



HAL
open science

Extraction of giant Dzyaloshinskii–Moriya interaction from ab initio calculations: First-order spin–orbit coupling model and methodological study

Mohammed-Amine Bouammali, Nicolas Suaud, Rémi Maurice, Nathalie Guihéry

► To cite this version:

Mohammed-Amine Bouammali, Nicolas Suaud, Rémi Maurice, Nathalie Guihéry. Extraction of giant Dzyaloshinskii–Moriya interaction from ab initio calculations: First-order spin–orbit coupling model and methodological study. *J.Chem.Phys.*, 2021, 155 (16), pp.164305. 10.1063/5.0065213. hal-03428828

HAL Id: hal-03428828

<https://hal.science/hal-03428828>

Submitted on 24 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Extraction of giant Dzyaloshinskii–Moriya interaction from *ab initio* calculations: First-order spin–orbit coupling model and methodological study

Cite as: J. Chem. Phys. 155, 164305 (2021); doi: 10.1063/5.0065213

Submitted: 30 July 2021 • Accepted: 5 October 2021 •

Published Online: 27 October 2021



View Online



Export Citation



CrossMark

Mohammed-Amine Bouammali,¹  Nicolas Suaud,¹  Rémi Maurice,^{2,3}  and Nathalie Guihéry^{1,a)} 

AFFILIATIONS

¹Laboratoire de Chimie et Physique Quantiques, UMR5626, University of Toulouse 3, Paul Sabatier, 18 route de Narbonne, 31062 Toulouse, France

²Subatech, UMR CNRS 6457, IN2P3/IMT Atlantique/University of Nantes, 4 rue A. Kastler, 44307 Nantes Cedex 3, France

³University of Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, 35700 Rennes, France

^{a)}Author to whom correspondence should be addressed: nathalie.guihery@irsamc.ups-tlse.fr

ABSTRACT

The Dzyaloshinskii–Moriya interaction is expected to be at the origin of interesting magnetic properties, such as multiferroicity, skyrmionic states, and exotic spin orders. Despite this, its theoretical determination is far from being established, neither from the point of view of *ab initio* methodologies nor from that of the extraction technique to be used afterward. Recently, a very efficient way to increase its amplitude has been demonstrated near the first-order spin–orbit coupling regime. Within the first-order regime, the anisotropic spin Hamiltonian involving the Dzyaloshinskii–Moriya operator becomes inappropriate. Nevertheless, in order to approach this regime and identify the spin Hamiltonian limitations, it is necessary to characterize the underlying physics. To this end, we have developed a simple electronic and spin–orbit model describing the first-order regime and used *ab initio* calculations to conduct a thorough methodological study.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0065213>

I. INTRODUCTION

The anisotropic antisymmetric exchange interaction, also called Dzyaloshinskii–Moriya Interaction (DMI), was introduced phenomenologically in 1958 by Dzyaloshinskii^{1,2} in order to describe the magnetic properties of R-Fe₂O₃. This interaction was theorized by Moriya two years later,^{3,4} leading to the well-known DM vector involved in the anisotropic spin Hamiltonian which, for binuclear systems with spin $S = 1/2$ magnetic centers, writes

$$\hat{H}^{model} = J_{AB} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B + \hat{\mathbf{S}}_A \cdot \overline{\overline{\mathbf{D}}}_{AB} \cdot \hat{\mathbf{S}}_B + \mathbf{d}_{AB} \cdot \hat{\mathbf{S}}_A \times \hat{\mathbf{S}}_B, \quad (1)$$

where $\hat{\mathbf{S}}_i$ is the spin vector operator on center $I = \{A, B\}$, J_{AB} is the isotropic magnetic exchange, $\overline{\overline{\mathbf{D}}}_{AB}$ is the symmetric anisotropy tensors of exchange, and \mathbf{d}_{AB} is the DM vector, the three

components of which are here labeled d_x , d_y , and d_z relatively to the X , Y , and Z axes. Since its introduction, the DMI has been used in the rationalization of many exotic magnetic properties.^{5–10} For instance, it favors a canting of the magnetic moments that may stabilize magnetic texture such as skyrmions, which are promising candidates for spintronic devices. It is also of interest in multiferroics, provided that the magneto-electric coupling is large enough. Indeed, it has been established that polarization arising from the through-ligand spin current is proportional to the vector product between the centers A and B distance vector, \mathbf{e}_{AB} , and the DM \mathbf{d}_{AB} vector.

As for the other parameters of magnetic anisotropy, the microscopic origin lies in the concomitant presence of spin–orbit couplings (SOCs) and particular symmetry conditions.^{11,12} Magnetic anisotropy parameters have been intensively studied using quantum

chemistry approaches,^{13–15} and the procedure of extraction of various parameters from the Hamiltonian theory has been proven to be very efficient.^{12,16–21} Nevertheless, only a few papers from theoretical chemistry reporting calculations of the DMI^{22–25} have been published and none of these works were devoted to a methodological study. As this interaction comes from the spin–orbit coupling (SOC) between the electronic ground and excited magnetic states, it is expected that its amplitude is affected by electron correlation. Furthermore, as we show here, this property not only strongly depends on the state energies, which is essentially the case for the other anisotropic parameters, but also strongly depends on the wave functions. A method that revises the coefficients of the wave function under the effect of electron correlation is required as well as a procedure of extraction that accounts for these corrections. For this reason, we have developed a computational procedure that allows us to use dynamically correlated wave functions instead of the non-dynamically correlated complete active space self-consistent field ones. This procedure is general, i.e., not solely applicable to the computation of the DMI, since it is applicable to any situation for which coupling between two relativistic (read M_S components of spin–orbit free states) references is required.

A very recent paper²⁵ has identified through analytical derivations and *ab initio* calculations the main chemical ingredients that govern both the orientation and amplitude of the DMI. We have also proposed an analytical formula that reproduces very well the magnitude of the DMI components far from the first-order SOC regime. One of the main conclusions of this article was that an efficient way to increase the DMI is to approach without reaching the first-order SOC regime, i.e., to design complexes with geometries where $d_{x^2-y^2}$ and d_{xy} (or eventually d_{xz} and d_{yz}) orbitals are quasi-degenerate. Unfortunately, as soon as we approach this regime, the usual method of extraction of DMI (i.e., directly from the spin–orbit coupling of the lowest electronic states) fails. Moreover, in the first-order SOC regime, the anisotropic multi-spin model Hamiltonian [Eq. (1)] becomes unreliable and a first-order model that describes all the almost degenerate states is required.

In this paper, we will therefore extract the matrix of this first-order SOC model and show that the DMI results from both electronic and spin–orbit couplings involving excited states. The impact

of electron correlation on these matrix elements and consequently on the DMI will be studied. Finally, a second-order expression of the DMI only valid far enough from the first-order SOC regime will be proposed.

The effective Hamiltonian theory^{26,27} is a very good method for the extraction of parameters. Nevertheless, near the first-order SOC regime, the projection of the *ab initio* states onto the model space may become small. As this extraction procedure makes use of the projected wave functions, one may wonder whether it is still valid in such cases. We will show that the intermediate Hamiltonian theory, which is specially designed to overcome this difficulty, gives exactly the same value in the peculiar case of the extraction of the DMI, i.e., the effective Hamiltonian theory remains valid even when the projections onto the model space are weak.

This paper is organized as follows: In Sec. II, we have presented the analytical derivation of the first-order SOC matrix, followed by the *ab initio* methods used, the theory of extraction, and the computational details. Section III, divided in two subsections, discusses the results obtained on a model complex made of two Cu(II) ions. In Subsection III A, dedicated to the methodological study, the impact of (i) basis set expansion, (ii) active space content, (iii) electron correlation, and (iv) extraction procedures is analyzed in detail with the aim of determining the calculation conditions required to accurately determine the DMI. Subsection III B is dedicated to unravel the physical origin of the DMI close to the first-order SOC regime.

