Effective Hamiltonian Crystal Field As Applied to Magnetic Exchange Parameters in μ-Oxo-Bridged Cr(III) Dimers

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ABSTRACT: The calculation of the 3d-intrashell excitations in coordination compounds by means of the Effective Hamiltonian Crystal Field (EHCF) method is generalized to their polynuclear analogues to properly describe several open d-shells and their magnetic interactions. This challenge requires improving the precision of ca. 1000 cm^{-1} to ca. 100 cm^{-1} characteristic for the spin-reorientation energies. The method follows the successful EHCF paradigm, namely, the concerted usage of McWeeny's group-function approximation and Löwdin's partitioning technique, for an effective description of the multicenter d-systems. The novel approach is implemented in the MagAîxTic package and validated against a series of binuclear complexes of Cr(III) featuring μ-oxygen superexchange paths. The trends in the compound series in terms of exchange constants are correctly reproduced, despite differing details of composition and structure, and the numerical results agree by order of magnitude with available experimental data and other theoretical methods.
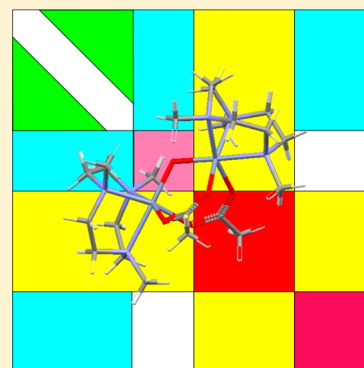
1. INTRODUCTION

The dinuclear *basic rhodo* [derived from Greek "ῥόδον" for "rose" as in *Rhododendron*, although the *basic* compounds are largely blue[1]] chromium compounds were synthetized 130 years ago by Jørgensen,[1] shortly before Werner formulated his famous coordination theory[2] of transition-metal complexes (TMC). The qualitative understanding of the spectral properties of this colorful family was reached through the seminal work by Bethe,[3] which also served as a basis for describing its electronic structure. Finally, the magnetic interactions in the polynuclear TMCs (PTMCs), descendants of the original rhodo species, have been qualitatively understood by van Vleck[4] and Anderson.[5]

The story of the numerical modeling of the magnetic properties of this molecular class is less spectacular. Although ab initio methods are potentially capable to solve the problem,[6−8] very unfortunately, however, the systems of interest may contain hundreds of transition-metal ions (TMI's),[9,10] such that electronic correlations allow the necessary computational resources scale as $N,[7]$ where N is the number of orbitals. Despite recent progress,[11] it will be hardly ever possible to apply such an approach within an entire setting of chemical problems. When it comes to the DFT-based methods, they have shown considerable success,[12−14] but in relation to the problems of magnetic interactions, they strongly rely upon the possibility to obtain the broken-symmetry solutions in the unrestricted Hartree−Fock setting. Although trivial for binuclear complexes, the usual "guinea pigs" in the field, DFT may become very problematic. It happens when odd-numbered cycles of spins coupled through antiferromagnetic exchange become dominant and induce magnetic

frustration, like in CuNCN,[15] where spins form a triangular lattice (examples of similar arrangements are amply represented in ref 10) or in FeNCN[16] where the DFT-based technique yields a metallic ground state instead of experimentally observed antiferromagnetic phase. Despite these problems, Neese and co-workers have significantly contributed to the DFT modeling of PTMCs, an admirable success within the principal DFT limitations.[17]

Eventually, TMCs turned out to be problematic for semiempirical quantum chemistry. Although considerable efforts had been applied in this direction,[18] the success achieved is indeed moderate, particularly for the detailed description of open *d*-shells, the most fundamental issue. This is in a visible contrast with the general theoretical understanding as based on Bethe's work[3] and its semiquantitative descendants such as the angular-overlap model (AOM).[19,20] Thus, the concept of semiempirism must be reconsidered since taking it simply as a parametrized self-consistent field (SCF) in the valence basis, led to the aforementioned problems whose more technical reasons are explained elsewhere.[21,22] The solution[23] is given by the concerted usage of McWeeny's group-function formalism[24] and Löwdin's partition technique[25] as described in reviews[26,27] and in a monograph.[28] This combination provides a new concept of semiempirism in quantum chemistry: taking the form of the wave function on the basis of observable electronic groups such as d-shells, π-systems, two-center bonds, and so on—chromophores, as we will call them in the sequel in a

somewhat generalized sense—which characterize the molecular class and which effective Hamiltonians need to be parametrized. The effective Hamiltonian technique serves as a formal implementation of the above concept. It allows for constructing semiempirical electronic structure methods targeted to the particular classes of molecules containing specific types of chromophores.

