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 MagAlxTic 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 “ῥόδων” for “rose” as in Rhododendron, although the basic compounds are largely blue¹] chromium compounds were synthesized 130 years ago by Jørgensen,¹ shortly before Werner formulated his famous coordination theory² 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 Vleck⁴ 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 N² 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 ample represented in ref 10) or in FeNCN¹⁶ 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 work¹ and its semiqualitative descendants such as the angular-overlap model (AOM).¹⁹,²⁰ Thus, the concept of semiempiricism 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 solution²³ is given by the concerted usage of McWeeny’s group-function formalism²⁴ and Löwdin’s partition technique²⁵ as described in reviews²⁶,²⁷ and in a monograph.²⁸ This combination provides a new concept of semiempiricism 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

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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\textsuperscript{29–31} that culminated in works\textsuperscript{32,33} devoted to the oxo-bridged copper(II) and iron(III) oxygen carriers. After having introduced the necessary corrections, other contributions\textsuperscript{34–36} provided a direct connection between the spectral AOM parameters $e_\sigma$, $e_\pi$ of the bridging ligand and the exchange parameters in binuclear TMCs including their geometrical dependence. Previously\textsuperscript{37}, the AOM parameters $e_\sigma$, $e_\pi$ 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.\textsuperscript{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 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 chromophores 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\textsuperscript{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 $e_\sigma$ and $e_\pi$.

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

$$\Psi = \Phi_3 \times \Phi_1$$

where $\Phi_3$ is the correlated function of the electrons in the d-shell of the TMI, and $\Phi_1$ is the function of all other electrons of the system; the product sign “$\times$” indicates that the resulting function is antisymmetric. The wave function $\Psi$ of eq 1 cannot be exact because the one-electron hopping terms in the Hamiltonian, effective the electron transfers between the d-shell and the rest of the complex. The states given by eq 1 span the model subspace\textsuperscript{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 $\mu$th d-AO and the $\kappa$th ligand MO; $D^{(1\pm)}(\kappa)$ are the inverse energies of the LMCT/MLCT excited states so that $D$ 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 $x$ of the ligand MOs of the products of the multipliers shown in the rectangles/square.](image)

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 $\Phi_1$ 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 ($\sigma$ or $\pi$) 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:

$$\beta_{\mu\kappa}$$

$$D^{(1\pm)}(\kappa)$$
\[ \epsilon_{\mu} = \beta_{\mu} D^{(1+)}(\kappa) \]  

(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. In addition, their dependence on geometry variations has been achieved, inaccessible for both ab initio and DFT-based methods.

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

\[ \Psi = \Phi_{A,B}(n_{A,B}; S) \times \Phi_{\alpha}(n_{\alpha}; S_{\alpha}) \times \Phi_{l} \]  

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-electron hopping (yellow rectangles) acts on the states in the d-shells of the A th and B th TMCs. The model subspace is spanned by the functions as given in eq 3. The outer subspace of Figure 2 (green triangles) do not calculationally belong to the model subspace di er by the exchange energy of the (MMCT) subspace with the characteristic energies \( [D^{(0)}_{A \rightarrow B}]^{-1} \) and the double ligand-to-metal or metal-to-ligand charge-transfer (\((LM)^{2}\)CT) subspace with the characteristic energies \( [D^{(2)}_{\kappa \kappa \rightarrow \kappa \kappa}]^{-1} \) 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 \( \beta_{\alpha}(B) \) 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:

\[ \beta_{\alpha}(A)\beta_{\alpha}(B)\beta_{\kappa}(A)\beta_{\kappa}(B) \]  

(4)

further multiplied by the products of the energy denominators:

\[ (a) \ n_{A}n_{B}D^{(1+)}(A)D^{(1+)}(B)D^{(0)}_{A \rightarrow B} \]

\[ (b) -n_{A}(1-n_{A})D^{(1+)}(B)D^{(1-)}(A)D^{(0)}_{A \rightarrow B} \]

\[ (c) -(1-n_{A})n_{B}D^{(1-)}(A)D^{(1+)}(B)D^{(0)}_{A \rightarrow B} \]

\[ (d) (1-n_{A})(1-n_{B})D^{(1-)}(A)D^{(1-)}(B)D^{(0)}_{A \rightarrow B} \]

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

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

(5)

\( n_{k} = 0 \) or 1 is the occupation number of the \( k \)th ligand MO 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 \((LM)^{2}\)CT states when the ligands are doubly ionized in either sense.