II. THEORY AND COMPUTATION

In this article, we focus on the effective coupling between two $S = 1/2$ magnetic sites. Let a (a') and b (b') be the magnetic orthogonal atomic orbitals (OAOs) of the triplet (singlet) state, i.e., the orthogonalized orbitals bearing the unpaired electrons optimized for the two states in a state specific manner. The magnetic orbitals are different in the triplet and singlet states when they are optimized in a state specific manner. The spin–orbit interaction couples the M_S components of the two electronic states differently generating the components of both symmetric and antisymmetric anisotropic tensors. The matrix of the model Hamiltonian of Eq. (1) in the basis of the singlet and triplet spin components writes

$$\begin{array}{cccc}
 T_1^+ = |ab\rangle & T_1^0 = \left| \frac{-b\bar{a} + a\bar{b}}{\sqrt{2}} \right\rangle & T_1^- = |\bar{a}\bar{b}\rangle & S_1 = \left| \frac{b'\bar{a}' + a'\bar{b}'}{\sqrt{2}} \right\rangle \\
 \langle ab| & \frac{J_1 + D_{zz}}{4} & \frac{D_{xz} - iD_{yz}}{2\sqrt{2}} & \frac{(D_{xx} - D_{yy} - 2iD_{xy})}{4} & \frac{d_y + id_x}{2\sqrt{2}} \\
 \left\langle \frac{-b\bar{a} + a\bar{b}}{\sqrt{2}} \right| & \frac{D_{xz} + iD_{yz}}{2\sqrt{2}} & \frac{J_1 - D_{zz} + (D_{xx} + D_{yy})}{4} & \frac{D_{xz} - iD_{yz}}{2\sqrt{2}} & \frac{id_z}{2} \\
 \langle \bar{a}\bar{b}| & \frac{(D_{xx} - D_{yy} + 2iD_{xy})}{4} & \frac{D_{xz} + iD_{yz}}{2\sqrt{2}} & \frac{J_1 + D_{zz}}{4} & \frac{d_y - id_x}{2\sqrt{2}} \\
 \left\langle \frac{b'\bar{a}' + a'\bar{b}'}{\sqrt{2}} \right| & \frac{d_y - id_x}{2\sqrt{2}} & \frac{id_z}{2} & \frac{d_y + id_x}{2\sqrt{2}} & \frac{-3J_1}{4} - \frac{D_{zz}}{4} - \frac{(D_{xx} + D_{yy})}{4},
 \end{array} \quad (2)$$

where T_1^+ , T_1^0 , T_1^- are, respectively, the $M_S = 1$, $M_S = 0$, $M_S = -1$ components of the lowest triplet state T_1 and S_1 is the lowest singlet state; J_1 is the isotropic magnetic exchange; D_{xy} , D_{xz} , etc. are the components of the symmetric \bar{D}_{AB} tensor of anisotropic exchange; and d_x , d_y , and d_z are the respective X, Y, and Z components of the DM vector. The DMI only couples the singlet with the three M_S components

of the triplet. Its determination therefore requires the calculation of the SOCs between these two electronic states. It should be noted that as the DM components are related to off-diagonal matrix elements, their amplitudes are completely determined by the coefficients of the various determinants involved in the singlet and triplet wave functions. As such, the DMI extracted from *ab initio* calculations should be strongly dependent on the effects of both non-dynamic and dynamic correlations on the wave functions.

A. Analytical derivation of the first-order SOC matrix

Let us determine the spin-orbit matrix in the basis of the non-coupled functions, i.e., the functions of a centrosymmetric molecule, such as complex **1** with $\theta = 180^\circ$ (see Fig. 1), that cannot couple for symmetry reasons. As the system will be distorted with the angle $\theta = 170^\circ$, the following demonstration uses the symmetries of the C_{2v} point group. One should pay attention to the fact that the irreducible representations have been relabeled in order to be compatible with the C_2 axis along the Y Cartesian axis. Considering two local d orbitals per center, that can mix when applying a distortion, and the six electrons that populate them, one may build four triplet and four singlet states. Let us call a_1 (a_2) and b_1 (b_2) the $d_{x^2-y^2}$ (d_{xy}) OAOs located on centers A and B, respectively. The lowest (O_1 and O_2) and highest (O_1^* and O_2^*) molecular orbitals (MOs) resulting from the through bridging ligand interaction between the orthogonalized atomic orbitals write

$$O_1 = \frac{a_1 + b_1}{\sqrt{2}}, \quad O_2 = \frac{a_2 + b_2}{\sqrt{2}}, \quad O_1^* = \frac{a_1 - b_1}{\sqrt{2}}, \quad O_2^* = \frac{a_2 - b_2}{\sqrt{2}}. \quad (3)$$

According to the values of the angles θ and φ , the MO diagram will adopt two different profiles that are represented in Scheme 1. Far from the first-order SOC regime, the MO diagram will be that shown in Scheme 1(a) where the two unpaired electrons will be in the $d_{x^2-y^2}$ orbitals. For a degeneracy of the local d orbitals [see Scheme 1(b)], i.e., in the first-order SOC regime, the ground state will have the unpaired electrons in both $d_{x^2-y^2}$ and d_{xy} orbitals.

Before distortion, i.e., when the angle $\widehat{CuClCu} = 180^\circ$, the four lowest triplet and singlet states are not coupled. They will be called “uncoupled” functions in the following and serve as basis for future analysis. They can be written as linear combinations of determinants expressed as functions of MOs or OAOs,

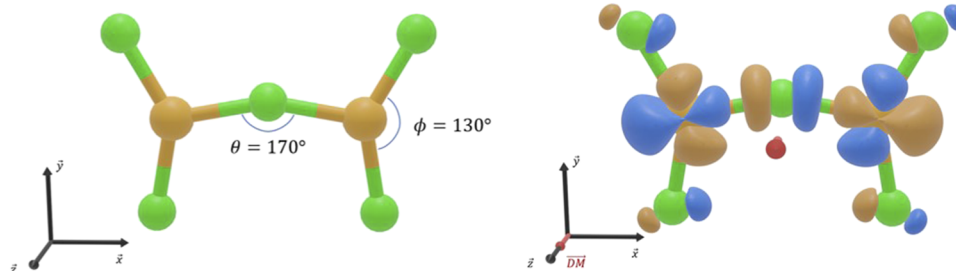


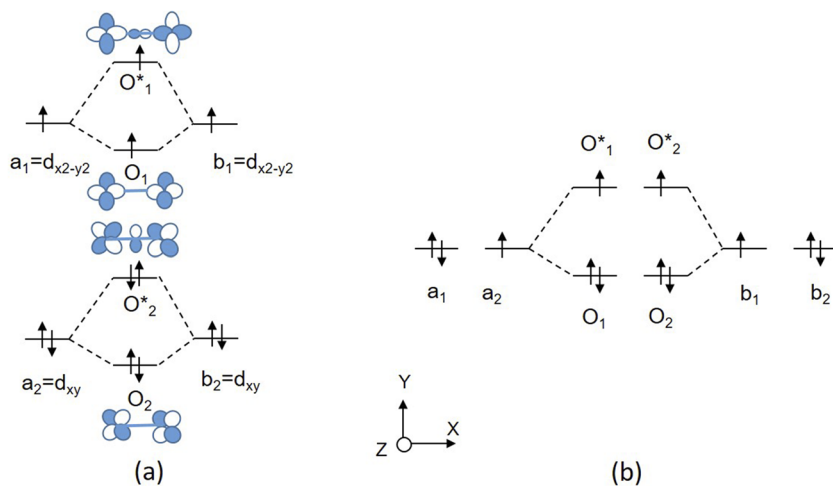
FIG. 1. Model complex **1** Cu_2Cl_5^- (left) with angular deformations θ and φ generating a d_z component of the DMI; one magnetic MO (right) of the triplet state resulting from the mixing between $d_{x^2-y^2}$ and d_{xy} orbitals for the angles $\theta = 170^\circ$ and $\varphi = 130^\circ$. The calculated DM vector (in red) is also represented (right) centered on the origin of the axes frame [middle of the segment $\text{Cu(II)}-\text{Cu(II)}$].