The effective Hamiltonian crystal field (EHCF) method implements the above philosophy for TMCs identifying two types of the involved chromophores: d-shells and the ligands. Then, it numerically estimates the parameters of the crystal-field theory (CFT) or of the AOM method by means of (semiempirical) quantum chemistry. Hence, EHCF is only successful when CFT or AOM yield an acceptable phenomenological description. Establishing relations between the (optical) spectral and magnetic characteristics of PTMCs is an old topic[29−31] that culminated in works[32,33] devoted to the oxo-bridged copper(II) and iron(III) oxygen carriers. After having introduced the necessary corrections, other contributions[34−36] provided a direct connection between the spectral AOM parameters e_σ, e_π of the bridging ligand and the exchange parameters in binuclear TMCs including their geometrical dependence. Previously,[37] the AOM parameters e_σ, e_π were reproduced by a local version of EHCF. In the present paper we address the magnetic exchange parameters of PTMCs. In the following section we pictorially represent the EHCF formalism and its necessary modifications for the PTMCs, and we describe contributions to the effective d-electron Hamiltonian that arise from this treatment. The details of the derivation are quite cumbersome and can be found elsewhere.[38] Two more sections describe relevant details of the implementation and the calculation results as compared to previous ones and the experiment. Finally, a conclusion is given.

2. ACCOUNT OF THE UNDERLYING THEORY

2.1. EHCF Model of d–d Spectra of Mononuclear TMCs. The quantum-chemical treatment of a many-electron molecular system ultimately reduces to diagonalizing its Hamiltonian matrix. In the case of truly polyatomic systems, as PTMCs are, the dimension of such a matrix turns out to be so large that the result becomes either numerically intractable or incomprehensible. Thus, a more empirical but physically (and chemically) substantiated approach is necessary. The analysis starts from identifying and localizing (on experimental grounds) the low-energy excitations of the system which are responsible for its behavior. [In other words, the chomophores in the molecule whatever they are must be identified.] In fact, CFT states that the lowest-energy electronic excitations of mononuclear TMCs are those of the d-shell, and their excitation energies are controlled by the effective crystal (ligand) field. The ionic CFT model, however, faces a serious problem: although the field symmetry is perfectly reproduced, at best 20% of the observed splitting results even if unrealistically large charges are ascribed to ligands. This unsatisfactory situation called for the development of the ligand field theory[39] (LFT) including a more realistic picture of the ligands. Specifically, the LFT splitting results from *covalent interactions* (one-electron transfers) between the d-shells and the ligands. Its semiquantitative version (AOM) expresses the effective crystal field in terms of the empirical ligand-specific parameters e_σ and e_π.

The EHCF theory recognizes that CFT implicitly assumes the wave function of a TMC to have the form

$$\Psi = \Phi_d \times \Phi_l \tag{1}$$

where Φ_d is the correlated function of the electrons in the d-shell of the TMI, and Φ_l is the function of all other electrons of the system; the product sign "×" indicates that the resulting function is antisymmetric. The wave function Ψ eq 1 cannot be exact because the one-electron hopping terms in the Hamiltonian effectuate the electron transfers between the d-shell and the rest of the complex. The states given by eq 1 span the *model subspace*[40] corresponding to the CFT setting. The one-electron hopping term *mixes* the states in the model space with those in the *outer subspace* spanned by the ligand-to-metal and metal-to-ligand charge-transfer (LMCT and MLCT) states. With this physically based classification of the electronic states, the Hamiltonian matrix acquires the form as represented in Figure 1.
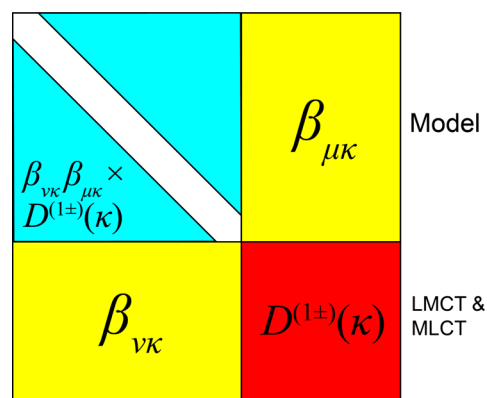

Figure 1. Pictorial representation of the partition of the mononuclear TMC Hamiltonian matrix relevant for the EHCF method. The quantities in the yellow blocks couple the model subspace with the LMCT/MLCT subspaces: $\beta_{\mu\kappa}$ are the one-electron hopping integrals between the μth d-AO and the κth ligand MO; $[D^{(1\pm)}(\kappa)]^{-1}$ are the inverse energies of the LMCT/MLCT excited states so that D's are the relevant energy denominators. The matrix elements of the effective crystal field induced by the ligands appear in the cyan triangle as sums over the index κ of the ligand MOs of the products of the multipliers shown in the rectangles/square.

