

Cite this: DOI: 00.0000/xxxxxxxxxx

# Spin-Orbit Coupling Descriptions of Magnetic Excitations in Lanthanide Complexes<sup>†</sup>

Shashank Vittal Rao, Matteo Piccardo, and Alessandro Soncini\*

Received Date  
Accepted Date

DOI: 00.0000/xxxxxxxxxx

We present a number of computationally cost-effective approaches to calculate magnetic excitations (i.e. crystal field energies and magnetic anisotropies in the lowest spin-orbit multiplet) in lanthanide complexes. In particular, we focus on the representation of the spin-orbit coupling term of the molecular Hamiltonian, which has been implemented within the quantum chemistry package CERES using various approximations to the Breit-Pauli Hamiltonian. The approximations include the (i) bare one-electron approximation, (ii) atomic mean field and molecular mean field approximations of the two-electron term, (iii) full representation of the Breit-Pauli Hamiltonian. Within the framework of the CERES implementation, the spin-orbit Hamiltonian is always fully diagonalized together with the electron repulsion Hamiltonian (CASCI-SO) on the full basis of Slater determinants arising within the  $4f$  ligand field space. For the first time, we make full use of the Cholesky decomposition of two-electron spin-orbit integrals to speed up the calculation of the two-electron spin-orbit operator. We perform an extensive comparison of the different approximations on a set of lanthanide complexes varying both the lanthanide ion and the ligands. Surprisingly, while our results confirm the need of at least a mean field approach to accurately describe the spin-orbit coupling interaction within the ground Russell-Saunders term, we find that the simple bare one-electron spin-orbit Hamiltonian performs reasonably well to describe the crystal field split energies and  $g$  tensors within the ground spin-orbit multiplet, which characterize all the magnetic excitations responsible for lanthanide-based single-molecule magnetism.

## 1 Introduction

The use of lanthanoid atoms as central metal ions in inorganic complexes seems to be the most promising way to achieve Single Molecule Magnets (SMM) with high operational temperatures<sup>1-5</sup>. This promise comes from the characteristic electronic structure properties of the lanthanide complexes, which involve only a weak mixing of the valence  $f$ -orbitals with the ligand. The valence space of these systems is more akin to atomic  $4f$ -orbitals, and like their atomic counterparts, the electronic structure of these complexes is dominated by spin-orbit  $J$ -multiplets, that are only weakly split by electronic interaction with the ligand field<sup>6,7</sup>. As a consequence, lanthanide based SMMs feature a large magnetic anisotropy arising from the crystal field splitting of the large unquenched angular momentum states in the ground multiplet.

Due to the typical over-parametrization afflicting phenomenological crystal field theory models<sup>6,8</sup>, nowadays the ab initio cal-

culations of the crystal field energy levels of lanthanide complexes play an important role in the interpretation of the experimental results. Among the various available ab initio approaches, the Complete Active Space Self-Consistent Field with Restricted Active Space State Interaction via Spin-Orbit coupling (CASSCF/RASSI-SO) method has been successfully used in the literature to compute the magnetic properties of the lanthanide complexes<sup>9-11</sup>. Such a method involves converging a set of molecular orbitals (MO) for each spin configuration in the CASSCF step. Then diagonalizing the Spin-Orbit Coupling (SOC) operator over the basis of the CASSCF wavefunctions. This is the method of choice in the popular package MOLCAS<sup>12</sup>, and it has extensively used to simulate the magnetic properties of lanthanide-based systems.

Recently, an alternative strategy has been proposed by us<sup>13,14</sup>, where a set of MO are optimized by minimizing the average-energy functional represented on the basis of all the possible CI configurations, which is called Configuration Averaged Hartree Fock (CAHF) method<sup>13,15,16</sup>. The optimizations of the MO and CI coefficients are then decoupled, and the latter coefficients are determined in a second step by direct diagonalization of the total Hamiltonian within the Complete Active Space Configuration In-

School of Chemistry, The University of Melbourne, Australia.

\*E-mail: [asoncini@unimelb.edu.au](mailto:asoncini@unimelb.edu.au)

<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 00.0000/00000000.

teraction with Spin-Orbit coupling (CASCI-SO) method.

CAHF/CASCI-SO method has been shown to produce consistent results with CASSCF/RASSI-SO approach with a significant saving in computational time, and it has been implemented into the Computational Emulator of Rare Earth Systems (CERES) quantum chemistry package<sup>17</sup>, an ad hoc tool specifically designed for the calculation of the electronic structure and magnetic properties of lanthanide complexes.

In this study, we focus our attention on the SOC operator, which enters the CASCI-SO step. Spin-orbit interaction plays an important role in the case of lanthanide complexes. It causes the splitting and mixing of the atomic terms. The SOC Hamiltonians arise naturally from the reduction of the Dirac equation and its many electron extensions to two components theory<sup>18</sup>. This reduction can be achieved in many different ways, and the most renowned spin-orbit Hamiltonian thus achieved is the Breit-Pauli Hamiltonian<sup>19</sup>, including both a one-electron (1e-SOC) term, and a two-electron (2e-SOC) term. However, the Breit-Pauli operator is quite complex, and different approximations are often used in the literature<sup>20</sup>. While many studies have been published on the performances of the different SOC approximations in the accurate modeling of spectroscopic transitions in organic molecules and inorganic complexes, including inter-multiplet transitions in lanthanide systems<sup>20–24</sup>, to our knowledge we present here the first extensive comparison of the performance of different approximations to the full Breit-Pauli Hamiltonian in the calculation of the crystal field splitting of the ground multiplets of lanthanide complexes, i.e. of their magnetic excitations.

Moreover, two of us have recently presented a new development that makes the evaluation of all the two-electron integrals entering the the Breit-Pauli Hamiltonian more efficient by the use of the Cholesky decomposition technique<sup>25</sup>. The aim of this work is then to (i) introduce working equations for the use of the Cholesky representation of the 2e-SOC integrals within the Breit-Pauli Hamiltonian and various mean-field approximations to it, (ii) apply our developments to the explicit ab initio calculation of the crystal field levels in a family of Ln(III) complexes, and finally (iii) compare the performances of the bare 1e-SOC and different mean-field approximations to the spin-orbit coupling Hamiltonian with respect to that of the full Breit-Pauli Hamiltonian, via a detailed analysis of the ensuing errors affecting the crystal field energy levels in the lowest energy multiplets for a series of Ln(III) complexes.

## 2 Spin-Orbit Coupling Hamiltonian

The Breit-Pauli spin-orbit Hamiltonian in atomic units for a system of  $N_e$  electrons and  $N_n$  nuclei has form<sup>18,19,26–28</sup>:

$$\begin{aligned} \mathcal{H}_{\text{SO}}^{\text{BP}} &= \mathcal{H}_{\text{SO}}^{(1)} + \mathcal{H}_{\text{SO}}^{(2)} \\ &= \frac{\alpha^2}{2} \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} \hat{\mathbf{l}}_{iI} \cdot \hat{\mathbf{s}}_i \\ &\quad - \frac{\alpha^2}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^3} \hat{\mathbf{l}}_{ij} \cdot (\hat{\mathbf{s}}_i + 2\hat{\mathbf{s}}_j) \end{aligned} \quad (1)$$

where  $\alpha = c^{-1}$  is the fine structure constant with  $c$  speed of light,  $\hat{\mathbf{l}}_{iI} = (\hat{\mathbf{r}}_i - \mathbf{R}_I) \times \hat{\mathbf{p}}_i$  is the angular momentum of the  $i$ -th electron relative to the  $I$ -th nucleus at position  $\mathbf{R}_I$  with charge  $Z_I$ , and  $\hat{\mathbf{l}}_{ij} = (\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j) \times \hat{\mathbf{p}}_i$  the angular momentum of the  $i$ -th electron relative to the  $j$ -th electron, with  $\hat{\mathbf{r}}_i$  and  $\hat{\mathbf{p}}_i$  position and momentum vector operators. Finally,  $\hat{\mathbf{s}}_i$  is the spin operator of the  $i$ -th electron.