$$\begin{aligned} T_1^1(^3B_2) &= -|O_1 O_1^*| = |a_1 b_1|, & T_1^0(^3B_2) &= \frac{|a_1 \bar{b}_1| - |b_1 \bar{a}_1|}{\sqrt{2}}, \\ S_1(^1A_1) &= \frac{|a_1 \bar{b}_1| + |b_1 \bar{a}_1|}{\sqrt{2}}, \\ T_2^1(^3B_2) &= \frac{|O_1 O_2| - |O_1^* O_2^*|}{\sqrt{2}} = \frac{|a_1 b_2| + |b_1 a_2|}{\sqrt{2}}, \\ T_2^0(^3B_2) &= \frac{|a_1 \bar{b}_2| + |b_1 \bar{a}_2| - |a_2 \bar{b}_1| - |b_2 \bar{a}_1|}{2}, \\ S_2(^1B_2) &= \frac{|a_1 \bar{b}_2| + |b_1 \bar{a}_2| + |a_2 \bar{b}_1| + |b_2 \bar{a}_1|}{2}, \\ T_3^1(^3A_1) &= \frac{|O_1 O_2^*| - |O_1^* O_2|}{\sqrt{2}} = \frac{-|a_1 b_2| + |b_1 a_2|}{\sqrt{2}}, \\ T_3^0(^3A_1) &= \frac{-|a_1 \bar{b}_2| + |b_1 \bar{a}_2| - |a_2 \bar{b}_1| + |b_2 \bar{a}_1|}{2}, \\ S_3(^1A_1) &= \frac{-|a_1 \bar{b}_2| + |b_1 \bar{a}_2| + |a_2 \bar{b}_1| - |b_2 \bar{a}_1|}{2}, \\ T_4^1(^3B_2) &= -|O_2 O_2^*| = |a_2 b_2|, & T_4^0(^3B_2) &= \frac{|a_2 \bar{b}_2| - |b_2 \bar{a}_2|}{\sqrt{2}}, \\ S_4(^1A_1) &= \frac{|a_2 \bar{b}_2| + |b_2 \bar{a}_2|}{\sqrt{2}}, \end{aligned} \quad (4)$$

where the valence bond ionic components ($\text{Cu}^{3+}-\text{Cu}^+$) have been neglected.

For symmetry reasons, the three triplets of B_2 symmetry T_1 , T_2 , and T_4 interact together while the three singlets of A_1 symmetry S_1 , S_3 , and S_4 interact together through the exact electronic Hamiltonian H^{El} when the geometrical distortion induces a mixing (hybridization) of the local d_{xy} and $d_{x^2-y^2}$ [i.e., a_1 (b_1) with a_2 (b_2)] orbitals. For the triplet states, these interactions are

$$\begin{aligned} h_1 &= \langle T_1^0 | H^{El} | T_2^0 \rangle = \frac{\langle a_1 b_1 | H^{El} | a_1 b_2 \rangle - \langle a_1 b_1 | H^{El} | a_2 b_1 \rangle}{\sqrt{2}} \\ &= \frac{\langle b_1 | F_{a_1}^{eff} | b_2 \rangle - \langle a_1 | F_{b_1}^{eff} | a_2 \rangle}{\sqrt{2}}, \\ h_2 &= \langle T_4^0 | H^{El} | T_2^0 \rangle = \frac{\langle a_2 b_2 | H^{El} | a_1 b_2 \rangle - \langle a_2 b_2 | H^{El} | a_2 b_1 \rangle}{\sqrt{2}} \\ &= \frac{\langle a_2 | F_{b_2}^{eff} | a_1 \rangle - \langle b_2 | F_{a_2}^{eff} | b_1 \rangle}{\sqrt{2}}, \end{aligned} \quad (5)$$



SCHEME 1. Molecular orbital diagrams in the two limit cases: (a) far from the first-order SOC regime; the unpaired electrons occupy the $d_{x^2-y^2}$ orbitals (S_1 and T_1 uncoupled functions) and (b) in the first-order SOC regime; one of the unpaired electrons occupies the MO delocalized over the two $d_{x^2-y^2}$, while the other occupies the MO delocalized over the two d_{xy} orbitals (S_3 and T_3 uncoupled functions).

where F^{eff} are effective Fock operators. The Fock operators are here effective, as they would be zero for symmetry reasons if one calculates them within the subspace of the d orbitals only. These interactions are mediated by the ligand orbitals that can mix with both of them when distorting the system. This is what is usually called hybridization in the language of chemists. Their values differ in the singlet and triplet states since, due to the exchange integrals, the Fock operators are different for these two states. For this last reason, we will call h' the interactions between the singlet states ($h'_1 = \langle S_1 | H^{el} | S_3 \rangle$ and $h'_2 = \langle S_3 | H^{el} | S_4 \rangle$). Let us call $E_1, E_2 \approx E_3$ and E_4 the energies of the singlet functions and $K_1, K_2 \approx K_3$ and K_4 the energy difference between the uncoupled singlet and triplet states of the same electronic configuration (these effective interactions should be close to twice the direct exchange integrals). All these electronic interactions give rise to the coupled electronic states $S'_1, S'_2, S'_3, S'_4, T'_1, T'_2, T'_3$, and T'_4 that are computed using *ab initio* methods. They are linear combinations of the previously uncoupled states plus other

determinants (ionic and also excited configurations at dynamically correlated levels of calculations). The energy differences between the coupled singlet and triplet states of the same configuration are the magnetic couplings and are called here after J_1, J_2, J_3 , and J_4 . They are known to be very sensitive to electron correlation.²⁸

The state interaction method introduces the SOC between all M_s components of the coupled states (S'_i and T'_i). In order to develop a model that introduces both the electronic and spin-orbit interactions, the here proposed SOC matrix is expressed in the basis of the uncoupled states (S_i and T_i). The off-diagonal elements of the SOC matrix can be analytically calculated using the spin-orbit operator $\hat{H}^{SO} = \xi (\vec{l}_1 \cdot \vec{s}_1 + \vec{l}_2 \cdot \vec{s}_2)$, where \vec{l}_i and \vec{s}_i are the angular and spin momenta, respectively, of electron i and ξ is the spin-orbit constant (we consider a spherical approximation of the SOC). In the $M_s = 0$ subspace, the Hamiltonian matrix involving both the electronic Hamiltonian H^{el} and spin-orbit H^{SO} interactions writes