The basic assumption is that the energies of the states in the LMCT/MLCT subspaces (the quantities $[D^{(1\pm)}(\kappa)]^{-1}$ are the inverses of the *energy denominators* entering in the formulas) are much larger than the characteristic energies in the model subspace such that the off-diagonal blocks (shown by yellow rectangles in Figure 1) can be treated perturbatively. After doing so, one may deal not with the entire Hamiltonian matrix shown in Figure 1, but only with its smaller block operating in the model subspace. In this lowest-order theory, the state of the electrons outside the d-shell does not change: in all cases it is described by the wave function Φ_l so that the variables of the corresponding electrons can be integrated out, and the TMC is now described by the effective Hamiltonian for the d-shell only, as proposed by Bethe. For the local ligand MOs (e.g., lone pairs) having a definite symmetry (σ or π) with respect to the axis connecting the TMI and the ligand (donor atom), the matrix elements of the effective crystal field transform to the AOM parameters:

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$$e_\mu = \beta_{\mu\kappa}^2 D^{(1+)}(\kappa) \qquad (2)$$

Hence, the CFT matrix elements are *not* taken as parameters, but are calculated within the EHCF procedure, and this basically rounds up the EHCF theory of mononuclear TMCs.

This general approach has turned out to be enormously successful when applied to TMCs: the EHCF method correctly reproduces not only the ground-state symmetries and spin multiplicities of all important classes of the Werner complexes, as well as their d−d-excitation spectra at the experimental geometries.[41−44] In addition, their dependence on geometry variations[45−50] including a successful modeling of the spin-transitions in Fe(II) complexes of nitrogen-containing ligands[51] has been achieved, inaccessible for both ab initio and DFT-based methods.

2.2. Extension of EHCF to PTMCs. The magnetic interactions in PTMCs can be described along the lines sketched in the previous section. The wave functions in the model subspace are now

$$\Psi = \Phi_A(n_A; S_A) \times \Phi_B(n_B; S_B) \times \Phi_1 \qquad (3)$$

where the functions $\Phi_{A,B}(n_{A,B}; S_{A,B})$ are those of the respective ground states of $n_{A,B}$ electrons in the EHCF-calculated d-shell such that definite values of total spin $S_{A,B}$ can be attributed to them. Here we assume that the electron numbers in each of the d-shells are fixed and, for the sake of simplicity, restrict ourselves to the case of a binuclear complex; more general formulas can be found in ref 38.

Partitioning the configuration space for calculating the effective magnetic exchange constants in PTMCs is shown in Figure 2. Like in the case of a mononuclear TMC, the one-
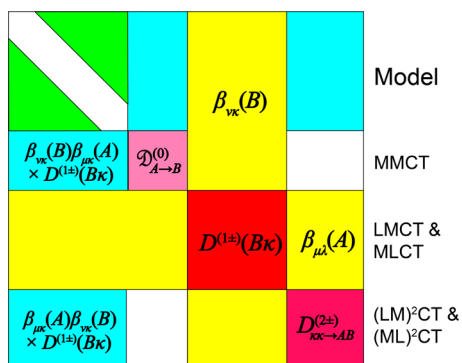

Figure 2. Pictorial representation of the partition of the PTMC Hamiltonian matrix relevant for estimating magnetic interactions between electrons in the d-shells of the *A*th and *B*th TMIs. The model subspace is spanned by the functions as given in eq 3. The outer subspace further decomposes in three subspaces: the old LMCT/MLCT and two more subspaces: that of the MMCT configurations and the $(LM)^2CT/(ML)^2CT$ states when the ligands get doubly ionized in either sense.

electron hopping (yellow rectangles) acts on the states in the model subspace and admixes the LMCT/MLCT states. At this stage, the only formal difference is that the diagonal energies $[D^{(1\pm)}(j\kappa)]^{-1}$ are additionally indexed by the label j = A,B of the specific TMI which is affected by the one-electron transfer. The wave functions of the individual TMIs in eq 3 are assumed to come from an EHCF procedure. Thus, second-order perturbation theory does not further shift their energies, but produces additional off-diagonal matrix elements (blue

rectangles) with the two subspaces in the outer space which so far did not appear: the metal-to-metal charge-transfer (MMCT) subspace with the characteristic energies $[\mathcal{D}^{(0)}_{A\rightarrow B}]^{-1}$ and the double ligand-to-metal or metal-to-ligand charge-transfer $((LM)^2CT/(ML)^2CT)$ subspace with the characteristic energies $[D^{(2\pm)}_{\kappa\kappa\rightarrow AB}]^{-1}$ where the ligands get doubly ionized in either sense. Both admixtures are sensitive to the way the local spins S_A and S_B arrange in the overall state of the total spin S. This allows one to obtain direct estimates of the exchange parameters without addressing the (*a priori* unknown) magnetic ground state of the complex in any form, instead of obtaining them as energy differences between various broken symmetry and other (high-spin and/or nonmagnetic) solutions by this lifting the though and hard-accessible precision requirements imposed on these energies in the DFT-based approaches.