From now on let us use  $\psi_a(\mathbf{x}) = \phi_a(\mathbf{r})\eta_a$  to indicate a single electron molecular spin-orbital, with spatial part  $\phi_a(\mathbf{r})$  and spin  $\eta_a (= \alpha \text{ or } \beta)$ , and define the 1e-SOC and the 2e-SOC integrals on the spatial coordinates as:

$$(\phi_a | \mathbf{g} | \phi_b) = \frac{\alpha^2}{2} \left\langle \phi_a(1) \left| \sum_I \frac{Z_I \hat{\mathbf{l}}_{iI}}{|\mathbf{r}_1 - \mathbf{R}_I|^3} \right| \phi_b(1) \right\rangle \quad (2)$$

and:

$$\begin{aligned} &(\phi_a \phi_b | \mathbf{g} | \phi_c \phi_d) \\ &= -\frac{\alpha^2}{2} \left\langle \phi_a(1) \phi_c(2) \left| \frac{\hat{\mathbf{l}}_{12}}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \right| \phi_b(1) \phi_d(2) \right\rangle \\ &= -\frac{\alpha^2}{2} \left\langle \phi_c(1) \phi_a(2) \left| \frac{\hat{\mathbf{l}}_{21}}{|\mathbf{r}_1 - \mathbf{r}_2|^3} \right| \phi_d(1) \phi_b(2) \right\rangle \end{aligned} \quad (3)$$

As usual when dealing with the CI approach, more direct developments rely on the second quantization formalism<sup>29–31</sup>. In second quantization,  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  has form<sup>22,32</sup>:

$$\begin{aligned} \mathcal{H}_{\text{SO}}^{\text{BP}} &= \sum_{ab} (\phi_a | \mathbf{g} | \phi_b) \cdot \mathbf{T}_{ab} \\ &\quad + \sum_{abcd} [(\phi_a \phi_b | \mathbf{g} | \phi_c \phi_d) + 2(\phi_c \phi_d | \mathbf{g} | \phi_a \phi_b)] \\ &\quad \cdot (\mathbf{T}_{ab} E_{cd} - \delta_{bc} \mathbf{T}_{ad}) \end{aligned} \quad (4)$$

where  $E_{cd}/\mathbf{T}_{ab}$  are the singlet/triplet excitation operators:

$$E_{cd} = a_{c\alpha}^+ a_{d\alpha} + a_{c\beta}^+ a_{d\beta} \quad (5)$$

$$T_{ab}^x = \frac{1}{2} (a_{a\alpha}^+ a_{b\beta} + a_{a\beta}^+ a_{b\alpha}) \quad (6)$$

$$T_{ab}^y = \frac{1}{2i} (a_{a\alpha}^+ a_{b\beta} - a_{a\beta}^+ a_{b\alpha}) \quad (7)$$

$$T_{ab}^z = \frac{1}{2} (a_{a\alpha}^+ a_{b\alpha} - a_{a\beta}^+ a_{b\beta}) \quad (8)$$

with  $a_{c\sigma}^+/a_{c\sigma}$  creation/annihilation operator of an electron in the spin-orbital  $\psi_c$ , with spatial part  $\phi_c$  and spin  $\eta_c$ .

Within all the CI methods, the molecular orbitals are partitioned in two main groups: (i) one set collecting the  $N_i$  orbitals that are doubly occupied in all the configurations, called inactive orbitals, (ii) the second set collecting the  $N_a$  orbitals which allow for an occupation number from 0 to 2, called active orbitals. Pointing out that the operator  $\mathbf{T}_{ab}$  can not connect two doubly occupied orbitals, the Hamiltonian in eq. (4) can be re-written

making explicit the non-null terms as:

$$\begin{aligned} \mathcal{H}_{\text{SO}}^{\text{BP}} = & \sum_{ab}^{N_a} h_{ab} \cdot \mathbf{T}_{ab} + \sum_{abcd}^{N_a} \left[ (\phi_a \phi_b | \mathbf{g} | \phi_c \phi_d) \right. \\ & \left. + 2(\phi_c \phi_d | \mathbf{g} | \phi_a \phi_b) \right] \cdot \mathbf{T}_{ab} E_{cd} \end{aligned} \quad (9)$$

where now  $a$  and  $b$  indices run just on the active set of orbitals, and

$$h_{ab} = (\phi_a | \mathbf{g} | \phi_b) + F_{ab}^{\text{I}} + F_{ab}^{\text{A}} \quad (10)$$

$F_{ab}^{\text{I}}$  term in the previous equation has form:

$$\begin{aligned} F_{ab}^{\text{I}} = & \sum_e^{N_i} \left[ 2(\phi_a \phi_b | \mathbf{g} | \phi_e \phi_e) \right. \\ & \left. - 3(\phi_a \phi_e | \mathbf{g} | \phi_e \phi_b) - 3(\phi_e \phi_b | \mathbf{g} | \phi_a \phi_e) \right] \end{aligned} \quad (11)$$

and it represents the interaction between the electrons sitting in the active orbitals and the mean field generated by the electrons sitting in the inactive orbitals, than it is the analogue of the Fock matrix for the Coulomb interactions<sup>22,31</sup>.  $F_{ab}^{\text{A}}$  term in eq. (10) is given by:

$$F_{ab}^{\text{A}} = - \sum_c^{N_a} \left[ (\phi_a \phi_c | \mathbf{g} | \phi_c \phi_b) + 2(\phi_c \phi_b | \mathbf{g} | \phi_a \phi_c) \right] \quad (12)$$

### 3 Spin-Orbit Mean Field

To avoid dealing explicitly with the 2e-SOC terms during the evaluation of the elements for the CI matrix, in the literature it is often used the mean field (MF) approximation. The latter is based on two assumptions:

1. the second term in the right-hand side of eq. (9) and  $F_{ab}^{\text{A}}$  term in eq. (10) are ignored. This reduces  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  to an effective one-electron operator on the MO basis;
2. the two-electron interactions within the active space are accounted for in an mean field approach within the  $F_{ab}^{\text{I}}$  term in eq. (10).

Under these simplifications, eq. (9) reduces to:

$$\mathcal{H}_{\text{SO}}^{\text{MF}} = \sum_{ab}^{N_a} \left[ (\phi_a | \mathbf{g} | \phi_b) + F_{ab}^{\text{MF}} \right] \cdot \mathbf{T}_{ab} \quad (13)$$

with:

$$\begin{aligned} F_{ab}^{\text{MF}} = & \sum_c^{N_c} \frac{n_c}{2} \left[ (\phi_a \phi_b | \mathbf{g} | \phi_c \phi_c) \right. \\ & \left. - \frac{3}{2}(\phi_a \phi_c | \mathbf{g} | \phi_c \phi_b) - \frac{3}{2}(\phi_c \phi_b | \mathbf{g} | \phi_a \phi_c) \right] \end{aligned} \quad (14)$$

In the previous equation,  $n_c$  is the occupation number of the orbital  $\phi_c$  ( $n_c = 2$  for an inactive orbital,  $n_c = n_a^{\text{el}}/N_a$  for an active orbital, with  $n_a^{\text{el}}$  the number of active electrons), and now the index  $c$  runs over all the complete set of  $N_e$  molecular orbitals.

## 4 The Atomic Approximation

Although the  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  operator in eq. (13) defines an effective one-electron operator, the number of atomic spin-orbit integrals which must be calculated it is not reduced if the Cholesky representation is not used. A widely used approximation used in the literature to reduce the computational effort is to restrict to calculation of the two-electron integrals on the AO basis to comprise only the one-center terms. This methodology is based on the assumption that the spin-orbit two-electron operator is a short-range operator, which can be justified by the presence of  $1/|\mathbf{r}_i - \mathbf{r}_j|^3$  terms in  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ . This is called the atomic approximation.

Moreover, the development that has gained larger popularity in the literature is the atomic mean field implementation (AMFI) proposed by Hess and Schimmelpfennig<sup>21,34</sup>, where the  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  operator is used together with two additional approximations: (i) only one-center integrals are retained throughout, and (ii) the molecular orbitals  $\phi_a$  in eq. (14) are replaced by atomic self-consistent field (SCF) orbitals obtained from spherically averaged atomic SCF calculations with predetermined valence shell occupations rather than using the complete non-spherical molecular density. While the combination of these approximations reduces the time needed for the SOC integrals evaluation to a negligible amount, it has been shown that the inclusion of all the significant multicenters two-electron SOC integrals is of primary importance to achieve a good accuracy<sup>20</sup>.