	$ S_1\rangle$	$ S_2\rangle$	$ S_3\rangle$	$ S_4\rangle$	$ T_1^0\rangle$	$ T_2^0\rangle$	$ T_3^0\rangle$	$ T_4^0\rangle$
$\langle S_1 $	E_1		h'_1			$i\xi\sqrt{2}$		
$\langle S_2 $		E_2						
$\langle S_3 $	h'_1		$E_3 \sim E_2$	h'_2	$i\xi\sqrt{2}$			$i\xi\sqrt{2}$
$\langle S_4 $			h'_2	E_4		$i\xi\sqrt{2}$		
$\langle T_1^0 $			$-i\xi\sqrt{2}$		$E_1 + K_1$	h_1		
$\langle T_2^0 $	$-i\xi\sqrt{2}$			$-i\xi\sqrt{2}$	h_1	$E_2 + K_2$		h_2
$\langle T_3^0 $							$E_3 + K_3 =$ $\sim E_2 + K_2$	
$\langle T_4^0 $			$-i\xi\sqrt{2}$			h_2		$E_4 + K_4$

where some bielectronic integrals that are expected to be small have not been reported, in particular, those between T_1^0 and T_4^0 and between S_1 and S_4 that interact for symmetry reasons. Looking at this matrix, one may first note that for symmetry reasons, the states S_2 and T_3^0 do not interact with any other function and can be erased from the model. It also appears that the SOC between S_1 and T_1^0 is strictly zero, showing that the d_z component of the DM vector is not a direct interaction but arises from complex mechanisms that go through both a SOC between S_1 and T_2^0 (T_1^0 and S_3) and an electronic coupling between T_2^0 and T_1^0 (S_3 and S_1). When these states are far apart in energy, a second-order estimation of the matrix element between the coupled singlet S_1' and triplet $T_1'^0$ states would be given by

$$\langle S_1' | H^{SO} | T_1'^0 \rangle^{(2)} = \frac{\langle S_1 | H^{SO} | T_2^0 \rangle \langle T_2^0 | H^{El} | T_1^0 \rangle}{E_2 + K_2 - E_1} + \frac{\langle S_1 | H^{El} | S_3 \rangle \langle S_3 | H^{SO} | T_1^0 \rangle}{E_3 + K_3 - E_1}. \quad (6)$$

Higher-order mechanisms also contribute such as, for instance, the following fourth-order one:

$$\langle S_1 | H^{El} | S_3 \rangle \langle S_3 | H^{SO} | T_4^0 \rangle \langle T_4^0 | H^{El} | T_2^0 \rangle \langle T_2^0 | H^{El} | T_1^0 \rangle, \quad (7)$$

and their contribution is expected to become important close to the first-order SOC regime.

B. Computational information and procedure of extraction

The MOLCAS(8.0)^{31–33} code has been used to perform Complete Active Space Self-Consistent Field (CASSCF) calculations in order to introduce non-dynamic correlation. To study the impact of dynamic correlation on both the energies and wave functions, Difference Dedicated Configuration (DDCI)^{34,35} calculations have been performed with the CASDI code.³⁶ To take into account the relativistic contributions, the *ab initio* Spin–Orbit–State–Interaction (SO-SI)³⁷ method implemented in MOLCAS has then been used. It proceeds in two steps: (i) the calculation of the electronic states energies which can be performed at various levels of correlations and (ii) the diagonalization of the SO-SI matrix obtained by calculating the SOC between the M_S components of the lowest states. While the electronic energies introduced in the SO-SI matrix (diagonal elements) can be easily changed in order to evaluate the impact of dynamic correlation, the wave functions used in this method are usually the CASSCF ones. To appreciate the impact of correlated wave functions on the DMI, we have projected the DDCI vectors onto the CASSCF ones and orthonormalized these projections. These new correlated functions even if re-expressed in the CASSCF determinant basis are “decontracted” under the effect of dynamic correlation. They are then used in the second step of the *ab initio* calculations, i.e., the SO-SI procedure. To evaluate the impact of the basis set extension, we have used three different basis ANO–RCC–V(D,T,Q)ZP,³⁸ where D, T, and Q stand for double, triple, and quadruple.

Concerning the values of the DMI, we have used three different procedures of extractions: (i) the direct SO-SI matrix element between the lowest triplet and singlet states, (ii) the effective Hamiltonian theory, and (iii) the intermediate Hamiltonian theory. Since

the effective and intermediate Hamiltonian theories provide identical results and as the former has been explained in many articles, we have detailed these two procedures of extraction in the [supplementary material](#). Finally, the numerical matrices of our electronic and spin–orbit model expressed in the space of the six uncoupled functions have been extracted from the *ab initio* results using the effective Hamiltonian.

The effective Hamiltonian theory²⁶ is a method of choice for both the determination of appropriate model Hamiltonians and the attribution of values to their various effective interactions. Nevertheless, in the present study, we are looking for geometrical structures close to those in which first-order SOC applies. As a consequence, the low energy spectrum is not limited to S_1' and $T_1'^0$. If one wants to restrict to these two states, the projections of the *ab initio* wave functions onto the model space may become quite low and one may wonder whether the effective Hamiltonian theory is still valid. In order to demonstrate the reliability of the effective Hamiltonian theory, we have also used another method of extraction based on the intermediate Hamiltonian theory that works on the six above mentioned states. This last method was first proposed in the context of a multireference coupled cluster theory^{29,30} and has been adapted here for the extraction of effective interactions. In order to explain the advantages of the intermediate Hamiltonian theory over the effective Hamiltonian one, we recall both methods in the [supplementary material](#) and detail both procedures of extractions in the simple case of the extraction of d_z . In the case where it is possible to calculate *ab initio* all the target states, the intermediate Hamiltonian theory provides exactly the same results as the effective Hamiltonian one, which shows that the latter method is still reliable even if the projection of the states becomes low. We invite the interested reader to refer to Sec. S1. Nevertheless, one should stress that when the projections are too low, it is the model Hamiltonian that becomes unreliable.

III. RESULTS AND DISCUSSION

Calculations have been performed on a model dinuclear system of Cu(II) bridged by a Cl^- ion, namely, the Cu_2Cl_5^- system (see [Fig. 1](#)). This choice is guided by three reasons: (i) we are not aware of any available experimental data on dicopper(II) complexes, (ii) cases for which experimental data are available are very rare and too complicated as explained in [Ref. 25](#), and (iii) this small and easily deformable toy model allows a detailed study of the first-order SOC regime and of electron correlation effects.

In the studied geometries, an angle $\theta = \widehat{\text{CuClCu}} = 170^\circ$ (with the bridging Cl^-) has been introduced in order to create a DM vector along the Z direction and a value of the angle $\varphi = \widehat{\text{ClCuCl}} = 130^\circ$ (with external Cl^-) has been imposed such that the local environment of both Cu(II) is close to D_{3h} symmetry point group, i.e., a non-negligible first-order SOC contribution to the DMI is expected. In order to appreciate the impact of the first-order SOC on the reliability of both the calculation of DMI and its extraction, calculations have also been performed for angles varying between $\varphi = 120^\circ$ and 170° . As already seen in [Ref. 25](#) for the angle $\varphi = 120^\circ$, the first-order SOC results in an almost degenerate spectrum and the spin Hamiltonian of [Eq. \(1\)](#) that is spanned on the product of a single doublet per center is no more valid. The considered distortions only create a DM vector in the Z direction; hence, only the magnitude of the algebraic

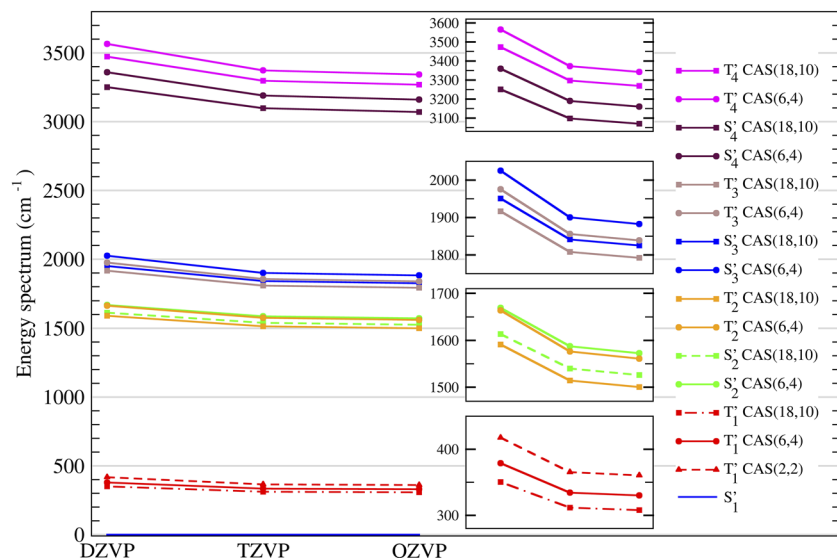


FIG. 2. Cu_2Cl_5^- with angles $\theta = 170^\circ$ and $\varphi = 130^\circ$. Vertical spectrum in cm^{-1} of the four triplet (noted T') and four singlet (noted S') states obtained from the CAS(18,10)SCF (dashed lines) and CAS(6,4)SCF (plain lines) calculations with double zeta (VDZP), triple zeta (VTZP), and quadruple zeta (VQZP) basis sets. The triplet states obtained at the CAS(2,2)SCF level appear with dotted-dashed lines. The lowest singlet is taken as zero of energy in all calculations.