3. IMPLEMENTATION

The effective exchange interactions splitting the model subspace of Figure 2 (green triangles) do not calculationally require any additional quantities except those already available within the EHCF method. These are the d-AO-l-MO one-electron hopping integrals $\beta_{\nu\kappa}(B)$ and the l-MO LCAO orbital energies, necessary for calculating the energy denominators. The amount of the splitting (i.e., the effective exchange constants) between the states of different total spin is given by summing the products of the four one-electron hopping integrals between the d-shells and the ligands:

$$\beta_{\mu\kappa}(A)\beta_{\nu\kappa}(B)\beta_{\mu\lambda}(A)\beta_{\nu\lambda}(B) \qquad (4)$$

further multiplied by the products of the energy denominators:

$$(a) \quad n_\kappa n_\lambda D^{(1+)}(A\kappa) D^{(1+)}(B\lambda) \mathcal{D}^{(0)}_{A\rightarrow B}$$

$$(b) \quad -n_\kappa(1 - n_\lambda) D^{(1+)}(B\kappa) D^{(1-)}(A\lambda) \mathcal{D}^{(0)}_{A\rightarrow B}$$

$$(c) \quad -(1 - n_\kappa) n_\lambda D^{(1-)}(A\kappa) D^{(1+)}(B\lambda) \mathcal{D}^{(0)}_{A\rightarrow B}$$

$$(d) \quad (1 - n_\kappa)(1 - n_\lambda) D^{(1-)}(A\kappa) D^{(1-)}(B\lambda) \mathcal{D}^{(0)}_{A\rightarrow B}$$

$$(e) \quad \delta_{\kappa\lambda} n_\kappa n_\lambda D^{(1+)}(B\lambda) [D^{(1+)}(A\kappa) + D^{(1+)}(B\kappa)] D^{(2+)}_{\kappa\kappa\rightarrow AB}$$

$$(f) \quad \delta_{\kappa\lambda}(1 - n_\kappa)(1 - n_\lambda) D^{(1-)}(B\lambda) [D^{(1-)}(A\kappa) + D^{(1-)}(B\kappa)] D^{(2-)}_{AB\rightarrow\kappa\kappa}$$

$$(5)$$

(n_κ = 0 or 1 is the occupation number of the κth ligand MO) each corresponding to a specific electron transfer path depicted in Figure S1 in the Supporting Information. Namely, these latter depend on the interrelations between the numbers of unpaired electrons in the involved d-shells and between their spins.

The energy denominators in the products (5) are chosen with account of the spin of the formed states. That is to say that the energies of the MMCT or $(LM)^2CT$ states with the spin of either of the d-shells increasing or decreasing relative to those in the model subspace differ by the exchange energy of the respective d-shell $(n_i + 1)K_i$, with i = A,B and K_i is the parameter of the intrashell exchange interaction responsible for conformance with Hund's rule. In the available literature,[34−36] the products of the energy denominators had been expanded assuming K_i was small, but we do not employ this approximation and perform the required calculations of the energy denominators exactly.
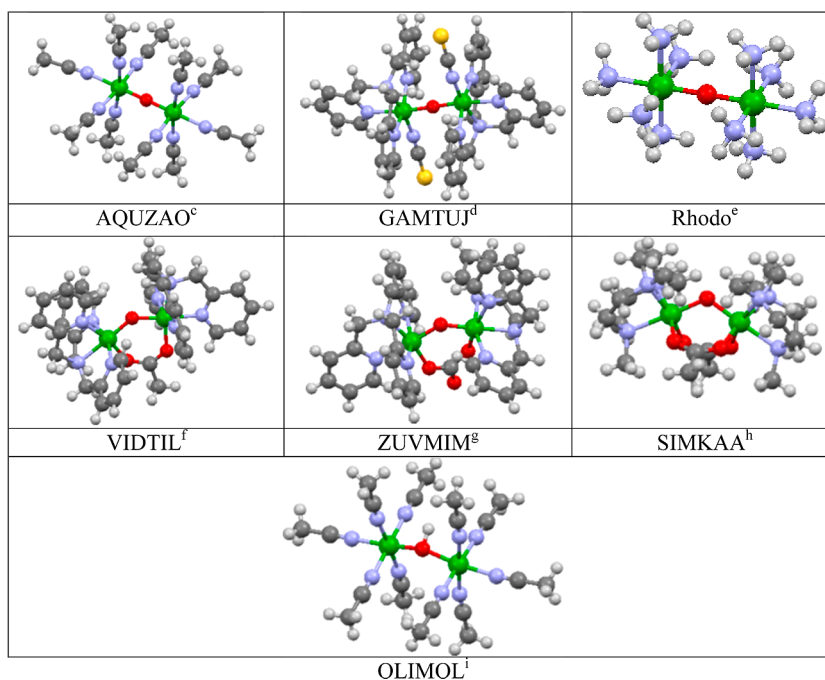
Figure 3. Graphic representation of the molecules addressed in the present study. Molecules are identified by name or CCSD code. Color code: oxygen − red; chromium − green; carbon − dark gray; sulfur − yellow; nitrogen − light blue; hydrogen − light gray. 3D rotatable images in xyz format are available. [c]AQUZAO = $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$; for geometry see ref 54. [d]GAMTUJ = $[\{(tmpa)(NCS)Cr\}_2O]^{2+}$, tmpa stands for tris(2-pyridylmethyl)amine; for geometry see ref 55. [e]Rhodo = $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$; for geometry see ref 56a. [f]VIDTIL = $[\{(tmpa)Cr\}_2(O)(CH_3COO)]^{3+}$; for geometry see ref 57. [g]ZUVMIM = $[\{(tmpa)Cr\}_2(O)(CO_3)]^{2+}$; for geometry see ref 58. [h]SIMKAA = $[\{(Me_3tacn)Cr\}_2(O)(CH_3COO)_2]^{2+}$, tacn stands for 1,4,7-trimethyl-1,4,7-triazacyclononane-N,N',N''; for geometry see ref 59. [i]OLIMOL = $[(CH_3CN)_5Cr(OH)Cr(NCCH_3)_5]^{5+}$; for geometry see ref 60.