In this work, we study how the atomic approximation affects the energy levels when applied to both  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  and  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  operators. In both cases, the density used in our SOC atomic calculations is always from the *true* molecular density, optimized at CAHF level on the whole system.

## 5 Cholesky representation

The integrals entering eqs. (9) and (13) are usually evaluated by expanding the functions  $\phi_a$  on a set of  $N_{\text{AO}}$  atomic basis functions  $\{\varphi_a\}$ :

$$\phi_a(\mathbf{r}) = \sum_{\mu}^{N_{\text{AO}}} c_{\mu a} \varphi_{\mu}(\mathbf{r}) \quad (15)$$

Here come the intense computational effort of a molecular calculation which aims to include explicitly both the  $\mathcal{H}_{\text{SO}}^{(1)}$  and  $\mathcal{H}_{\text{SO}}^{(2)}$  term in eq. (1), that is the evaluation of all the 2e-SOC integrals in atomic orbitals (AO) basis, and their transformations to the molecular orbitals (MO) basis:

$$\begin{aligned} & (\phi_a \phi_b | \mathbf{g} | \phi_c \phi_d) \\ & = \sum_{\mu\nu\tau\kappa}^{N_{\text{AO}}} c_{\mu a} c_{\nu b} c_{\kappa c} c_{\tau d} (\varphi_{\mu} \varphi_{\nu} | \mathbf{g} | \varphi_{\kappa} \varphi_{\tau}) \end{aligned} \quad (16)$$

Different approximations have been proposed in the literature to reduce the time needed for SOC integrals evaluation<sup>20,21,33</sup>. We propose here a new approach, which allows for significant speed ups of the calculations without loss of accuracy. This can be achieved by the use of the Cholesky representation for the 2e-SOC integrals

recently presented in the literature by some of us<sup>25</sup>:

$$\begin{aligned}
& (\varphi_\mu \varphi_\nu | g_\alpha | \varphi_\kappa \varphi_\tau) \\
&= \frac{-i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \left[ (\varphi_\mu \nabla_\gamma \varphi_\nu | \nabla_\beta \varphi_\kappa \varphi_\tau) + (\varphi_\mu \nabla_\gamma \varphi_\nu | \varphi_\kappa \nabla_\beta \varphi_\tau) \right] \\
&\approx \frac{-i\alpha^2}{2} \sum_J^{N_{\text{CH}}} \left( [L_{\mu\nu}^\gamma]^J [L_{\tau\kappa}^\beta]^J + [L_{\mu\nu}^\gamma]^J [L_{\kappa\tau}^\beta]^J \right) \quad (17)
\end{aligned}$$

where  $\varepsilon_{\alpha\beta\gamma}$  is the Levi-Civita symbol,  $(\varphi_\mu \varphi_\nu | g_\alpha | \varphi_\kappa \varphi_\tau)$  is an Coulomb electron repulsion integral (ERI), and  $[L_{\mu\nu}^\gamma]^J$  is an element of the  $J$ -th Cholesky vector in AO basis.  $N_{\text{CH}}$  the dimension of the Cholesky basis, i.e. the number of the Cholesky vectors. In ref.<sup>25</sup>, we showed that chosen the Cholesky  $\delta$  threshold, the errors  $\Delta_{\text{SOC}}$  affecting the integrals evaluated by eq. (17) is always  $\Delta_{\text{SOC}} \leq 2\delta$ . Then, the 2e-SOC integrals in MO basis can be expressed on the Cholesky basis by substituting eq. (17) into eq. (16):

$$\begin{aligned}
& (\phi_a \phi_b | g_\alpha | \phi_c \phi_d) \\
&= \sum_{\mu\nu\tau\kappa}^{N_{\text{AO}}} c_{\mu a} c_{\nu b} c_{\kappa c} c_{\tau d} (\varphi_\mu \varphi_\nu | g_\alpha | \varphi_\kappa \varphi_\tau) \\
&= \frac{-i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \sum_{\mu\nu\tau\kappa}^{N_{\text{AO}}} c_{\mu a} c_{\nu b} c_{\kappa c} c_{\tau d} \\
&\quad \left[ (\varphi_\mu \nabla_\gamma \varphi_\nu | \nabla_\beta \varphi_\kappa \varphi_\tau) + (\varphi_\mu \nabla_\gamma \varphi_\nu | \varphi_\kappa \nabla_\beta \varphi_\tau) \right] \\
&\approx \frac{-i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \sum_J^{N_{\text{CH}}} \left( [L_{ab}^\gamma]^J [L_{dc}^\beta]^J + [L_{ab}^\gamma]^J [L_{cd}^\beta]^J \right) \quad (18)
\end{aligned}$$

where  $[L_{ab}^\gamma]^J \neq [L_{ba}^\gamma]^J$  is an element of the  $J$ -th Cholesky vector transformed in the MO basis:

$$[L_{ab}^\gamma]^J = \sum_{\mu\nu}^{N_{\text{AO}}} c_{\mu a} [L_{\mu\nu}^\gamma]^J c_{\nu b} \quad (19)$$

Moreover, the term in eq. (11) on AO basis reads:

$$F_{ab}^I = \sum_{\mu\nu}^{N_{\text{AO}}} c_{\mu a} c_{\nu b} F_{\mu\nu} \quad (20)$$

where:

$$\begin{aligned}
F_{\mu\nu} &= \sum_{\kappa\tau}^{N_{\text{AO}}} D_{\kappa\tau} \left[ (\varphi_\mu \varphi_\nu | \mathbf{g} | \varphi_\kappa \varphi_\tau) \right. \\
&\quad \left. - \frac{3}{2} (\varphi_\mu \varphi_\kappa | \mathbf{g} | \varphi_\tau \varphi_\nu) - \frac{3}{2} (\varphi_\tau \varphi_\nu | \mathbf{g} | \varphi_\mu \varphi_\kappa) \right] \quad (21)
\end{aligned}$$

and  $D_{\kappa\tau}$  is an element of the molecular density  $\mathbf{D}$  for the inactive electrons in AO basis:

$$D_{\kappa\tau} = 2 \sum_c^{N_i} c_{\kappa c} c_{\tau c} \quad (22)$$

By the use of the Cholesky representation for the 2e-SOC inte-

grals,  $F_{\mu\nu}$  becomes:

$$\begin{aligned}
F_{\mu\nu} &\approx -\frac{i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \sum_J^{N_{\text{CH}}} \sum_{\kappa\tau}^{N_{\text{AO}}} D_{\kappa\tau} \\
&\quad \left[ [L_{\mu\nu}^\gamma]^J \left( [L_{\kappa\tau}^\beta]^J + [L_{\tau\kappa}^\beta]^J \right) \right. \\
&\quad \left. - \frac{3}{2} \left( [L_{\mu\kappa}^\gamma]^J [L_{\nu\tau}^\beta]^J + [L_{\tau\nu}^\gamma]^J [L_{\kappa\mu}^\beta]^J \right) \right] \\
&= -\frac{i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \sum_J^{N_{\text{CH}}} \left[ [L_{\mu\nu}^\gamma]^J \sum_{\kappa\tau}^{N_{\text{AO}}} D_{\kappa\tau} \left( [L_{\tau\kappa}^\beta]^J + [L_{\kappa\tau}^\beta]^J \right) \right. \\
&\quad \left. - 3 \sum_c^{N_i} \left( [K_{\mu c}^\gamma]^J [K_{\nu c}^\beta]^J + [K_{c\nu}^\gamma]^J [K_{c\mu}^\beta]^J \right) \right] \quad (23)
\end{aligned}$$

where  $[K_{\mu c}^\gamma]^J \neq [K_{c\mu}^\gamma]^J$  are the semi-transformed Cholesky vectors:

$$[K_{\mu c}^\gamma]^J = \sum_{\kappa}^{N_{\text{AO}}} [L_{\mu\kappa}^\gamma]^J c_{\kappa c} \quad (24)$$

$$[K_{c\mu}^\gamma]^J = \sum_{\kappa}^{N_{\text{AO}}} [L_{\kappa\mu}^\gamma]^J c_{\kappa c} \quad (25)$$