value d_z of the vector varies (and not its orientation). The magnetic orbitals are linear combinations of the $d_{x^2-y^2}$ and d_{xy} orbitals; one magnetic MO obtained using a state specific CAS(2,2)SCF for the triplet state is depicted in Fig. 1. One should mention that visually, it is difficult to appreciate the difference between this orbital and those optimized with a larger active space and/or in an average way.

Our *ab initio* methodological study consists in testing the effect of the basis sets, the impact of the active space extent, the role of having different orbitals sets, and the impact of dynamic correlation. We will also endeavor to show the impact of the extraction method on the DMI values in cases where we approach a situation where the first-order SOC becomes non-negligible.

A. Spin-orbit free results

Three different active spaces have been considered including (i) the five 3d orbitals of each Cu(II) leading to a CAS(18,10)SCF in which the orbitals have been averaged separately for 25 triplets and 25 singlets (corresponding to all single excitations on each copper), (ii) only the $d_{x^2-y^2}$ and d_{xy} orbitals of each copper (as only these orbitals mix in the distorted structure), leading to a CAS(6,4)SCF in which the orbitals have been averaged separately for four triplets

and four singlets, and (iii) the two magnetic orbitals leading to a state specific CAS(2,2)SCF (that are linear combinations of $d_{x^2-y^2}$ and d_{xy}). Finally, a CAS(2,2) singlet state calculation has been performed using the CAS(2,2)SCF orbitals of the triplet state in order to illustrate the importance of having two different orbitals sets to calculate the DMI. Figure 2 reports the spectra obtained for these three active spaces and using double-, triple-, and quadruple-zeta plus polarization basis sets.

While it is quite well known that the electronic energies slowly converge as functions of the basis set extension, we may see that the vertical spectrum is converged here as soon as we use the triple zeta basis set. As the VDZP basis set is not reliable enough, we will only study the dependence of the parameters on the VTZP and VQZP basis sets in the following.

The spectrum changes little for the different choices of active spaces and the largest discrepancy is obtained for the highest triplet and singlet states indexed 4. Nevertheless, one may note that the magnetic couplings $J_i = E(T'_i) - E(S'_i)$ are very similar for the CAS(6,4) and CAS(18,10) active spaces as can be seen in Table I. Two kinds of calculations were carried out using (i) two sets of average MOs: one for the singlets and the other for the triplets (noted CASSCF) and (ii) a single set of MOs averaged on the triplets (noted CASCI).

TABLE I. Cu_2Cl_5^- with angle $\theta = 170^\circ$ and $\varphi = 130^\circ$. Magnetic couplings (see the text) obtained with the three different active spaces and the VTPZ and VQZP basis sets. CASCI results appear in bold.

cm^{-1}	CAS(2,2)SCF/ CAS(2,2)CI		CAS(6,4)SCF/ CAS(6,4)CI		CAS(18,10)SCF*/ CAS(18,10)CI *	
	VTZP	VQZP	VTZP	VQZP	VTZP	VQZP
J_1	365/254	361/251	335/310	331/306	312/303	307/301
J_2	-12/-29	-12/-30	-25/-31	-26/-31
J_3	-43/-28	-42/-27	-33/-30	-33/-30
J_4	182/183	182/183	199/194	198/195

TABLE II. Cu_2Cl_5^- with angles $\theta = 170^\circ$ and $\varphi = 130^\circ$. Magnetic couplings (see the text) in cm^{-1} obtained at the CAS(6,4) + DDCI level using the averaged MOs of the triplets and the VTZP basis set.

cm^{-1}	E(triplet)-E(singlet) CAS(6,4)DDCI
J_1	843
J_2	-33
J_3	-5
J_4	424

Although the results are quite consistent, it is well known that magnetic couplings are very sensitive to dynamic correlation, meaning that an important part of the physics is still missing. DDCI calculations were therefore performed using the CAS(6,4) zeroth-order space and the triple zeta basis, which both happen to provide similar results than CAS(18,10) and the quadruple zeta basis. The validity of the DDCI method is based on the non-differential effect of inactive di-excitations on the states generated by the CAS. This strict cancellation at the second-order of perturbations of the di-excitations effect on the spectrum is only possible if the MOs are identical for all states. Calculations have therefore been performed on the triplet averaged orbitals as it is usually done in magnetic systems. The magnetic couplings obtained at the DDCI level are reported in Table II. It

reveals the dramatic effect of dynamic correlation and, in particular, the expected important increase of the antiferromagnetic contribution.²⁸ The coefficients of these coupled functions on the uncoupled functions are given at both levels of calculations (CASCI and CAS + DDCI) in Table III. The DDCI wave functions have been projected onto the CAS space and the projections have been renormalized. One may notice that dynamic correlation increases the mixings between S_1 and S_3 slightly, and between T_1^0 and T_2^0 dramatically, which should have consequences on the value of the DMI. Finally, the norms of the projections of the coupled electronic states S'_i onto the coupled functions S_i are reported in Table IV.

B. Spin-orbit results

The physical origin of DMI lies in the relativistic effects. Its magnitude has been extracted from the *ab initio* calculations either directly from the elements of the SO-SI method between the lowest singlet and triplet states or using the effective and intermediate Hamiltonian theories that provide the same values. Results are reported in Table V. The diagonal elements of the SO-SI matrix are the energies of the mentioned functions (either CASSCF or CASCI).

First of all, one may notice that the two kinds of extractions using either the effective or intermediate Hamiltonian theory lead to the same values for the CAS(2,2)SCF calculations, as already

TABLE III. Cu_2Cl_5^- with angles $\theta = 170^\circ$ and $\varphi = 130^\circ$. Coefficients of the uncoupled wave function S_i and T_i in the coupled functions S'_i and T'_i , obtained at the CAS(6,4)CI or CAS(6,4) + DDCI (in bold) levels with the MOs average on the triplets. The DDCI functions have been projected onto the CAS(6,4) and renormalized.

	S'_1 CASCI/DDCI	S'_2 CASCI/DDCI	S'_3 CASCI/DDCI	S'_4 CASCI/DDCI	T'_1^0 CASCI/DDCI	T'_2^0 CASCI/DDCI	T'_3^0 CASCI/DDCI	T'_4^0 CASCI/DDCI
S_1	0.9874/ 0.9814	0.0/0.0	-0.1520/- 0.1672	+0.0019/+ 0.0228	T_1^0 0.9986/ 0.9924	0.0512/- 0.1232	0.0/0.0	-0.0114/- 0.0164
S_2	0.0/0.0	0.9985/ 0.9954	0.0/0.0	0.0/0.0	T_2^0 -0.0518/ 0.1165	0.9869/ 0.9757	0.0/0.0	-0.1477/- 0.1626
S_3	0.1499/ 0.1629	0.0/0.0	0.9854/ 0.9850	+0.0693/- 0.0146	T_3^0 0.0/0.0	0.0/0.0	1.0/ 0.9999	0.0/0.0
S_4	- 0.0128 /- 0.0194	0.0 /0.0	- 0.0675 /+ 0.0180	0.9964/ 0.9961	T_4^0 0.0042/ 0.0348	0.1465/ 0.1545	0.0/0.0	0.9884/ 0.9856

TABLE IV. Cu_2Cl_5^- with angle $\theta = 170^\circ$ and $\varphi = 130^\circ$. Weight of the coupled singlet and triplet functions onto the uncoupled ones, calculated at the DDCI level for an angle of 130° .