The calculation of the products given in 4 and 5 and their summation to the effective exchange parameters J_{AB} is technically implemented in the package MagAîxTic[52] accepting a standard quantum-chemical input (molecular composition and geometry; see Supporting Information Section S2). It uses the GEOMO package[53] (QCPE No 290) and its subroutines to calculate the integrals and perform semiempirical SCF-MO-LCAO calculations for the ligands. The parametrization procedure follows the general EHCF methodology and is briefly described in the Supporting Information Section S2.3. The package which is universally applicable to any combination of first-row TMIs has been presently tested against the compounds of the Cr(III)OCr(III) family. We provide graphical representation of all studied complexes in Figure 3. Results are presented and discussed in the following Section. Further applications of the package are to follow.

4. RESULTS AND DISCUSSION

Applying the developed procedure to the test set of compounds immediately results in the crystal-field states of the individual ions. The splitting pattern as coming from the EHCF procedure and depicted in Figure 4 is expected for TMIs in the tetragonally distorted octahedral environment characteristic for all considered molecules. The strong crystal field of the O^{2-} bridge pushes up the θ-orbitals (uppermost orbital in Figure 4; the z^2-orbital in the linear geometry coming from the octahedral e_g-manifold).

The general expressions as given in eqs 4 and 5 and used for the programming significantly simplify by assuming that only the filled orbitals of the O^{2-} bridge contribute to the transfer processes. After this and having taken the symmetry into account, the expression for the effective exchange constant in
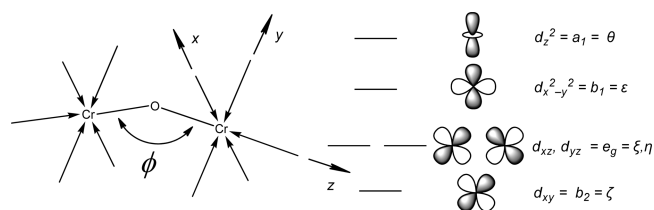

Figure 4. Schematic representation of the archetypical geometry characteristic for the μ-oxo bridged Cr(III) dimers and one-electron states of the d-shells in the respective effective crystal field.

the CrOCr dimers converts to the sum of the "elementary" exchange constants corresponding to specific superexchange paths going through the suitable ligand MO κ:

$$J_{AB} = \frac{4}{9}(J_{\xi\xi} + J_{\eta\eta} + J_{\zeta\zeta}) - \frac{4}{3}J_{\eta\vartheta}$$

$$J_{\mu\mu} = [\beta_{\mu O\pi}(Cr_A)\beta_{\mu O\pi}(Cr_B)D^{(1+)}(Cr_BO\pi)]^2$$
$$[\mathcal{D}^{(0)}_{Cr\to Cr} + 2D^{(2+)}_{O\pi O\pi \to CrCr}]$$

$$J_{\eta\vartheta} = [\beta_{\eta O\pi}(Cr_A)\beta_{\vartheta O\pi}(Cr_B)D^{(1+)}(Cr_BO\pi)]^2$$
$$[\mathcal{D}^{(0)}_{Cr\to Cr} + 2D^{(2+)}_{O\pi O\pi \to CrCr}]^2 \times K \qquad (6)$$

where the numerical coefficients 4/9 and 4/3 are the combinations of the Racah $6j$ symbols and genealogical coefficients specific for a pair of high-spin d^3 Cr^{3+} ions (the calculation of the analogous coefficients required for arbitrary combination of numbers of (unpaired) electrons in the d-shells is built in the MagAîxTic package). K is the amount of the intrashell exchange characteristic for the Cr^{3+} ion.

