} \quad (6)$$

size as  $\text{Cr}^{\text{III}}$  but without d-electrons is replaced for one of the  $\text{Cr}^{\text{(III)}}$  ion, while keeping the

Table 4  
Matrix of the Hamiltonian in a basis of SD constructed from localized magnetic orbitals and its parameterization using DFT

Basis functions	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_4$	$\phi_5$	$\phi_6$	$\phi_7$	$\phi_8$	$\phi_9$
$\phi_1$	$2K_{ae} + K_{aa} + 2K_{ae}$	$-K_{ae}$	$-k_{ae}$	$-K_{aa}$	$-K_{ae}$	$-K_{ae}$	$-\sqrt{2}(t_{aa} + R_{aa})$	0	0
$\phi_2$	$-k_{ae}$	$k_{ae} + k_{ee} + K_{ee} + K_{ae} + K'_{ee}$	$-k_{ee}$	$-K_{ae}$	$-K_{ee}$	$-K'_{ee}$	0	$-\sqrt{2}(t_{ee} + R_{ee})$	0
$\phi_3$	$-k_{ae}$	$-k_{ee}$	$k_{ae} + k_{ee} + K_{ee} + K_{ae} + K'_{ee}$	$-K_{ae}$	$-K'_{ee}$	$-K_{ee}$	0	0	$-\sqrt{2}(t_{ee} + R_{ee})$
$\phi_4$	$-K_{aa}$	$-K_{ae}$	$-K_{ae}$	$2k_{ae} + K_{aa}$	$-k_{ae}$	$-k_{ae}$	$\sqrt{2}(t_{aa} + R_{aa})$	0	0
$\phi_5$	$-K_{ae}$	$-K_{ee}$	$-K'_{ee}$	$-k_{ae}$	$k_{ae} + k_{ee} + K_{ee} + K_{ae} + K'_{ee}$	$-k_{ee}$	0	$\sqrt{2}(t_{ee} + R_{ee})$	0
$\phi_6$	$-K_{ae}$	$-K'_{ee}$	$-K_{ee}$	$-k_{ae}$	$k_{ae} + k_{ee} + K_{ee} + K_{ae} + K'_{ee}$	0	0	0	$\sqrt{2}(t_{ee} + R_{ee})$
$\phi_7$	$-\sqrt{2}(t_{aa} + R_{aa})$	0	0	$\sqrt{2}(t_{aa} + R_{aa})$	0	0	$U_{aa} + 2k_{ae} + K_{aa}/2 + 2K_{ee}$	$-K_{11}^{22} + K_{12}^{21}$	$-K_{11}^{22} + K_{12}^{21}$
$\phi_8$	0	$-\sqrt{2}(t_{ee} + R_{ee})$	0	0	$\sqrt{2}(t_{ee} + R_{ee})$	0	$-K_{11}^{22} + K_{12}^{21}$	$U_{ee} + k_{ae} + k_{ee} + K_{ae} + K'_{ee} + K_{ee}/2 + K_{11}^{22}$	$X_{12}^{21} - X_{11}^{22}$
$\phi_9$	0	0	$-\sqrt{2}(t_{ee} + R_{ee})$	0	0	$\sqrt{2}(t_{ee} + R_{ee})$	$-K_{11}^{22} + K_{12}^{21}$	$X_{12}^{21} - X_{11}^{22}$	$U_{ee} + k_{ae} + k_{ee} + K_{ae} + K_{ee}/2 + K_{ee} + K'_{ee}$

cluster geometry unchanged. For these purposes we have chosen  $\text{Ga}^{3+}$ , including its 10 d-electrons in a frozen core ( $\text{SD}'_1\text{--SD}'_3$ , Table 6). In addition in Eq. (6) use was made of the finding that combinations  $K_{12}^{21} + K_{11}^{22}$  and  $X_{12}^{21} + X_{11}^{22}$  have been found negligibly small (0.001 eV) and thus neglected. Values of all model parameters are listed in Table 8 along with  $J_{12} = -0.016$  eV, as calculated from the difference between the lowest eigenvalue of  $S = 2(M_s = 2)$  (of the form  $\phi_1 + \phi_2 + \phi_3 - \phi_4 - \phi_5 - \phi_6$ ) and  $S = 3(M_s = 3)$  (of the form  $\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$ , divided by 3, Lande rule  $E_{S-1} - E_S = S \cdot J_{12}$ ). It compares nicely with the one from experiment ( $-0.020 \pm 0.002$  eV [13]) but is definitely smaller than the BS-DFT result ( $-0.041$  eV). Using perturbation theory (Eq. (7)) yields a smaller value of  $J_{12}(p) = -0.012$  eV and allows to further decompose this quantity into orbital terms yielding ferro- and antiferromagnetic contributions to  $J_{12}(p)$ . It is interesting to compare our results