S'_1 onto S_1	S'_2 onto S_2	S'_3 onto S_3	S'_4 onto S_4	T'_1^0 onto T_1^0	T'_2^0 onto T_2^0	T'_3^0 onto T_3^0	T'_4^0 onto T_4^0
0.8681	0.8945	0.9408	0.8851	0.8991	0.8599	0.9134	0.8859

TABLE V. Cu_2Cl_5^- with angles $\theta = 170^\circ$ and $\varphi = 130^\circ$. Values in cm^{-1} of the DMI extracted from either the SO matrix element of the SO-SI method or the effective and intermediate Hamiltonian theories. Two different MO sets are used, see the text. CASCI results appear in bold.

(cm^{-1})	Basis set	CAS(2,2)SCF/ CAS(2,2)CI	CAS(6,4)SCF/ CAS(6,4)CI	CAS(18,10)SCF/ CAS(18,10)CI
d from SO matrix	VTZP	250/ 1.8	228/ 221	231/ 228
	VQZP	251/ 1.8	228/ 221	232/ 228
d from H^{eff} or H^{int}	VTZP	250/ 1.8	156/ 151	153/ 151
	VQZP	251/ 1.8	155/ 150	152/ 149

mentioned in Sec. II. We will therefore only use the effective Hamiltonian theory procedure in the following.

DMI values obtained using both basis sets are very similar, confirming that VTZP is enough for the DMI calculation. The comparison of the results obtained with different active spaces shows that while the CAS(6,4) and CAS(18,10) provide similar results, the CAS(2,2) gives quite different DMI values. One should note that, as expected from the analytical derivation reported in a previous article,²⁵ the use of a unique set of MOs produces zero (or almost zero) DMI values if the two states are obtained using two magnetic orbitals resulting from the simple combination of the local d orbitals (plus “tails” on the ligands of course), i.e., at the state average CAS(2,2)CI level.

When using two different sets of MOs, i.e., at the state specific CAS(2,2)SCF level, the mixing of the $d_{x^2-y^2}$ and d_{xy} orbitals takes place with a somewhat larger flexibility, which is reflected in the appearance of different coefficients in the following magnetic orbitals $a(b)$ and $a'(b')$ for the two states:

$$\begin{aligned} a &= \alpha a_1 + \beta a_2, & b &= -\alpha b_1 + \beta b_2, \\ a' &= \alpha' a_1 + \beta' a_2, & b' &= -\alpha' b_1 + \beta' b_2, \end{aligned} \quad (8)$$

where the α (α') and β (β') coefficients are the mixing coefficients between the d orbitals in the triplet (singlet) state. This hybridization of the orbitals actually mixes T_1 with T_2 and T_4 and S_1 with S_3 and S_4 in a constrained manner that results in the following functions:

$$\begin{aligned} T_1^0 &= -\alpha^2 T_1^0 + \beta^2 T_4^0 + \alpha\beta\sqrt{2}T_2^0, \\ S_1' &= -\alpha'^2 S_1 + \beta'^2 S_4 + \alpha'\beta'\sqrt{2}S_3, \end{aligned} \quad (9)$$

As soon as the active space contains both local $d_{x^2-y^2}$ and d_{xy} orbitals, i.e., CAS(6,4), one sees that the $\alpha\beta$ ($\alpha'\beta'$) product [that is actually the coefficient on the T_2 (S_3) state] is not strictly equal to $\sqrt{\alpha^2\beta^2}$ ($\sqrt{\alpha'^2\beta'^2}$), i.e., the optimization of the four states simultaneously revises the coefficients of the uncoupled states in the coupled ones. Then, a state specific optimization of the MOs is no more compulsory and the flexibility of both wave functions in the state average enlarged CASCI calculations is enough to provide accurate results. This reasoning is generalizable to geometries that would mix more than two local d orbitals. Indeed, as already observed previously for distortions that create two component DMI,²⁵ the active space must contain all d orbitals that mix in the magnetic MOs.

One should note that at the CAS(2,2)SCF level, the variational procedure tries to capture this effect only through the SCF procedure and the flexibility of the wave function is not enough as soon as the state mixing is important, i.e., when approaching the first-order SOC regime. To verify this statement, the results obtained for various angles φ are reported in Table VI. It is interesting to note that far from the first-order SOC regime, the two active spaces [CAS(2,2)CI and CAS(6,4)CI] provide similar results, which can be attributed to the fact that simple rotations of the orbitals can capture the main physics in this regime. Another important result is that the DMI values extracted from the SO matrix and from the effective Hamiltonian theory are very similar far for the first-order SOC regime and become more and more different when approaching first-order SOC. Let us note that for $\varphi = 130^\circ$, while the spectrum is far from being degenerate, the impact of the first-order SOC is already quite

TABLE VI. Values in cm^{-1} of the DMI extracted either from the SO matrix element of the SO-SI method or from the effective Hamiltonian theory for various φ angles. CASCI calculations have been performed using the triplet average orbitals.

φ (deg)	CAS(2,2)SCF	CAS(6,4)CI	
	$ d $ from SO matrix = $ d $ from H^{eff}	$ d $ from SO matrix ^a	$ d $ from H^{eff}
120	1252	1270	812
130	250	221	151
140	120	106	93
150	85	75	70
160	71	61	59
170	63	54	52

^aDirectly taken from the relevant off-diagonal element of the SO-SI matrix (i.e., excited state contributions being neglected).

important: a CAS(6,4) calculation is compulsory and the effective Hamiltonian theory must be used to extract the DMI value.

Let us now analyze the impact of dynamic correlation. Table VII reports the values obtained using (i) the CASCI energies and wave functions, (ii) the DDCI energies and the CASCI wave functions, and (iii) the DDCI energies and wave functions. First of all, we can note the same discrepancy at the DDCI level that observed at the CASCI level between the values extracted from the SO matrix and the effective Hamiltonian theory. For the two first calculations, the wave functions are identical and the DMI values obtained from the SO matrix are of course identical as the off-diagonal elements do not depend on the energies but only on the wave functions. On the contrary, the effective Hamiltonian theory uses the energies of the excited states and therefore provides different values for different spectra. In the last column, both the energies and the wave functions are obtained at the correlated level. The impact of dynamic correlation is dramatic with both methods of extraction, showing that using a correlated wave function is crucial to calculate the DMI. One may note that the norms of the projections of the two lowest SO states onto the S_1 and T_1 uncoupled functions are 62% and 65%, respectively.

We would like now to understand why dynamic correlation increases the DMI. In the first place, we report the SO matrices (see Table VIII) of the SO-SI method obtained using both the CAS(6,4) and CAS(6,4) + DDCI energies and their corresponding S' and T' wave functions projected onto the CAS space.

TABLE VII. Cu_2Cl_5^- with angle $\theta = 170^\circ$ and $\varphi = 130^\circ$. DMI values obtained from (i) CAS(6,4)CI energies and wave functions (column 2), (ii) CAS(6,4) DDCI energies and CAS(6,4)CI wave functions (column 3), and (iii) CAS(6,4) + DDCI energies and wave functions (column 4). Calculations have been performed using the triplet averaged orbitals.

cm^{-1}	CAS(6,4)CI	CAS(6,4) + DDCI	CAS(6,4) + DDCI
	CASCI WF	CASCI WF	DDCI WF
$ d $ from SO matrix	226	226	622
$ d $ from H^{eff}	155	80	444

TABLE VIII. Cu_2Cl_5^- with angle $\theta = 170^\circ$ and $\varphi = 130^\circ$. SOC matrix in the basis of the coupled functions extracted using either the CAS(6,4)CI or from the CAS(6,4) + DDCI (in bold) electronic calculations. Values are in cm^{-1} .