Using for $[D^{(2+)}{}_{O\pi O\pi \rightarrow CrCr}]^{-1}$—the energy in the $(LM)^2CT$ subspace—a handy estimate as twice the energy $[D^{(1+)}(Cr_BO\pi)]^{-1}$ of the LMCT state, one identifies the second square bracket in eq 6 with the inverse of the effective MMCT energy:[36]

$$U_{eff}^{-1} = D^{(1+)}(O\pi) + \mathcal{D}_{Cr \rightarrow Cr}^{(0)} \qquad (7)$$

The authors[34] ingeniously used the structure of the quadratic multiplier in eq 6 and rewrote it as

$$[\beta_{\mu O\pi}(Cr_A)\beta_{\nu O\pi}(Cr_B)D^{(1+)}(Cr_BO\pi)]^2 =$$

$$[\beta_{\mu O\pi}^2(Cr_A)D^{(1+)}(Cr_BO\pi)][\beta_{\nu O\pi}^2(Cr_B)D^{(1+)}(Cr_BO\pi)]$$

$$= e_\mu e_\nu$$

This expresses the exchange constant through the AOM parameters of the effective crystal field, which can be determined independently either from experiment or numerically.

By using these latter considerations, the elementary exchange constants turn out to be

$$J_{\xi\xi} \approx \frac{e_\pi^2}{U_{eff}}$$

$$J_{\eta\eta} \approx \frac{e_\pi^2}{U_{eff}} \cos^2 \phi$$

$$J_{\eta\vartheta} \approx \frac{e_\pi e_\sigma}{U_{eff}} \times \frac{K}{U_{eff}} \sin^2 \phi \qquad (8)$$

where ϕ is the bending angle $\angle$MOM. The key result of the series of papers[34−36] was that *universal* (transferable) estimates of the exchange parameters and their geometry dependence for a variety of μ-oxo bridged complexes can be obtained in terms of the AOM parameters of the bridging O^{2-} anion. [The elementary exchange $J_{\zeta\zeta}$ was assumed to be negligibly small in the phenomenological model. This is confirmed by our direct calculation.] Hence, any difference between the complexes with different composition of the ligand sphere is only possible when it manifests through the variation of the bridging geometry: the $\angle$MOM bending angle ϕ. By contrast, our numerical procedure accepts usual information on composition and geometry of a PTMC as input and produces the numerical estimates of the exchange parameters as output. The intermediate quantities (AOM parameters e_μ and effective charge transfer energies U_{eff}), which can be used to obtain simpler estimates of the exchange by eq 8, are also produced. We shall refer to the latter estimates as J_{WG} in Table 1. [The abbreviation WG stands for the method by Weihe and Güdel.[32−34]] Using the program suite MagAîxTic[52] we checked the results of the phenomenological approach based on eq 8, however, employing the above intermediate quantities produced by the MagAîxTic package, and those of direct calculation of the exchange parameters by this package against experiment.

The original phenomenological treatment[34−36] is based on the quantities entering eq 8 but estimated largely from experiment. The value of the AOM parameter e_π for the bridging oxide anion is most important. It was fixed[34] at 4000 cm^{-1} (0.5 eV) on the basis of experimental data. The simplest estimate of U_{eff} is the intrashell electron−electron repulsion and amounts to 18.14 eV, which is clearly too high. The value of U_{eff} necessary to reach the concordance between the above

Table 1. Calculated and Experimental Values of the Exchange Constants in a Series of μ-Oxo-Bridged Cr(III) Dimers^a

compound^b	d_{Cr-O} (Å)	$\phi = \angle$MOM (°)	J_{WG}, cm^{-1}	J_{calc}, cm^{-1}	J_{exp}, cm^{-1}
AQUZAO	1.76	180	553	568	1067
GAMTUJ	1.80	180		424	510
Rhodo	1.82	180	389	408	450
VIDTIL	1.83	132	164	190	101
ZUVMIM	1.83	128	136	150	61
SIMKAA	1.85	121	90	82	56
OLIMOL	1.92	148	274	16	36

$^a J_{WG}$ stands for the values obtained by summing the relevant terms in eq 8 calculated with use of the estimates of the AOM parameters and energy denominators obtained in the MagAîxTic package. ^{b}Name or CCSD code.
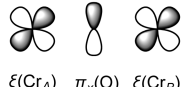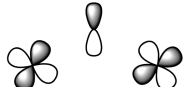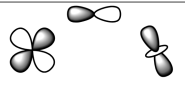
AOM value and experimental exchange parameter within the WG scheme[34−36] in the basic rhodo compound $[(NH_3)_5CrOCr(NH_3)_5]^{4+}$ is 3.9 eV. This amount can hardly be explained by whatever screening or relaxation mechanism. The required value of U_{eff} had been obtained by including the $(LM)^2CT$ states and estimating the characteristic energy of the involved LMCT state to be between 5 and 7 eV and also by setting the intrashell repulsion to ca. 9.25 eV without further elaboration[34]