Within the MF approximation, the 2e-SOC integrals can be efficiently evaluated by the use of their Cholesky representation leading to:

$$\begin{aligned}
F_{\mu\nu}^{\text{MF}} &\approx -\frac{i\alpha^2}{2} \varepsilon_{\alpha\beta\gamma} \sum_J^{N_{\text{CH}}} \left[ [L_{\mu\nu}^\gamma]^J \sum_{\kappa\tau}^{N_{\text{AO}}} D_{\kappa\tau} \left( [L_{\tau\kappa}^\beta]^J + [L_{\kappa\tau}^\beta]^J \right) \right. \\
&\quad \left. - \frac{3}{2} \sum_c^{N_e} n_c \left( [K_{\mu c}^\gamma]^J [K_{\nu c}^\beta]^J + [K_{c\nu}^\gamma]^J [K_{c\mu}^\beta]^J \right) \right] \quad (26)
\end{aligned}$$

with:

$$D_{\kappa\tau} = \sum_c^{N_e} n_c c_{\kappa c} c_{\tau c} \quad (27)$$

The computation of the spin-orbit coupling contributions implemented in CERES includes five steps: (i) evaluation and storage of the Cholesky representation for the 2e-SOC integrals as presented in ref.<sup>25</sup>, (ii) evaluation of  $F_{ab}^I$  in eq. (9) by direct contraction of the inactive density matrix with the Cholesky vectors (eq. (23)) and transformation on the molecular basis (iii) transformation of the Cholesky vectors on the molecular basis within the chosen active space and construction of the 2e-SOC integrals (iv) evaluation of the effective one-electron integrals in eq. (10) via eq. (12) (v) update and diagonalization of the CI-SOC matrix.

The here proposed approach allows the following advantages: (i) rigorous evaluation of the most important contributions for 2e-SOC integrals, (ii) full control on the needed accuracy by the choice of the unique Cholesky  $\delta$  threshold, and (iii) the one-off calculation and the storage of the smallest amount of data needed to numerically represent all the 2e-SOC integrals with absolute accuracy smaller than  $2\delta$ , which are then readily available for

transformations as in eqs. (18) and (23) (this can be really favorable within the self-consistent approaches which include the SOC contribution in the iterative procedure).

## 6 Computational Methods

CAHF/CASCI-SO calculations were carried out on a set of Ln(III) complexes to analyze how different approximations for  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  Hamiltonian affect the energy gaps of the lowest energy spin-orbit multiplets.

In CAHF/CASCI-SO strategy<sup>13,14</sup>, at first the CAHF method is used to generate the set of  $\phi_a$  molecular orbitals which minimizes the average-energy functional represented on the basis of all possible Slater determinants, of any  $M_S$  quantum number, built up allowing  $n_a^{\text{el}}$  active electrons to be distributed in all the possible ways in  $N_a$  active orbitals. Then, in the CASCI-SO step, the CAHF orbitals are used to construct the representation of the total Hamiltonian of the system, which includes both the Born-Oppenheimer electrostatic and spin-orbit Hamiltonian, still on the basis of all possible Slater determinants in the CAS space of  $n_a^{\text{el}}$  electrons in  $N_a$  orbitals. Finally, the total Hamiltonian is diagonalized to obtain the energy levels.

The number  $N_a = 7$  active orbitals have been used for all the Ln ions studied (i.e. 4f atomic shell), and the number  $n_a^{\text{el}} = 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13$  active electrons for Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III) ions, respectively.

The geometries of the Ln complexes analyzed have been fixed to their experimental X-ray structures taken from the literature.<sup>35-41</sup> We indicate the ligands with acac = acetylacetonate, dppz = dipyrrophenazine, dpq = dipyrroquinoxaline, phen = 1,10-phenanthroline, hfac = hexafluoroacetylacetonate, glyme = dimethoxyethane.

All atoms were described by the ANO-RCC basis set<sup>42</sup>, with the contraction [8s7p5d3f2g1h] for Ln atoms, [4s3p2d1f] for O, [3s2p] for C and N, [2s] for H.

Scalar relativistic terms were included in the one-electron part of the electrostatic Hamiltonian both in the CAHF and CASCI-SO steps, within the second order Douglas-Kroll-Hess (DKH2) approximation<sup>28</sup>.

Four different approximations to the Breit-Pauli Hamiltonian  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  were studied: (i) bare  $\mathcal{H}_{\text{SO}}^{(1)}$ , (ii)  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  complete, (iii) atomic  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  (referred to as  $\mathcal{H}_{\text{SO}}^{\text{AMF}}$ ), and (iv) atomic  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  (referred to as  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$ ). Note that the atomic approximation is applied just to  $\mathcal{H}_{\text{SO}}^{(2)}$  term, while  $\mathcal{H}_{\text{SO}}^{(1)}$  always include both one- and two-centers SOC integrals. The CASCI-SO energies within a given multiplet have been compared with the CASCI-SO results which include the true  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ .

The Cholesky representation of the 2e-SOC integrals as proposed in this paper was used to speed up the calculations when the atomic approximation is not used. Different Cholesky  $\delta$  thresholds have been tested at first to reach the best compromise between time performance and accuracy. It has been fixed at  $\delta = 10^{-4}$ , which shows a significant speed up in the calculations with a loss of accuracy on the energy gaps smaller than  $0.01 \text{ cm}^{-1}$  with respect to the results which include all the 2e-SOC integrals.

All the calculation were performed using the software package CERES<sup>17</sup>, an ab initio quantum chemistry package specifically designed for the calculation of the electronic structure and magnetic properties of lanthanide complexes.

The errors affecting the energy gaps  $\Delta E_i^{\text{APP}} = E_i^{\text{APP}} - E_0^{\text{APP}}$ , calculated within a given spin-orbit multiplet  $M = (2S+1)L_J$  by the use of the approximation APP, were analyzed by the statistical indicators:

$$(\% \text{error})_i^{\text{APP}} = \frac{\Delta E_i^{\text{APP}} - \Delta E_i^{\text{BENC}}}{\Delta E_i^{\text{BENC}}} \times 100 \quad (28)$$

$$\mu_M^{\text{APP}} = \frac{\sum_{i=1}^N (\% \text{error})_i^{\text{APP}}}{N} \quad (29)$$

$$\sigma_M^{\text{APP}} = \sqrt{\frac{\sum_{i=1}^N [(\% \text{error})_i^{\text{APP}} - \mu_M^{\text{APP}}]^2}{N-1}} \quad (30)$$

$$\text{MAE}_M^{\text{APP}} = \frac{\sum_{i=1}^N |(\% \text{error})_i^{\text{APP}}|}{N} \quad (31)$$

where  $\Delta E_i^{\text{BENC}} = E_i^{\text{BENC}} - E_0^{\text{BENC}}$  are the energy gaps calculated by the use of the true  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ , and  $N$  is the total number of states in the multiplet (minus one for the ground state in the ground spin-orbit multiplet). The results were graphically represented by the use of the probability density of the normal distribution:

$$P(\% \text{error}; \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(\% \text{error} - \mu)^2 / (2\sigma^2)} \quad (32)$$

For Dy(III) complexes, the principal values of the  $g$  tensor were calculated within the pseudo-spin  $\tilde{S} = 1/2$  formalism as the square roots of the eigenvalues of the  $\mathbf{G}$  matrix<sup>43,44</sup>:

$$G_{\alpha\beta} = 2 \sum_{r,s=0,1} \langle \Psi_r | m_{\alpha} | \Psi_s \rangle \langle \Psi_s | m_{\beta} | \Psi_r \rangle \quad (33)$$

where  $\mathbf{m} = \mathbf{L} + g_e \mathbf{S}$  is the magnetic moment, with  $\mathbf{L} = \sum_i^{N_e} \mathbf{l}_{i\text{Dy}}$  the total electronic angular momentum with respect to the position of the Dy(III) atom,  $\mathbf{S} = \sum_i^{N_e} \mathbf{s}_i$  the total spin angular momentum, and  $g_e$  the magnetic  $g$  factor of the electron. The electronic wavefunctions  $\Psi_0$  and  $\Psi_1$  are a Kramers pair for the system at zero magnetic field. The three eigenvectors of  $\mathbf{G}$  are the directions of the three principal magnetic axes.