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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 MagAixTic\textsuperscript{32} accepting a standard quantum-chemical input (molecular composition and geometry; see Supporting Information Section S2). It uses the GEOMO package\textsuperscript{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\textsuperscript{2−} bridge pushes up the $\theta$-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\textsuperscript{2−} bridge contribute to the transfer processes. After this and having taken the symmetry into account, the expression for the effective exchange constant in the CrOCr dimers converts to the sum of the “elementary” exchange constants corresponding to specific superexchange paths going through the suitable ligand MO $\kappa$:

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

$$J_{\mu\nu} = [\beta_{\mu\nu}(Cr_A)\beta_{\mu\nu}(Cr_B)D^{(1+)}(Cr,O\mu)]^2\left[D^{(0)}_{Cr-Cr} + 2D^{(2+)}_{O\nu O\nu-Cr-Cr}\right]$$

$$J_{\theta\theta} = [\beta_{\theta\theta}(Cr_A)\beta_{\theta\theta}(Cr_B)D^{(1+)}(Cr,O\theta)]^2\left[D^{(0)}_{Cr-Cr} + 2D^{(2+)}_{O\theta O\theta-Cr-Cr}\right]^2 \times K$$

(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 MagAixTic package). $K$ is the amount of the intrashell exchange characteristic for the Cr$^{3+}$ ion.
Using for \([D^{(2+)}_{O\text{XO} \rightarrow \text{CrO}_2}]^{-1}\)—the energy in the \((\text{LM})^2\text{CT}\) subspace—a handy estimate as twice the energy \([D^{(1+)}_{\text{CrO}_2 \rightarrow \text{Cr}}]^{-1}\) of the LMCT state, one identifies the second square bracket in eq 6 with the inverse of the effective MMCT energy: 36

\[
U_{\text{eff}}^{-1} = D^{(1+)}(\text{CrO}_2) + D^{(0)}_{\text{Cr} \rightarrow \text{Cr}}.
\]

(7)

The authors34 ingeniously used the structure of the quadratic multiplier in eq 6 and rewrote it as

\[
\begin{align*}
\left[ \beta_{\text{O} \text{XO}}(\text{Cr}_A) \beta_{\text{O} \text{XO}}(\text{Cr}_B) D^{(1+)}(\text{CrO}_2) \right]^2 &= \\
\left[ \beta_{\text{O} \text{XO}}^2(\text{Cr}_A) D^{(1+)}(\text{CrO}_2) \right][\beta_{\text{O} \text{XO}}^2(\text{Cr}_B) D^{(1+)}(\text{CrO}_2)] &= \epsilon_e^2 \epsilon_s
\end{align*}
\]

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

\[
\begin{align*}
J_{\text{ss}} &\approx \frac{e^2}{U_{\text{eff}}} \\
J_{\text{jj}} &\approx \frac{e^2}{U_{\text{eff}}} \cos^2 \phi \\
J_{\text{ij}} &\approx \frac{e^2 \sin^2 \phi}{U_{\text{eff}}} \times \frac{K}{U_{\text{eff}}}
\end{align*}
\]

(8)

where \(\phi\) is the bending angle \(\angle \text{MOM}\). The key result of the series of papers34–36 was that universal (transferable) estimates of the exchange parameters and their geometry dependence for a variety of \(\mu\)-oxo bridged complexes can be obtained in terms of the AOM parameters of the bridging \(O^2-\) anion. The elementary exchange \(J_{\text{ss}}\) 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 \(\angle \text{MOM}\) bending angle \(\phi\). 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 \(\epsilon_e \) and effective charge transfer energies \(U_{\text{eff}}\)), 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 \(J_{\text{eff}}\) in Table 1. (The abbreviation WG stands for the method by Weihe and Güdel32–34. Using the program suite MagAiTic52 we checked the results of the phenomenological approach based on eq 8, however, employing the above intermediate quantities produced by the MagAiTic package, and those of direct calculation of the exchange parameters by this package against experiment.

The original phenomenological treatment34–36 is based on the quantities entering eq 8 but estimated largely from experiment. The value of the AOM parameter \(\epsilon_e\) for the bridging oxide anion is most important. It was fixed34 at 4000 cm\(^{-1}\) (0.5 eV) on the basis of experimental data. The simplest estimate of \(U_{\text{eff}}\) is the intrashell electron–electron repulsion and amounts to 18.14 eV, which is clearly too high. The value of \(U_{\text{eff}}\) necessary to reach the concordance between the above AOM value and experimental exchange parameter within the WG scheme34–36 in the basic rhodo compound \([(\text{NH}_3)_5\text{CrO}\text{Cr(\text{NH}_3)_5}]^{4+}\) is 3.9 eV. This amount can hardly be explained by whatever screening or relaxation mechanism. The required value of \(U_{\text{eff}}\) had been obtained by including the \((\text{LM})^2\text{CT}\) 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 elaboration34.