$$J_{12}(p) = (1/9)[(J_{aa}) + 2(J_{ee}) + 2(J'_{ee}) + 4(J_{ae})]$$

$$J_{12}^{\text{af}} (1/9)[(-0.325) + 2(-0.105) + 2(0) + 4(0)] \\ = -0.059 \text{ eV}$$

$$J_{12}^{\text{f}} (1/9)[(0.040) + 2(0.122) + 2(0.028) + 4(0.022)] \\ = 0.047 \text{ eV}$$

$$\text{Total } (1/9)[(-0.285) + 2(0.017) + 2(0.028) \\ + 4(0.022)] = -0.012 \text{ eV}$$

$$\text{Empirical[13]} (1/9)[(-0.145) + 2(-0.009) + 0 + 0] \\ = -0.018 \quad (7)$$

with those deduced from magnetic and spectroscopic data [13]. In the latter estimation the ferromagnetic contributions to  $J_{aa}$ ,  $J_{ee}$ ,  $J_{ae}$  and  $J'_{ee}$  have been neglected. However the overall  $J_{12}$  values do not differ much though,  $J_{aa}^{\text{af}}$ ,  $J_{ee}^{\text{af}}$  are numerically quite different: ferromagnetic terms are not negligible. Both sets of data show however, that direct Cr–Cr coupling ( $J_{aa}$ ) dominates in  $J_{12}$ .

Table 5

Symmetry based parameterization of exchange ( $g_i$ ,  $i = 1, \dots, 9$ ) and Coulomb repulsion ( $f_i$ ,  $i = 1, \dots, 13$ ) integrals between  $M_1$  and  $M_2$  dimer orbitals of a homonuclear complex with face shared octahedra ( $D_{3h}$  symmetry)

Orbital	$ 1\rangle, a_1'$	$ 2\rangle, e''\zeta$	$ 3\rangle, e''\eta$	$ 4\rangle, a_2''$	$ 5\rangle, e'\varepsilon$	$ 6\rangle, e'\zeta$
$\langle 1 , a_1'$	$f_1$	$g_1, f_2$	$g_1, f_2$	$g_2, f_3$	$g_3, f_4$	$g_3, f_4$
$\langle 2 , e''\zeta$	$g_1, f_2$	$f_5$	$g_4, f_6$	$g_5, f_7$	$g_6, f_9$	$g_7, f_{10}$
$\langle 3 , e''\eta$	$g_1, f_2$	$g_4, f_6$	$f_5$	$g_5, f_7$	$g_7, f_{10}$	$g_6, f_9$
$\langle 4 , a_2''$	$g_2, f_3$	$g_5, f_7$	$g_5, f_7$	$f_8$	$g_8, f_{11}$	$g_8, f_{11}$
$\langle 5 , e'\varepsilon$	$g_3, f_4$	$g_6, f_9$	$g_7, f_{10}$	$g_8, f_{11}$	$f_{12}$	$g_9, f_{13}$
$\langle 6 , e'\zeta$	$g_3, f_4$	$g_7, f_{10}$	$g_6, f_9$	$g_8, f_{11}$	$g_9, f_{13}$	$f_{12}$

Table 6

Energies (in eV) of selected SD and their expressions in terms of the exchange and repulsion parameters of Table 3 for  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$  calculated using DFT, as well as for a  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Ga}^{\text{III}}(\text{NH}_3)_3^{3+}$  with  $\text{Ga}^{3+}$  3d-orbitals, included in a frozen core to allow calculation also of  $k_{\text{ac}}$  and  $k_{\text{ce}}$