CAS/DDCI	S'_1	S'_2	S'_3	$T'_1{}^0$	$T'_2{}^0$	$T'_3{}^0$
S'_1	0	0	0	-110i/- 311i	1078i/ 1031i	-4.3i/- 6.1i
S'_2	0	1860/ 2618	0	-1087i/- 1082i	-23.5i/- 120i	-1082i/- 1064i
S'_3	0	0	3166/ 3898	-18.5i/- 114i	1087i/ 1086i	87.5i/ 196i
$T'_1{}^0$	110i/ 311i	1087i/ 1082i	18.5i/ 114i	310/ 843	0	0
$T'_2{}^0$	-1078i/ 1031i	23.5i/ 120i	-1087i/- 1086i	0	1546/ 1892	0
$T'_3{}^0$	4.3i/ 6.1i	1082i/ 1064i	-87.5i/- 196i	0	0	3349/ 4322

Then, in order to check the validity of our analytical approach of the first-order SOC regime, we have extracted the SO matrices in the uncoupled (S and T) functions basis using the effective Hamiltonian theory working on the model space of the six electronic states. Table IX reports the matrix elements obtained using the CAS(6,4) and CAS(6,4)+DDCI energies and their corresponding S' and T' wave functions projected onto the uncoupled functions.

The spin-orbit part of the matrices is identical to that calculated analytically, except for the numerical uncertainties. It allows us to extract a spin-orbit constant of $\sim 770 \text{ cm}^{-1}$ in agreement with the expected value for a Cu(II) in a complex, i.e., slightly less than that of the free ion 830 cm^{-1} .³⁹ Regarding the electronic part, we also observe very similar matrices to that derived analytically with fairly low values of the bielectronic integrals $\langle S_1 | H^{El} | S_4 \rangle$ and $\langle T_4^0 | H^{El} | T_1^0 \rangle$ assumed to be small in the model matrix (but that could be accounted for if necessary).

The important point here is to note that the direct coupling between S_1 and T_1 is strictly zero, as expected from the analytical derivation. This shows the crucial role of the mixings with excited uncoupled functions. A second-order perturbative estimate of their effective coupling (i.e., between S'_1 and T'_1) after mixing with T_2 and S_3 can be obtained using Eq. (5),

$$\begin{aligned} & \frac{1}{2} (\langle S'_1 | H^{SO} | T_1^0 \rangle + \langle T'_1 | H^{SO} | S_1^0 \rangle)_{(CASC I)} \\ &= \frac{1}{2} \left(\frac{h'_1 \sqrt{2} i \xi}{E(S_3) - E(S_1)} + \frac{h'_1 \sqrt{2} i \xi}{E(S_3) - E(T_1)} \right) \\ &+ \frac{1}{2} \left(\frac{\sqrt{2} i \xi h_1}{E(T_2^0) - E(S_1)} + \frac{\sqrt{2} i \xi h_1}{E(T_2^0) - E(T_1)} \right) \\ &= -184i + 52i = -132i \text{ (cm}^{-1}\text{)}, \end{aligned} \quad (10)$$

where we have taken the mean value of the off-diagonal elements since the quasi-degenerate perturbation theory provides non-Hermitian matrices. Note that, despite the fact that we approach the first-order SOC regime, the values are quite close to those of the SO matrix elements provided by SO-SI, i.e., in the S' and T' coupled function basis: $-i|d|/2 = -220i/2$ (Table V) = $-110i$ (Table VII). One may also note that the contributions of the S_3 and T_2 excited states to the effective coupling are of opposite sign.

A comparison of the matrices obtained using either the CASCI or the CAS + DDCI electronic results enables us to measure the impact of electron correlation. One first sees that electronic interactions increase with dynamic correlation while the spectrum expands. The second-order perturbative estimate of the SOC between the two lowest singlet and triplet states is $-92.8i - 231.8i = -324.6i \text{ cm}^{-1}$, which here again compares quite well with the value extracted from the SO-SI method ($-i|d|/2 = -622i/2 = -311i$) (see Tables VII and VIII). The qualitative impact of dynamic correlation lies in the change of sign of the h_1 effective interaction between T_1 and T_2 , resulting in the two contributions of the same sign that sum up to give a very large negative value. A deep inspection of the mechanisms involved in this effective interaction would of course be of interest, even if quite tedious, but is out of the scope of the present study that focuses more specifically on the procedures of calculation and extraction. It is worth noting for a reader unfamiliar with the effective Hamiltonian theory that effective interactions between functions of the model space can be very different from those of the exact Hamiltonians since they take into account effects passing through excited configurations up to the infinite order of perturbations. It is not surprising that these effective interactions can even change sign and sometimes values by orders of magnitude.

TABLE IX. Cu_2Cl_5^- with angle $\theta = 170^\circ$ and $\varphi = 130^\circ$. SOC matrix in the basis of the uncoupled functions extracted using either the CAS(6,4)CI or CAS(6,4) + DDCI (in bold) electronic calculations. Values are in cm^{-1} .

CAS/DDCI	S_1	S_3	S_4	T_1^0	T_2^0	T_4^0
S_1	0/0	-277/- 428	26/ 80	0	1086i	0
S_3	-277/- 428	1781/ 2472	93/- 10	1086i	0	1086i
S_4	26/ 80	93/- 10	3116/ 3822	0	1086i	0
T_1^0	0	-1086i	0	270/ 785	67/- 117	-26/- 76
T_2^0	-1086i	0	-1086i	67/- 117	1538/ 1866	-262/- 389
T_4^0	0	-1086i	0	-26/- 76	-262/- 389	3266/ 4183

Usually in magnetic systems based on transition metal ions, unpaired electrons are sheltered by well-defined magnetic orbitals, i.e., having an occupancy close to 1. They are coupled through exchange integrals, the amplitude of which determines most of the spectrum characteristics. The resulting states have wave functions very close to those of the S_1 and T_1 uncoupled states described above. In most transition metal complexes, SOC has a low amplitude effect: it slightly affects the energies of the states and removes degeneracy between M_S components of non-zero spin states. When approaching the first-order SOC regime, the physical content of these states changes dramatically. The functions of the two states differ from those of the functions S_1 and T_1 by (i) their spatial part that results from an electronic coupling with excited electronic states; it is impossible to identify only two local singly occupied orbitals from which a zeroth-order wave function possessing the essentials of physics could be constructed as the functions are multireferential and (ii) the spin part. Indeed, a strong mixing of different spin states due to non-negligible SOC occurs. Finally, the functions S_A and S_B used in Eq. (1) could be seen as pseudo-orbital pseudo-spin functions, as it is quite often the case in lanthanide complexes.