The EHCF methodology as implemented in the MagAîxTic package permits to calculate all the intermediate quantities entering eq 8 independently. They can be extracted from the calculations on the linear highly symmetric basic "rhodo" complex and its recently synthetized acetonitril analog (AQUZAO). In either case, the highest occupied π-MOs of the ligands are at the 90% level contributed by the p_π-AOs of the bridging O atom. Thus, for e_π the EHCF yields 3850 and 4730 cm^{-1} for the two compounds, respectively. Taking the standard value of the intrashell repulsion for Cr[23] and correcting it by the electron−hole attraction (an obvious move, however, not made previously[34−36]) results in the values 11.52 and 11.42 eV, respectively, which are somewhat larger than the value required by the phenomenological procedure.[34−36] Nevertheless, with use of the energies of the LMCT states $[D^{(1+)}(CrO\pi)]^{-1}$ coming from the EHCF procedure we arrive at the U_{eff} values pretty close to the phenomenological estimates and to the estimates J_{WG} of the exchange constants in these two compounds as given in Table 1. Thus, in general, the EHCF-based estimates are in agreement with phenomenological treatment[34−36] for the linear geometry. The complete summation of the products showing up in eqs 4 and 5 performed by our package yields realistic estimates for the rhodo compound but underestimates the value for the AQUZAO compound. It has to be noticed that in variance with other studied molecules, the exchange constant for AQUZAO had been determined[54] not from the temperature dependence of the susceptibility (like, e.g., for the Rhodo compound itself[56b]), but from the temperature dependence of the intensity of some one-center excitations. It cannot be excluded that the exchange constants coming from different methods may be different as well. With this reservation, one can consider the obtained agreement with experiment as adequate.[61] The same applies to the GAMTUJ compound as well having the linear bridge geometry.

Based on the above agreement of the EHCF derived intermediate quantities with the phenomenological estimates and of the calculated exchange parameters with experiment for linear configuration of the bridge, we applied the MagAîxTic package to a series of other Cr(III) complexes whose molecular geometry and effective exchange are available from experiment. The results are summarized in Table 1 as well. Two effects, the bridge bending and the bridge protonation, were particularly interesting.

The geometry (angular) dependence of the effective exchange is stipulated by two elementary exchange contributions of opposite sign: the antiferromagnetic $J_{\eta\eta}$ and ferromagnetic $J_{\eta\vartheta}$; $J_{\xi\xi}$ refers to the superexchange path going through the Op-orbital of the π-character with respect to the CrOCr plane in the bent structure and thus does not depend on the angle ϕ. We present the values of the elementary exchange constants derived from the EHCF-based estimates in Table 2. For the VIDTIL, ZUVMIM, and SIMKAA compounds

Table 2. Elementary Exchange Constants $J_{\mu\nu}$ Eq 8 (cm^{-1}), Corresponding Superexchange Paths for Considered Set of CoOCr Dimers Calculated with Use of the AOM Parameters e_μ and Effective Charge Transfer Energies U_{eff} Obtained from the MagAîxTic Package

$J_{\xi\xi}$	$\xi(Cr_A)$ $\pi_x(O)$ $\xi(Cr_B)$	435[d] 620[e]
$J_{\eta\eta}$	$\eta(Cr_A)$ $\pi_y(O)$ $\eta(Cr_B)$	435[d] 620[e] 196[f] 166[g] 116[h]
$J_{\eta\vartheta}$	$\eta(Cr_A)$ $\sigma(O)$ $\theta(Cr_B)$	88[f] 100[g] 117[h]

with the bent geometry of the bridge, the antiferromagnetic contributions (4/9 scaled sums of the elementary exchange constants $J_{\xi\xi}$ and $J_{\eta\eta}$ given in Table 2) estimated according to eq 8 amount 280, 269, and 264 cm^{-1}. These numbers have to be compared with 250, 200, and 164 cm^{-1} obtained by the complete summation of all relevant contributions by the MagAîxTic package. The ferromagnetic contributions (− 4/3 multiples of $J_{\eta\vartheta}$) in their turn amount to −117, − 32, and −156 cm^{-1}, respectively, when calculated according to eq 8. The AOM parameter e_σ necessary for this is made up by the highest occupied molecular orbital (HOMO) of the basic rhodo molecule which is contributed by the Op_σ-AO at the 85% level. It equals 13 700 cm^{-1}. The complete summation of the ferromagnetic terms by the MagAîxTic package yields smaller values of the ferromagnetic contributions: −54, −48, and −84 cm^{-1}, respectively. The reason is that performing the complete summation takes into account an additional increase of the MMCT energies by the amount of the crystal field splitting between the η- and θ-orbitals (see Figure 4) not taken into account in the phenomenological scheme.[34−36]

The SIMKAA compound is dubbed to be an outlier for the phenomenological model in ref 35, which is explained by its anomalously large μ−O−Cr separation. This is reproduced by

the EHCF based estimates either by eq 8 or by the complete summation by the MagAîxTic package.