Slater determinant	DFT energy	Energy expression
$\text{SD}_1 =  1^+ 2^+ 3^+ 4^+ 5^+ 6^+ $	0.0	0
$\text{SD}_2 =  1^- 2^+ 3^+ 4^+ 5^+ 6^+ $	1.6117	$4g_1 + 2g_2 + 4g_3$
$\text{SD}_3 =  1^+ 2^- 3^+ 4^+ 5^+ 6^+ $	1.6509	$2g_1 + 2g_4 + 2g_5 + 2g_6 + 2g_7$
$\text{SD}_4 =  1^+ 2^+ 3^- 4^+ 5^+ 6^+ $	1.6516	$2g_1 + 2g_4 + 2g_5 + 2g_6 + 2g_7$
$\text{SD}_5 =  1^+ 2^+ 3^+ 4^- 5^+ 6^+ $	1.7043	$2g_2 + 4g_5 + 4g_8$
$\text{SD}_6 =  1^+ 2^+ 3^+ 4^+ 5^- 6^+ $	1.5498	$2g_3 + 2g_6 + 2g_7 + 2g_8 + 2g_9$
$\text{SD}_7 =  1^+ 2^+ 3^+ 4^+ 5^+ 6^- $	1.5494	$2g_3 + 2g_6 + 2g_7 + 2g_8 + 2g_9$
$\text{SD}_8 =  1^+ 1^- 2^+ 3^+ 5^+ 6^+ $	0.8163	$e_1 - e_4 + f_1 + 2f_2 - f_3 + 2f_4 - 2f_7 - 2f_{11} + g_2 + 2g_5 + 2g_8$
$\text{SD}_9 =  2^+ 3^+ 4^+ 4^- 5^+ 6^+ $	2.5783	$e_4 - e_1 - 2f_2 - f_3 - 2f_4 + 2f_7 + f_8 + 2f_{11} + 2g_1 + g_2 + 2g_3$
$\text{SD}_{10} =  1^+ 2^+ 3^+ 3^- 4^+ 6^+ $	1.2287	$e_3 - e_5 + f_2 - f_4 + f_5 + f_6 + f_7 - f_{10} - f_{11} - f_{13} + g_3 + g_6 + g_7 + g_8 + g_9$
$\text{SD}_{11} =  1^+ 2^+ 4^+ 5^+ 5^- 6^+ $	2.2143	$e_5 - e_3 - f_2 + f_4 - f_6 - f_7 - f_{10} + f_{11} + f_{12} + f_{13} + g_1 + g_4 + g_5 + g_6 + g_7$
$\text{SD}_{12} =  1^+ 2^+ 2^- 3^+ 4^+ 5^+ $	1.2271	$e_2 - e_6 + f_2 - f_4 + f_5 + f_6 + f_7 - f_{10} - f_{11} - f_{13} + g_3 + g_6 + g_7 + g_8 + g_9$
$\text{SD}_{13} =  1^+ 3^+ 4^+ 5^+ 6^+ 6^- $	2.2146	$e_6 - e_2 - f_2 + f_4 - f_6 - f_7 - f_{10} + f_{11} + f_{12} + f_{13} + g_1 + g_4 + g_5 + g_6 + g_7$
$\text{SD}'_1 =  a_1^+ x_1^+ y_1^+ $	0	0
$\text{SD}'_2 =  a_1^- x_1^+ y_1^+ $	0.923	$2k_{\text{ac}}$
$\text{SD}'_3 =  a_1^+ x_1^+ y_1^- $	0.903	$k_{\text{ac}} + k_{\text{ce}}$

#### 4. Discussion and conclusions

The DFT based LF model for magnetic exchange coupling developed in [12] has been extended here to magnetic centers with more than one magnetic electrons per site. Using the  $(\text{NH}_3)_3\text{Cr}(\text{OH})_3\text{Cr}(\text{NH}_3)_3^{3+}$  complex as an example we deduce exchange parameters: transfer (hopping) integrals ( $t_{\text{aa}}$ ,  $t_{\text{ee}}$ ), charge transfer energies ( $U_{\text{aa}}$ ,  $U_{\text{ee}}$ ), intratomic ( $k_{\text{ac}}$ ,  $k_{\text{ce}}$ ) and interatomic ( $K_{\text{aa}}$ ,  $K_{\text{ee}}$ ,  $K_{\text{ac}}$  and  $K'_{\text{ce}}$ ) Heisenberg exchange integrals to allow calculations of the exchange split local multiplets. A mixed strategy to achieve this lies in using exchange coupling theory based on localized magnetic orbitals, but DFT calculations of the dimer allowing to extract the model pa-

rameters from the manifold energies of all SD resulting from electron replacements within orbitals which accommodate the magnetic electrons. We show, using this simple complex of  $D_{3h}$  symmetry, how exploiting symmetry helps to deduce symmetry based exchange parameters and to greatly simplify the exchange problem. Note, that exchange coupling energies for ground and excited states are obtained basically in one step (diagonalising one matrix – Table 4 in the considered example). Thus magnetic data on the ground and excited state (from spectroscopy) couplings can be treated on the same footing. One note of caution when dealing with degenerate excited states has to be added here. Exchange coupling for such states is described in terms of a non-Heisenberg

Table 7

Values of the exchange parameters  $g_i$  ( $i = 1, \dots, 9$ , in eV) as deduced from a fit of the expressions of all 64 SD, resulting from the flip of one, two and three spins imposed on the  $SD_1 = |1^+ 2^+ 3^+ 4^+ 5^+ 6^+|$  high-spin reference configuration to DFT energies of  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$ ; expressions of the  $g_i$  integrals in terms of two-electron integrals in the basis of the localized magnetic orbitals (Table 2) are also included