The EHCF methodology as implemented in the MagAiTic 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 synthesized acetonitril analog (AQUZAO). In either case, the highest occupied \(\pi\)-MOs of the ligands are at the 90% level contributed by the \(p_x\)-AOs of the bridging O atom. Thus, for \(\epsilon_e\) 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 previously34–36) 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 \([D^{(1+)}(\text{CrO}_2)]^{-1}\) coming from the EHCF procedure we arrive at the \(U_{\text{eff}}\) values pretty close to the phenomenological estimates and to the estimates \(J_{\text{eff}}\) 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 treatment34–36 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 determined34 not from the temperature dependence of the susceptibility (like, e.g., for the Rhodo compound itself36b), 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.

| Table 1. Calculated and Experimental Values of the Exchange Constants in a Series of \(\mu\)-Oxo-Bridged Cr(III) Dimers |
|----------------|------------------|-----------------|------------------|------------------|
| compound | \(d_{\text{Cr}-\text{O}}\) (\AA) | \(\phi\) = \(\angle \text{MOM}\) (\(^{\circ}\)) | \(J_{\text{eff}}\) (cm\(^{-1}\)) | \(J_{\text{calc}}\) (cm\(^{-1}\)) |
| AQUZAO | 1.76 | 180 | 553 | 568 | 1067 |
| GAMTUJ | 1.80 | 180 | 424 | 510 |
| Rhodo | 1.82 | 180 | 389 | 408 | 450 |
| VDYTIL | 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 |

\(J_{\text{eff}}\) 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 MagAiTic package.60 Name or CCSD code.
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 MagAxTic 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 \( J_{\alpha\beta} \) and ferromagnetic \( J_{\alpha\beta} \), with \( \alpha \) and \( \beta \) referring to the superexchange path going through the \( \pi \)-orbital of the \( \pi \)-character with respect to the CrOCr plane in the bent structure and thus does not depend on the angle \( \phi \). 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.

The results are summarized in Table 1 as well. Two effects, the bridge bending and the bridge protonation, were particularly interesting.

Table 2. Elementary Exchange Constants \( J_{\alpha\beta} \) Eq 8 (cm\(^{-1}\)), Corresponding Superexchange Paths for Considered Set of CoOCr Dimers Calculated with Use of the AOM Parameters \( \epsilon_p \) and Effective Charge Transfer Energies \( U_{e\text{ff}} \) Obtained from the MagAxTic Package

<table>
<thead>
<tr>
<th>( J_{\alpha\beta} )</th>
<th>( \xi(\text{Cr}) )</th>
<th>( \pi_p(\text{O}) )</th>
<th>( \zeta(\text{Cr}) )</th>
<th>( \eta_{\text{Cr}} )</th>
<th>( \sigma_{\text{Cr}} )</th>
<th>( \theta_{\text{Cr}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{\xi\xi} )</td>
<td>( \xi(\text{Cr}) )</td>
<td>( \pi_p(\text{O}) )</td>
<td>( \zeta(\text{Cr}) )</td>
<td>435 (^{4})</td>
<td>629 (^{5})</td>
<td></td>
</tr>
<tr>
<td>( J_{\eta\eta} )</td>
<td>( \eta_{\text{Cr}} )</td>
<td>( \sigma(\text{O}) )</td>
<td>( \theta_{\text{Cr}} )</td>
<td>38 (^{8})</td>
<td>109 (^{9})</td>
<td>117 (^{10})</td>
</tr>
</tbody>
</table>

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 MagAxTic package. The ferromagnetic contributions (\( 4/3 \) multiples of \( J_{\eta\eta} \)) in their turn amount to \(-117, -32, \) and \(-156\) cm\(^{-1}\), respectively, when calculated according to eq 8. The AOM parameter \( \epsilon_p \) necessary for this is made up by the highest occupied molecular orbital (HOMO) of the basic rhodo molecule which is contributed by the \( \eta \) and \( \theta \) orbitals of the CrOCr plane of the bent structure and thus does not depend on the angle \( \phi \).

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 MagAxTic and tested against a series of binuclear complexes of trivalent Cr featuring \( \mu \)-oxo 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\(^{52}\) 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...
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, 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$\rightarrow$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*

The authors declare no competing financial interest.

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(61) The authors54 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 $e_\pi$ values for the two compounds relate as 1.23, which gives the factor of 1.51 for the exchange constants (proportional to square of $e_\pi$) in good agreement with the estimate.54 This is, however, insufficient to explain the observed ratio of 2.2. The remaining discrepancy is attributed54 to the variation of the effective charge transfer energy $U_{\text{eff}}$ as coming from the nephelauxetic effect produced by the CN groups. The value of $U_{\text{eff}}$ 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 MagAxTic package does not implement the nephelauxetic effect and produces the values of $U_{\text{eff}}$ 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.