Finally we address the effect of bridge protonation. In the phenomenological model, the only reason for the variation of the exchange is the angular dependence of the one-electron hopping integrals resulting both in the decrease of the elementary antiferromagnetic exchange contributions and in the appearance of the ferromagnetic terms increasing by absolute value with bending. In Table 1 the entries AQUZAO and OLIMOL represent the $[(CH_3CN)_5CrOCr(NCCH_3)_5]^{4+}$ analogue of the basic rhodo molecule and its protonated (acidic rhodo) counterpart. Although OLIMOL noticeably deviates from the linear geometry, its bending angle is much smaller than in other bent molecules. The μ−O−Cr separation in OLIMOL is significantly longer than in AQUZAO. Thus, the effect of the protonation cannot be unequivocally isolated from other (geometry-induced) effects. The estimate obtained by the phenomenological model with use of the EHCF based AOM parameters and the energy denominators and thus taking into account the variation of the interatomic separations is completely unrealistic. It is, however, not unexpected since the protonation strongly affects the electronic states of the bridging oxygen atom. In variance with other considered compounds, the HOMO and its closest neighbors from below in the OLIMOL compound are only weakly contributed by the oxygen AOs. Even these manifest much higher LMCT energies than those characteristic for the nonprotonated compounds, which significantly damps the effective exchange as reflected in our numerical value.

Finally we can conclude that the calculated and measured exchange parameters for all compounds follow the same sequence without a single exception: for the compounds having larger experimental exchange, the calculated exchange is larger as well so that the order in the row: AQUZAO > GAMTUJ > Rhodo > VIDTIL > ZUVMIM > SIMKAA > OLIMOL is the same whether the experimental or calculated values of the exchange parameters are used for ranking. The order of magnitude of parameters calculated by our method conforms to that derived from the susceptibility experiments.

5. CONCLUSION

In the present paper we extend the EHCF method, originally targeted to calculating the effective crystal fields in isolated d-shells, to the modeling of magnetic interactions of effective spins residing in several open d-shells. This challenging problem is solved and the precision of ca. 1000 cm^{-1} (that of describing the excitation energies of the single d-shells by the EHCF method) is improved by an order of magnitude. The approach is implemented in the package MagAîxTic and tested against a series of binuclear complexes of trivalent Cr featuring μ-oxygen superexchange path. The calculational results are in reasonable agreement with available experimental data and improve the predictions of the phenomenological model.

The implemented method does not use any assumptions concerning either the number of TMIs to be considered (current version of the package[52] available to the users of the NetLaboratory system is configured for up to 5 TMIs) nor makes any assumptions concerning the nature of the magnetic state of the system and is thus independent of them.

The efficiency issues also cannot be ignored: according to estimates[62] for a dicopper complex of comparable number of atoms the required computer time ranges from 1 to 5 h as compared to the minute scale required by our method on a

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comparable processor (AMD Phenom2 × 6 1055T vs QuadCore Q9450).

With use of the developed software, it is possible to study coordination polymers or crystals. However, applying it to the infinite/translation invariant system can be done only in the cluster approximation, which introduces additional uncertainties due to cutting the cluster out of otherwise infinite system. Such procedure has been shown to be feasible when applied to the $d-d$ excitation spectra within the EHCF approach,[63−65] but on the scale of the exchange parameters, the cluster boundary effects may deteriorate the precision. Such development is under way, but requires additional efforts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures representing the configurations involved in electron transfer for the processes (5a−5f); sample input files for the Rhodo compound; brief description of the parametrization procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

Ⓦ Web-Enhanced Feature

3D rotatable images of the molecules in Figure 3 in xyz format are available in the HTML version of the paper.

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Notes
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(61) The authors[54] propose an explanation of that large difference between the exchange constants in the Rhodo compound and its acetonitril analogue. It is based on two points. First is the dependence of the hopping integrals on the Cr−O distance, which results in a factor of 1.45 in favor of AQUZAO. The EHCF method reproduces this: the e_π values for the two compounds relate as 1.23, which gives the factor of 1.51 for the exchange constants (proportional to square of e_π) in good agreement with the estimate.[54] This is, however, insufficient to explain the observed ratio of 2.2. The remaining discrepancy is attributed[54] to the variation of the effective charge transfer energy U_{eff} as coming from the nephelauxetic effect produced by the CN groups. The value of U_{eff} must thus be 1.52 smaller in the case of AQUZAO. This factor is by far too large: it does not conform even to the observations of ref 54 itself, where the variation of this quantity has been estimated only at the 12% level in favor of AQUZAO. Currently the MagAîxTic package does not implement the nepheauxetic effect and produces the values of U_{eff} to be 4.46 and 4.20 eV, but in favor of the Rhodo compound, thus giving the factor of 0.94 and the overall ratio of 1.42 in favor of AQUZAO. Thus we conclude that most probably an additional analysis of the experimental value of the exchange constant in the AQUZAO compound based on the susceptibility measurements is needed.

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