## 7 Results and Discussion

The mean  $\mu$ , standard deviation  $\sigma$ , and MAE for the %errors affecting the energy gaps within the lowest energy spin-orbit multiplet for Ln-acac<sub>3</sub>-(H<sub>2</sub>O)<sub>2</sub> complexes, estimated using different approximations to the Breit-Pauli Hamiltonian, are represented in Figure 1 (see also Table S17 in the Supporting Information (SI)). In the following, MAE =  $|\mu|$  if not explicitly reported.

The errors for  $\mathcal{H}_{\text{SO}}^{(1)}$  differ between the different ions. A quite large underestimation of the crystal field levels affects the results for Ho(III) ( $\mu \approx -11\%$ ,  $\sigma \approx 1\%$ ), while smaller deviations affect the results for Nd(III) ( $\mu \approx -6\%$ ,  $\sigma \approx 2\%$ ), Pr(III) ( $\mu \approx -5\%$ ,  $\sigma \approx 4\%$ ), and Dy(III) ( $\mu \approx -4\%$ ,  $\sigma \approx 1\%$ ). The energy gaps are well represented for Sm(III), Tb(III), Er(III), Tm(III), Yb(III) ( $\mu$  within  $\pm 1\%$  and  $\sigma < 2\%$ ). As an indication of the magnitude of these

errors, it has been shown in the literature that the discrepancies between the simulated ab initio and the experimental results can be larger than 10%<sup>45,46</sup>. As an example, the ab initio crystal field levels in Er(III)-trensal reported in Table 2 of ref.<sup>46</sup> are affected by a MAE  $\approx$  19% for CASSCF/RASSI-SO model A1 simulation, or MAE  $\approx$  8% for RASSCF/CASPT2/RASSI-SO model C4, and in both models the ab initio gap between the ground and the first excited Kramers doublet, which is experimentally observed at 54 cm<sup>-1</sup>, is affected by an error exceeding +13%.

$\mathcal{H}_{\text{SO}}^{(1)}$  is not sufficient to describe the SO coupling within the spin-only ground multiplet  $^8\text{H}_{7/2}$  of Gd(III). Here, the crystal field levels calculated by  $\mathcal{H}_{\text{SO}}^{(1)}$  ( $\Delta E = 1.2, 2.3, 4.3$  cm<sup>-1</sup>, see Table S6) are largely overestimated with respect to the  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  results ( $\Delta E = 0.3, 0.5, 1.0$  cm<sup>-1</sup>), leading to  $\mu \approx +350\%$ .

The  $3\sigma$  (99.7% confidence) is smaller than 6% for almost all the ions in Figure 1, which indicates a systematic nature of the errors introduced by the bare  $\mathcal{H}_{\text{SO}}^{(1)}$  approximation. Pr(III) ( $3\sigma \approx 12\%$ ) and Gd(III) ( $3\sigma \approx 52\%$ ) show an higher degree of randomness.

A large improvement in the results is shown by  $\mathcal{H}_{\text{SO}}^{\text{MF}}$ , where the two-electron interactions are accounted for in a mean field approach. Here,  $\mu$  never exceeds  $\pm 1\%$  for all the ions, with very narrow picked normal distributions.

Similar errors are shown by both the atomic  $\mathcal{H}_{\text{SO}}^{\text{AMF}}$  and  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  approximations, where  $\mu$  falls in the range  $\pm 1\%$  for all the ions, with the exception of Gd(III). For the latter, the exclusion of the 2e-SOC multi-center integrals in the computation leads to a quite large underestimation of the energy gaps ( $\Delta E = 0.2, 0.5, \text{ and } 0.8$  cm<sup>-1</sup>,  $\mu \approx -12\%$ ). Within the atomic approximation, Ho(III), Er(III), and Tm(III) show the largest  $3\sigma$  values ( $3\sigma \approx 2.0\%, 3.0\%$  and  $1.5\%$ , respectively), while  $3\sigma < 1.2\%$  for all the other metals. It is noteworthy that the use of the atomic approach does not introduce significant additional errors to the  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  results.

Next, we study the errors affecting the various approximations to the spin-orbit Hamiltonian in the calculation of the energy gap between ground and first excited multiplets. While due to lack of dynamical correlation in our approach these calculations would be of limited use to model experimental data, we are only interested here to estimate the typical error affecting spin-orbit Hamiltonians for the calculation of such energy gaps, as a term of comparison with that estimated for the ground multiplet magnetic excitations that are the focus of this study. The results are represented in Figure 2 (see Table S17 in SI). Here, the bare  $\mathcal{H}_{\text{SO}}^{(1)}$  fails completely, with a general overestimation of the crystal field gaps larger than +70% for all the ions but Gd(III). Differently, the  $^6\text{P}_{7/2}$  levels for Gd(III) are underestimated ( $\Delta E = 35631, 35687, 35728, 35822$  cm<sup>-1</sup> by  $\mathcal{H}_{\text{SO}}^{(1)}$  versus  $\Delta E = 38742, 38779, 38807, 38849$  cm<sup>-1</sup> by  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ , with  $\mu \approx -9\%$  and  $\sigma \approx 0.1\%$ ).

On the other hand,  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  approximation leads to errors within the acceptable range  $\pm 4\%$ , with generally small standard deviations ( $\sigma < 1\%$ ). As for the ground multiplets,  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  and  $\mathcal{H}_{\text{SO}}^{\text{AMF}}$  approximations lead to very comparable results, and  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  shows almost zero errors.

Overall,  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  Hamiltonian turns out to be a very good compromise between computational saving and accuracy in the evaluation of the energy gaps for both the ground (of large interest

for the magnetic properties) and the first excited (of large interest for the spectroscopic properties) multiplets of Ln(III) complexes. On the other hand,  $\mathcal{H}_{\text{SO}}^{(1)}$  works quite well for the gaps within the ground multiplets, but it can not be used for the estimation of the gaps in the excited levels.

Eu(III) ion deserves a special consideration. The ground level of Eu(III) is the  $^7\text{F}_0$  singlet, and the gaps between the lowest energy multiplets  $^7\text{F}_J$ , with  $J = 1, 2, 3, 4, 5, 6$ , are considerably small. CAHF/CASCI-SO[ $\mathcal{H}_{\text{SO}}^{\text{BP}}$ ] computations on the isolated Eu<sup>3+</sup> atom estimates the energy gaps within the ground Russell-Saunders term  $^7\text{F}$  as  $\Delta E = 369, 1028, 1889, 2880, 3949, 5056$  cm<sup>-1</sup>, which are in a very good agreement with the observed values from spectroscopy  $\Delta E = 370, 1040, 1890, 2860, 3910, 4940$  cm<sup>-1</sup> (see Table S1)<sup>47</sup>. On the isolated atom,  $\mathcal{H}_{\text{SO}}^{\text{MF}}$  approximation slightly overestimates the levels gaps with respect to  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  Hamiltonian (+3.5%, +3.8%, +4.1%, +4.5%, +5.0%, +5.5% for  $^7\text{F}_1, ^7\text{F}_2, ^7\text{F}_3, ^7\text{F}_4, ^7\text{F}_5, ^7\text{F}_6$  levels, respectively).

The errors affecting the crystal field splittings for Eu-acac<sub>3</sub>-(H<sub>2</sub>O)<sub>2</sub> are represented in Figure 3. As found for the excited multiplets in the other ions, bare  $\mathcal{H}_{\text{SO}}^{(1)}$  leads to errors larger than +100%, while the SOC mean field Hamiltonian, both within and without the atomic approximation, shows errors similar to those affecting Eu<sup>3+</sup> atom ( $\mu \approx +5\%$ ), with small standard deviations (systematic errors) whereas the size of the statistical sample is not too small, that is, for the  $^7\text{F}_J$  levels with  $J > 1$ . It is noteworthy that  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  accurately reproduces the true Breit-Pauli results for all the excited multiplets.