$g_i$	Value	Expression in terms of localized magnetic orbitals
$g_1$	0.2372	$(1/4)\{2k_{\text{ac}} + 2K_{\text{ac}} - 4K_{11}^{12} + 4K_{11}^{21} - 2K_{12}^{21} - 2K_{11}^{22}\}$
$g_3$	0.2113	$(1/4)\{2k_{\text{ac}} + 2K_{\text{ac}} + 4K_{11}^{12} + 4K_{11}^{21} + 2K_{12}^{21} + 2K_{11}^{22}\}$
$g_5$	0.2614	$(1/4)\{2k_{\text{ac}} + 2K_{\text{ac}} - 4K_{11}^{12} - 4K_{11}^{21} + 2K_{12}^{21} + 2K_{11}^{22}\}$
$g_8$	0.2334	$(1/4)\{2k_{\text{ac}} + 2K_{\text{ac}} + 4K_{11}^{12} - 4K_{11}^{21} - 2K_{12}^{21} - 2K_{11}^{22}\}$
$g_2$	0.7134	$(1/2)[J_{\text{a1a1}} - J_{\text{a1a2}}] = U_{\text{aa}}$
$g_7$	0.6647	$(1/2)[J_{\text{x1x1}} - J_{\text{x1x2}}] = (1/2)[J_{\text{y1y1}} - J_{\text{y1y2}}] = U_{\text{ee}}$
$g_4$	0.2584	$(1/4)[2k_{\text{ce}} + 2K'_{\text{ce}} + 2X_{21}^{12} - 2X_{11}^{22}]$
$g_6$	0.2282	$(1/4)[2k_{\text{ce}} + 2K'_{\text{ce}} - 2X_{21}^{12} - 2X_{11}^{22}]$
$g_9$	0.2106	$(1/4)[2k_{\text{ce}} + 2K'_{\text{ce}} + 2X_{11}^{21} + 2X_{21}^{12} + 2X_{11}^{22}]$

Notations:  $k_{\text{ac}} = [\text{a}_1\text{y}_1 | \text{a}_1\text{y}_1] = \int \int \text{a}_1(1)\text{y}_1(1)(1/r_{12})\text{a}_1(2)\text{y}_1(2)\text{d}\tau_1\text{d}\tau_2$ ;  $K_{\text{ac}} = [\text{a}_1\text{y}_2 | \text{a}_1\text{y}_2]$ ;  $K_{11}^{12} = [\text{a}_1\text{y}_1 | \text{a}_1\text{y}_2]$ ;  $K_{11}^{21} = [\text{a}_1\text{y}_1 | \text{a}_2\text{y}_1]$ ;  $K_{12}^{21} = [\text{a}_1\text{y}_2 | \text{a}_2\text{y}_1]$ ;  $K_{11}^{22} = [\text{a}_1\text{y}_1 | \text{a}_2\text{y}_2]$ ;  $J_{\text{a1a1}} = [\text{a}_1\text{a}_1 | \text{a}_1\text{a}_1]$ ;  $J_{\text{a1a2}} = [\text{a}_1\text{a}_1 | \text{a}_2\text{a}_2]$ ;  $J_{\text{x1x1}} = [\text{x}_1\text{x}_1 | \text{x}_1\text{x}_1]$ ;  $J_{\text{x1x2}} = [\text{x}_1\text{x}_1 | \text{x}_2\text{x}_2]$ ;  $k_{\text{ce}} = [\text{x}_1\text{y}_1 | \text{x}_1\text{y}_1]$ ;  $K'_{\text{ce}} = [\text{x}_1\text{y}_2 | \text{x}_1\text{y}_2]$ ;  $X_{21}^{12} = [\text{x}_2\text{y}_1 | \text{x}_1\text{y}_2]$ ;  $X_{11}^{22} = [\text{x}_1\text{y}_1 | \text{x}_2\text{y}_2]$ ;  $X_{11}^{21} = [\text{x}_1\text{y}_1 | \text{x}_2\text{y}_1]$ .

Table 8

DFT parameter values (eV) for the exchange coupling in  $(\text{NH}_3)_3\text{Cr}^{\text{III}}(\text{OH})_3\text{Cr}^{\text{III}}(\text{NH}_3)_3^{3+}$

$k_{\text{ac}}$ 3B+C	$k_{\text{ce}}$ 3B+C	$K_{\text{aa}}$	$K_{\text{ee}}$	$K_{\text{ac}}$	$K'_{\text{ce}}$	$U_{\text{aa}}$	$U_{\text{ee}}$	$t_{\text{aa}}$	$t_{\text{ce}}$	$J_{12}$
0.461	0.442	0.020	0.061	0.011	0.014	1.427	1.329	0.440	0.247	−0.016

(anisotropic) exchange Hamiltonian in which orbital- and spin-operators (degrees of freedom) have to be taken into account. The basic formalism and its applications are well documented [20–23]. In view of this, the present recipe is proper addition to such techniques.

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