IV. CONCLUSION AND PERSPECTIVES

A first objective of this work consisted in determining the methodological factors (basis sets, active spaces, level of dynamic correlation) appropriate to calculate the DMI. We focused on the determination of giant values of DMI, i.e., obtained when approaching the first-order SOC regime. For this purpose, we have studied a model system to which we have imposed a deformation that induces large single component DMI values (coming from an orbital mixing of the $d_{x^2-y^2}$ and d_{xy} orbitals). Beyond the analysis of that specific regime, this work has helped to better understand the physical origin of this interaction and, in particular, it revealed the following:

- (i) The direct term between the uncoupled functions that are supposed to be the basis of the model Hamiltonian in which the DMI is defined is strictly zero. It is therefore the indirect coupling via the excited states that determines the magnitude of this interaction and we have seen that it is possible to get a reasonable estimate of this coupling owing to the quasi-degenerate perturbation theory.
- (ii) The extraction of the DMI directly from the SO matrix calculated with the SO-SI method is valid far from the first-order SOC regime but it becomes irrelevant as soon as we enter this regime. In such a case, effective Hamiltonian theory extractions should be used. The intermediate Hamiltonian theory enabled us to extract this interaction in the case of poor projections of the target states onto the model space. In the two-state considered case, the two theories lead exactly to the same values, but this method could be of interest when some of the target states cannot be calculated. An important conclusion here is that the effective Hamiltonian theory may be relevant even in cases where the projections onto the model space are low.
- (iii) The values of the DMI are strongly dependent on dynamic correlation whatever the method of extraction is. Contrary to what has already been observed for the determination of the Zero-Field Splitting parameters, the sole use of the correlated energies is not sufficiently reliable to reach stable

values. Indeed, correlated wave functions lead to very different extracted values and it would be interesting to extend the proposed strategy that uses the dynamically correlated projected wave functions to calculate other spin-orbit properties.

This work shows an important discrepancy of the values determined from different *ab initio* methods, which are also strongly dependent on the extraction method. Establishing benchmarks on real molecules studied experimentally is obviously the next crucial step.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the effective Hamiltonian theory and a method of extraction based on the intermediate Hamiltonian theory.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹I. E. Dzyaloshinskii, *J. Exp. Theor. Phys.* **19**, 960 (1964), see <http://jetp.ras.ru/cgi-bin/e/index/e/19/4/p960?a=list>.
- ²I. Dzyaloshinsky, *J. Phys. Chem. Solids* **4**, 241 (1958).
- ³T. Moriya, *Phys. Rev.* **120**, 91 (1960).
- ⁴T. Moriya, *Solid State Commun.* **20**, 291 (1976).
- ⁵P. Bak and M. H. Jensen, *J. Phys. C: Solid State Phys.* **13**, L881 (1980).
- ⁶M. Kataoka and O. Nakanishi, *J. Phys. Soc. Jpn.* **50**, 3888 (1981).
- ⁷A. N. Bogdanov and D. A. Yablonskii, *J. Exp. Theor. Phys.* **68**, 101 (1989), see <http://jetp.ras.ru/cgi-bin/e/index/e/68/1/p101?a=list>.
- ⁸A.-O. Mandru, O. Yildirim, R. Tomasello, P. Heistracher, M. Penedo, A. Giordano, D. Suess, G. Finocchio, and H. J. Hug, *Nat. Commun.* **11**, 6365 (2020).
- ⁹X. Z. Yu, Y. Onose, N. Kanazawa, J. H. Park, J. H. Han, Y. Matsui, N. Nagaosa, and Y. Tokura, *Nature* **465**, 901 (2010).
- ¹⁰G. Chen, A. Mascaraque, H. Jia, B. Zimmermann, M. Robertson, R. L. Conte, M. Hoffmann, M. A. G. Barrio, H. Ding, R. Wiesendanger, E. G. Michel, S. Blügel, A. K. Schmid, and K. Liu, *Sci. Adv.* **6**, eaba4924 (2020).
- ¹¹A. D. Buckingham, P. Pyykkö, J. B. Robert, and L. Wiesenfeld, *Mol. Phys.* **46**, 177 (1982).
- ¹²R. Ruamps, R. Maurice, C. de Graaf, and N. Guihéry, *Inorg. Chem.* **53**, 4508 (2014).
- ¹³F. Neese, *J. Chem. Phys.* **127**, 164112 (2007).
- ¹⁴L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet, and D. Luneau, *J. Am. Chem. Soc.* **130**, 12445 (2008).
- ¹⁵E. Ruiz, J. Cirera, J. Cano, S. Alvarez, C. Loose, and J. Kortus, *Chem. Commun.* **2008**, 52.
- ¹⁶R. Maurice, “Zero-field anisotropic spin Hamiltonians in first-row transition metal complexes: Theory, models and applications,” Ph.D. thesis, Université de Toulouse, Université Toulouse III—Paul Sabatier, 2011.
- ¹⁷R. Maurice, N. Guihéry, R. Bastardis, and C. de Graaf, *J. Chem. Theory Comput.* **6**, 55 (2010).
- ¹⁸R. Maurice, R. Bastardis, C. de Graaf, N. Suaud, T. Mallah, and N. Guihéry, *J. Chem. Theory Comput.* **5**, 2977 (2009).
- ¹⁹R. Maurice, C. de Graaf, and N. Guihéry, *Phys. Chem. Chem. Phys.* **15**, 18784 (2013).

- ²⁰R. Maurice, K. Sivalingam, D. Ganyushin, N. Guihéry, C. de Graaf, and F. Neese, *Inorg. Chem.* **50**, 6229 (2011).
- ²¹R. Maurice, C. de Graaf, and N. Guihéry, *Phys. Rev. B* **81**, 214427 (2010).
- ²²R. Maurice, A.-M. Pradipto, C. de Graaf, and R. Broer, *Phys. Rev. B* **86**, 024411 (2012).
- ²³R. Maurice, A. M. Pradipto, N. Guihéry, R. Broer, and C. de Graaf, *J. Chem. Theory Comput.* **6**, 3092 (2010).
- ²⁴A.-M. Pradipto, R. Maurice, N. Guihéry, C. de Graaf, and R. Broer, *Phys. Rev. B* **85**, 014409 (2012).
- ²⁵M.-A. Bouammali, N. Suaud, C. Martins, R. Maurice, and N. Guihéry, *J. Chem. Phys.* **154**, 134301 (2021).
- ²⁶C. Bloch, *Nucl. Phys.* **6**, 329 (1958).
- ²⁷J. des Cloizeaux, *Nucl. Phys.* **20**, 321 (1960).
- ²⁸J. P. Malrieu, R. Caballol, C. J. Calzado, C. de Graaf, and N. Guihéry, *Chem. Rev.* **114**, 429 (2014).
- ²⁹L. Adamowicz, R. Caballol, J. P. Malrieu, and J. Meller, *Chem. Phys. Lett.* **259**, 619 (1996).
- ³⁰J.-P. Malrieu, *Mol. Phys.* **111**, 2451 (2013).
- ³¹F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. Li Manni, H. Lischka, D. Ma, P. Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata, and R. Lindh, *J. Comput. Chem.* **37**, 506 (2016).
- ³²G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, and L. Seijo, *Comput. Mater. Sci.* **28**, 222 (2003).
- ³³F. Aquilante, L. De Vico, N. Ferré, G. Ghigo, P. Å. Malmqvist, P. Neogrady, T. B. Pedersen, M. Pitoňák, M. Reiher, B. O. Roos, L. Serrano-Andrés, M. Urban, V. Veryazov, and R. Lindh, *J. Comput. Chem.* **31**, 224 (2010).
- ³⁴J. Miralles, J.-P. Daudey, and R. Caballol, *Chem. Phys. Lett.* **198**, 555 (1992).
- ³⁵J. Miralles, O. Castell, R. Caballol, and J.-P. Malrieu, *Chem. Phys.* **172**, 33 (1993).
- ³⁶D. Maynau and N. Ben Amor, *Chem. Phys. Lett.* **286**, 211 (1998).
- ³⁷P. Å. Malmqvist, B. O. Roos, and B. Schimmelpfennig, *Chem. Phys. Lett.* **357**, 230 (2002).
- ³⁸B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P.-O. Widmark, *J. Phys. Chem. A* **109**, 6575 (2005).
- ³⁹T. M. Dunn, *Trans. Faraday Soc.* **57**, 1441 (1961).