The data obtained varying the ligands' environment for a fixed central Dy(III) ion are represented in Figures 4 and 5 (see also Table S18). We find that the %error is largely unaffected by the choice of the ligands for the gaps within both the ground and the first-excited multiplets. As observed in Figures 1 and 2 for Dy-acac<sub>3</sub>-(H<sub>2</sub>O)<sub>2</sub> complex,  $\mathcal{H}_{\text{SO}}^{(1)}$  approximation underestimate/overestimate the energy gaps within the ground/first-excited multiplets of about  $-5\%/+100\%$  with respect to  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ , while the SOC mean field approximation well reproduces the results for the ground  $^6\text{H}_{15/2}$  level, and slightly underestimates ( $\mu \approx -3$ ) the gaps within the excited  $^6\text{H}_{13/2}$  level, for both the multi-center and one-center 2e-SOC integrals evaluations.  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  leads to almost negligible errors in all cases.

We studied the errors affecting the  $g$  tensors, and the orientation of the corresponding principal magnetic axes, for the ground Kramers doublets in the Dy(III) complexes, of large interest for the modeling for the magnetic behavior of lanthanide-based SMM complexes. The  $g$  tensor values calculated by  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  present almost zero transversal  $g_x$  and  $g_y$  components, and  $g_z$  axial component of about 19.4, which is close to the value expected for a pure  $M_J \pm 15/2$  Kramers doublet (i.e. 20), indicating a strong magnetic anisotropy, see Table 1.

All the SOC approximations well reproduce the strong axiality.  $\mathcal{H}_{\text{SO}}^{(1)}$  leads to a very small underestimation on the  $g_z$  values of about  $-1.4\%$ , with the corresponding principal magnetic axis tilted from the axis calculated by  $\mathcal{H}_{\text{SO}}^{\text{BP}}$  of less than 1 degree in all Dy(III) systems.  $\mathcal{H}_{\text{SO}}^{\text{MF}}$ ,  $\mathcal{H}_{\text{SO}}^{\text{AMF}}$ , and  $\mathcal{H}_{\text{SO}}^{\text{ABP}}$  approximations present effective  $g$  values and principal magnetic axes orientations almost coincident with the results obtained by  $\mathcal{H}_{\text{SO}}^{\text{BP}}$ .

## 8 Conclusions

In this paper we investigated a number of approximations to the full Breit-Pauli spin-orbit coupling operator for the calculation of the ground multiplet crystal field levels and effective  $g$  tensors for lanthanide-based compounds within the CAHF/CASCI-SO ab initio method<sup>13,14</sup>.

After briefly reviewing the most widely used approximations to the SOC Hamiltonian in the literature, we presented an implementation of a new approach to the calculation of the 2e-SOC integrals which makes use of their Cholesky representation, which was recently proposed by some of us<sup>25</sup>. This novel method allows for significant speed ups without loss of accuracy, and it can be applied to the true Breit-Pauli Hamiltonian, as well as to its approximations. The novel approach has been implemented in the CERES package<sup>14,17</sup>.

Via extensive comparison of the computed crystal field energies for a family of lanthanide complexes that are of interest to achieve single molecule magnetism, we showed that the use of the bare one-electron SOC Hamiltonian  $\mathcal{H}_{\text{SO}}^{(1)}$  reproduces the crystal field split energies of the ground multiplets with almost systematic errors of about  $-13\%$  to  $+2\%$  for Pr(III), Nd(III), Sm(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Yb(III), while the energy gaps are largely under-/over-estimated for Eu(III)/Gd(III) systems.

Among the approximations that aim to include part of the SOC two-electron interaction, the spin-orbit mean field approach almost completely reproduces the Breit-Pauli results for the ground multiplets, and remains within an error of  $\pm 4\%$  for the energies of the first excited multiplets. For both the ground and the excited multiplets, we showed that the atomic approximation, where only the one-center 2e-SOC integrals are retained throughout, and contracted with the true CAHF molecular density, does not introduce additional errors with respect to the results where all the 2e-SOC integrals are evaluated. The errors are quite stable varying the ligands' environment for all the approximations studied.

In Dy(III) complexes, the effective  $g$  values for the ground Kramers doublet are reproduced with an error of about  $-1.4\%$  for  $\mathcal{H}_{\text{SO}}^{(1)}$ , while the discrepancies in the orientation of the principal magnetic axes are almost negligible. No differences in the  $g$  tensors are shown by the other approximations.

These results indicate the atomic approximation as the best compromise between computational saving and high accuracy for both the ground and the excited multiplets. On the other hand, surprisingly the simple bare 1e-SOC Hamiltonian well reproduces the gaps within the lowest energy crystal field manifold for the main ions used in the literature for the design of the lanthanide-based SMMs (i.e. Dy, Tb, Er), with errors below 4% with respect to the evaluations made by the use of the complete Breit-Pauli Hamiltonian. Finally, it is noteworthy to mention that the  $g$  tensor for the lowest crystal field manifold in Dy(III) complexes are all well reproduced already using the bare 1e-SOC Hamiltonian  $\mathcal{H}_{\text{SO}}^{(1)}$ .

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

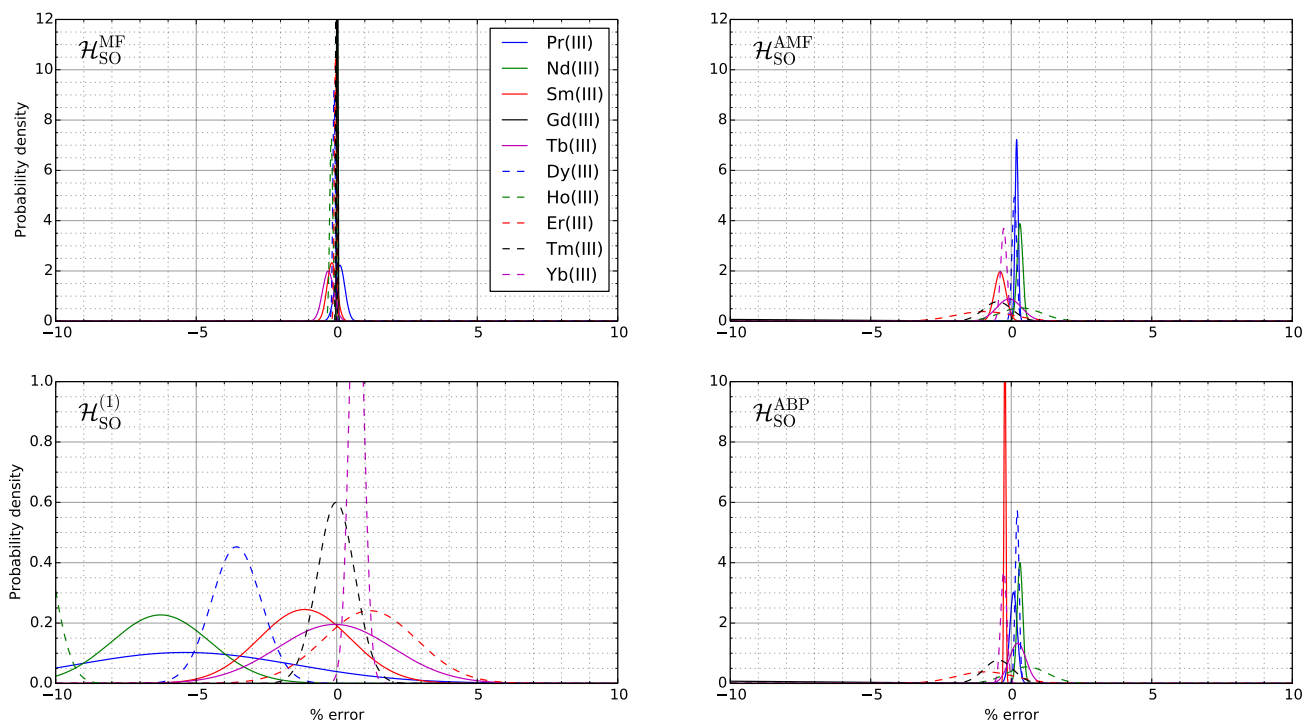
S.V.R. thankfully acknowledges support from the Melbourne India Postgraduate Program. A.S. thankfully acknowledges support from the Australian Research Council, Future Fellowship No. FT180100519. This research was supported by use of the Nectar Research Cloud (<https://nectar.org.au>), a collaborative Australian research platform supported by the National Collaborative Research Infrastructure Strategy (NCRIS).

## References

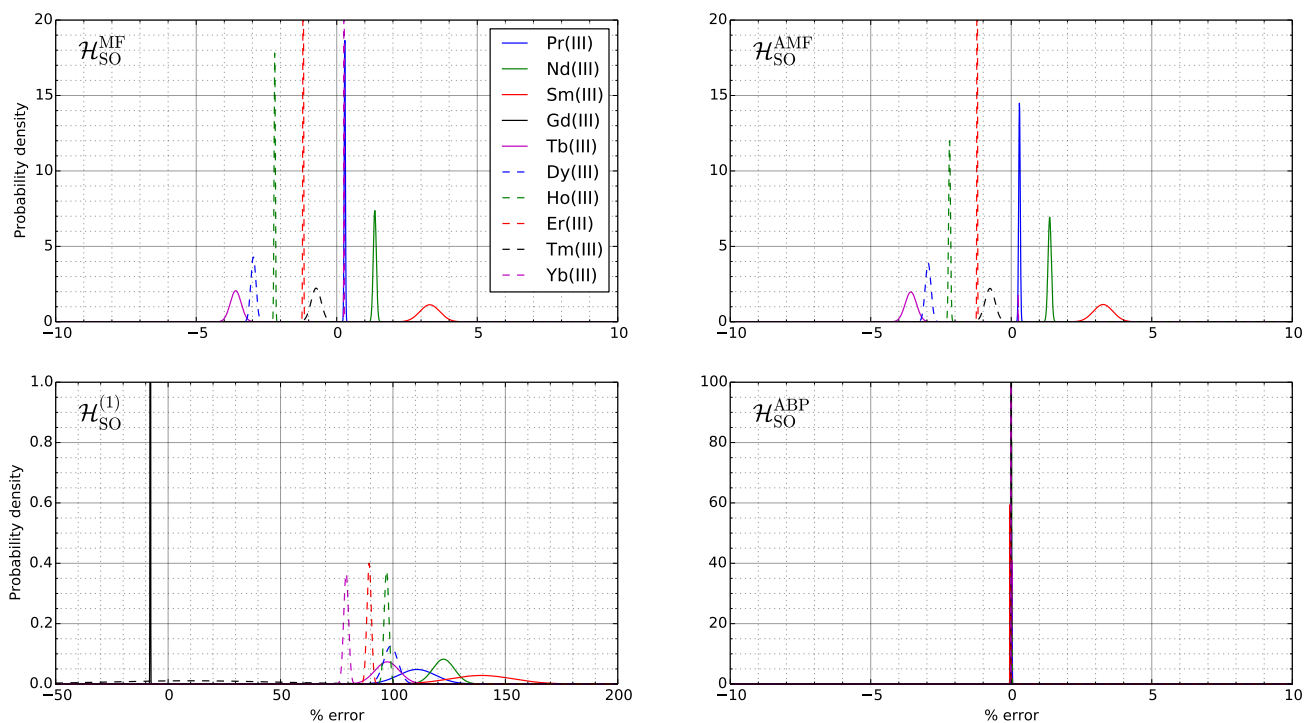
- 1 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143.
- 2 R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *Journal of the American Chemical Society*, 1993, **115**, 1804–1816.
- 3 D. Gatteschi and R. Sessoli, *Angewandte Chemie International Edition*, 2003, **42**, 268–297.
- 4 C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton and D. P. Mills, *Nature*, 2017, **548**, 439–442.
- 5 F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki and R. A. Layfield, *Science (New York, N.Y.)*, 2018, **362**, 1400–1403.
- 6 D. Gatteschi, R. Sessoli, J. Villain and J. V. Dante Gatteschi, Roberta Sessoli, *Molecular nanomagnets*, Oxford University Press, New York, 2006.
- 7 T. Jinkui and Z. Peng, *Lanthanide Single Molecule Magnets*, Springer, London, 2015.
- 8 C. Benelli and D. Gatteschi, *Introduction to Molecular Magnetism: From Transition Metals to Lanthanides*, Wiley-VCH, Weinheim, Germany, 2015.
- 9 B. O. Roos, P. R. Taylor and P. E. Siälřgbahn, *Chemical Physics*, 1980, **48**, 157–173.
- 10 P. E. M. Siegbahn, J. Almlöf, A. Heiberg and B. O. Roos, *The Journal of Chemical Physics*, 1981, **74**, 2384–2396.
- 11 P. Å. Malmqvist, B. O. Roos and B. Schimmelpfennig, *Chemical Physics Letters*, 2002, **357**, 230–240.
- 12 F. 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, *Journal of Computational Chemistry*, 2016, **37**, 506–541.
- 13 W. V. den Heuvel, S. Calvello, A. Soncini, W. V. den Heuvel, S. Calvello and A. Soncini, 2015.
- 14 S. Calvello, M. Piccardo, S. V. Rao and A. Soncini, *Journal of Computational Chemistry*, 2018, **39**, 328–337.
- 15 R. McWeeny, *Methods of molecular quantum mechanics*, Academic Press, 1992, p. 573.
- 16 R. McWeeny, *Molecular Physics*, 1974, **28**, 1273–1282.

- 17 A. Soncini, S. Calvello, M. Piccardo and S. V. Rao, *ÅIJCeres, an ab initio quantum chemistry package for the electronic structure and magnetic properties of lanthanide complexesÅI*, 2017.
- 18 K. G. Dyall and K. Fægri, *Introduction to relativistic quantum chemistry*, Oxford University Press, 2007, p. 530.
- 19 C. M. Marian, *Reviews in Computational Chemistry*, Wiley, 2001, ch. 3, pp. 99–204.
- 20 F. Neese, *The Journal of Chemical Physics*, 2005, **122**, 034107.
- 21 B. A. Heß, C. M. Marian, U. Wahlgren and O. Gropen, *Chemical Physics Letters*, 1996, **251**, 365–371.
- 22 A. Berning, Marcus Schweizer, Hans-Joa, *Molecular Physics*, 2000, **98**, 1823–1833.
- 23 C. M. Marian, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 2012, **2**, 187–203.
- 24 A. Van Yperen-De Deyne, E. Pauwels, V. Van Speybroeck and M. Waroquier, *Physical Chemistry Chemical Physics*, 2012, **14**, 10690.
- 25 M. Piccardo and A. Soncini, *Journal of Computational Chemistry*, 2017, **38**, 2775–2783.
- 26 M. Blume and R. E. Watson, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 1962, **270**, 127–143.
- 27 T. Nakajima and K. Hirao, *Chemical Reviews*, 2012, **112**, 385–402.
- 28 M. Reiher and A. Wolf, *Relativistic quantum chemistry: the fundamental theory of molecular science*, Wiley-VCH, 2015.
- 29 R. McWeeny and B. T. Sutcliffe, *Methods of molecular quantum mechanics*, Academic Press, San Diego, 1969.
- 30 T. Helgaker, P. Jørgensen and J. Olsen, *Molecular Electronic-Structure Theory*, John Wiley & Sons, Ltd, Chichester, UK, 2000.
- 31 P. Jensen and P. R. Bunker, *Computational molecular spectroscopy*, Wiley, 2000, p. 670.
- 32 M. Sjøvoll, O. Gropen and J. Olsen, *Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta)*, 1997, **97**, 301–312.
- 33 S. Itoh, R. Saito, T. Kimura and S. Yabushita, *Journal of the Physical Society of Japan*, 1994, **63**, 807–813.
- 34 B. Schimmelpfennig, *AMFI - An Atomic Mean Field Program*, 1996.
- 35 S.-D. Jiang, B.-W. Wang, G. Su, Z.-M. Wang and S. Gao, *Angewandte Chemie*, 2010, **122**, 7610–7613.
- 36 G.-J. Chen, C.-Y. Gao, J.-L. Tian, J. Tang, W. Gu, X. Liu, S.-P. Yan, D.-Z. Liao and P. Cheng, *Dalton Transactions*, 2011, **40**, 5579.
- 37 G.-J. Chen, Y.-N. Guo, J.-L. Tian, J. Tang, W. Gu, X. Liu, S.-P. Yan, P. Cheng and D.-Z. Liao, *Chemistry - A European Journal*, 2012, **18**, 2484–2487.
- 38 E. M. Fatila, E. E. Hetherington, M. Jennings, A. J. Lough and K. E. Preuss, *Dalton Trans.*, 2012, **41**, 1352–1362.
- 39 N. F. Chilton, S. K. Langley, B. Moubaraki, A. Soncini, S. R. Batten and K. S. Murray, *Chemical Science*, 2013, **4**, 1719.
- 40 Z.-G. Wang, J. Lu, C.-Y. Gao, C. Wang, J.-L. Tian, W. Gu, X. Liu and S.-P. Yan, *Inorganic Chemistry Communications*, 2013, **27**, 127–130.
- 41 Y. BiÅI, Y.-N. Guo, L. Zhao, Y. Guo, S.-Y. Lin, S.-D. Jiang, J. Tang, B.-W. Wang and S. Gao, *Chemistry - A European Journal*, 2011, **17**, 12476–12481.
- 42 B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark and A. C. Borin, *The Journal of Physical Chemistry A*, 2008, **112**, 11431–11435.
- 43 A. Abragam and B. Bleaney, *Electron paramagnetic resonance of transition ions*, Oxford University Press, 2012.
- 44 H. Bolvin, *ChemPhysChem*, 2006, **7**, 1575–1589.
- 45 J. J. Baldoví, Y. Duan, R. Morales, A. Gaita-Ariño, E. Ruiz and E. Coronado, *Chemistry - A European Journal*, 2016, **22**, 13532–13539.
- 46 L. Ungur and L. F. Chibotaru, *Chemistry - A European Journal*, 2017, **23**, 3708–3718.
- 47 W. C. Martin, R. Zalubas and L. Hagan, *Atomic energy levels - the rare-earth elements*, National bureau of standards technical report, 1978.

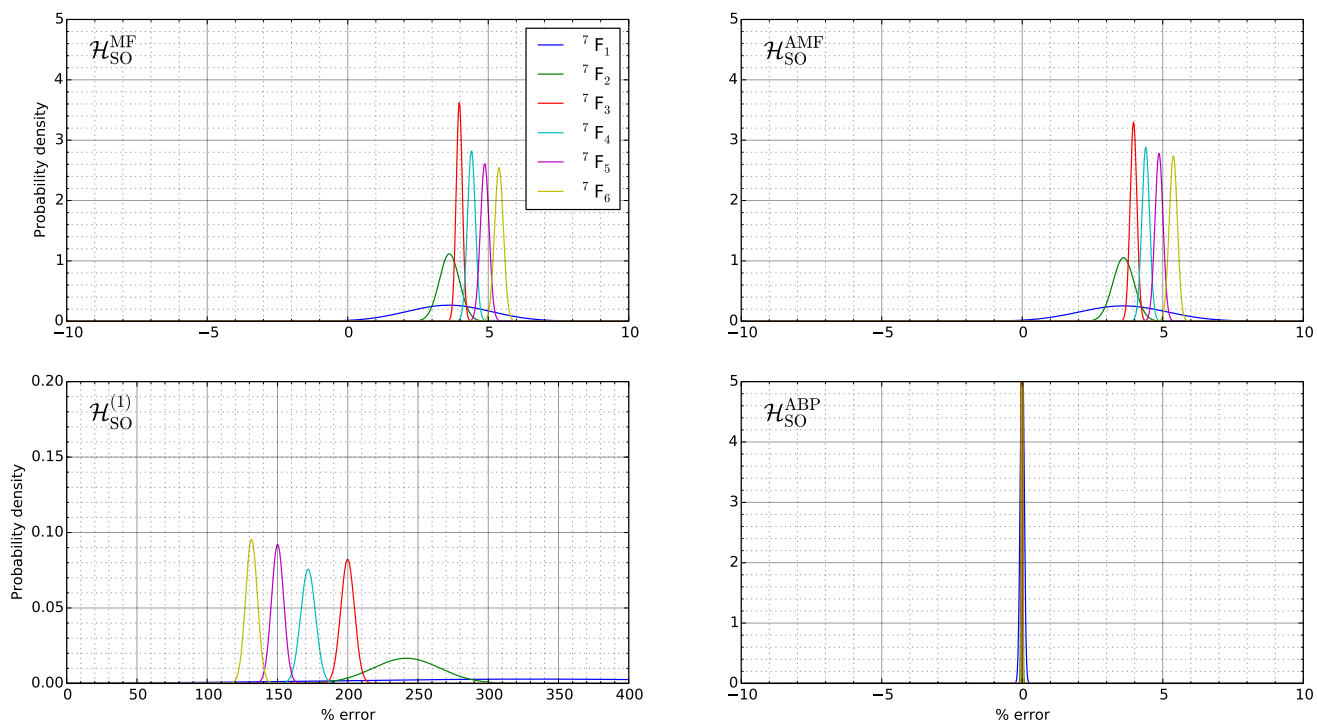




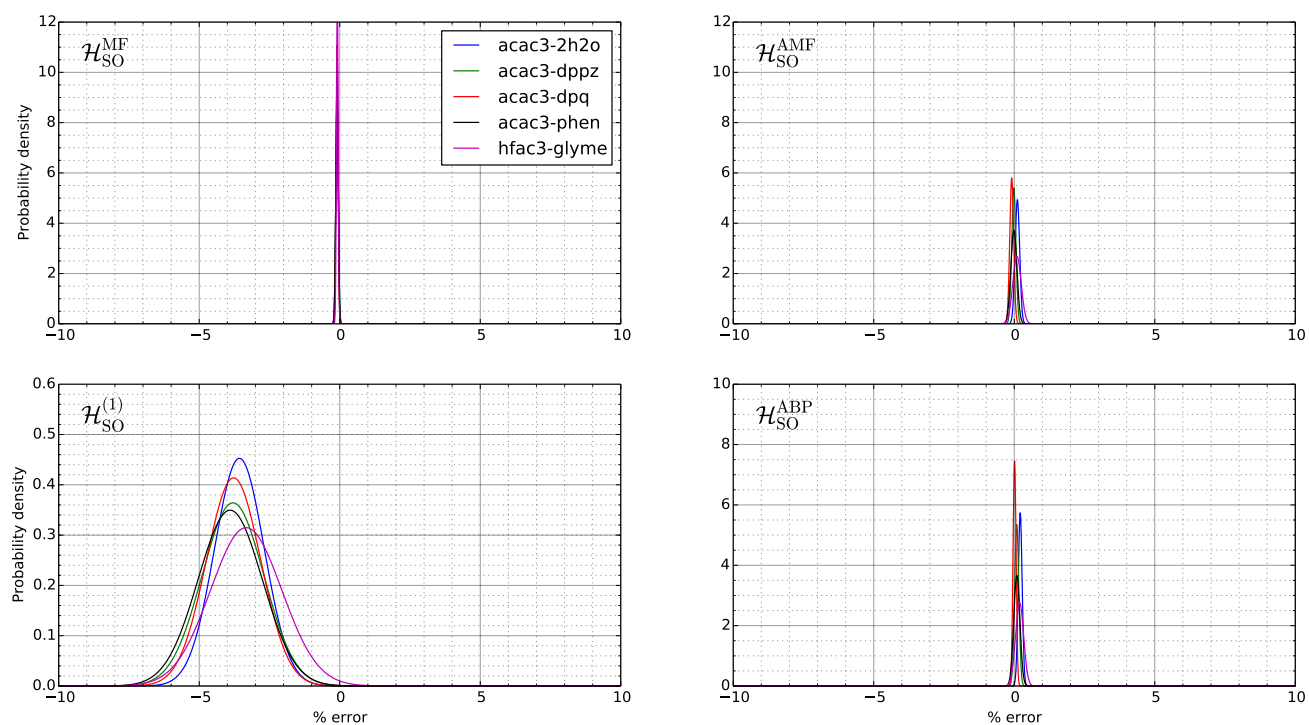
**Fig. 1** Graphical representation (by normal distribution function) of the mean  $\mu$  and standard deviation  $\sigma$  for the %errors affecting the energy gaps within the ground spin-orbit multiplet for Ln-acac<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> complexes, estimated using different approximations for the SOC interaction with respect to the Breit-Pauli Hamiltonian (see Table S1).



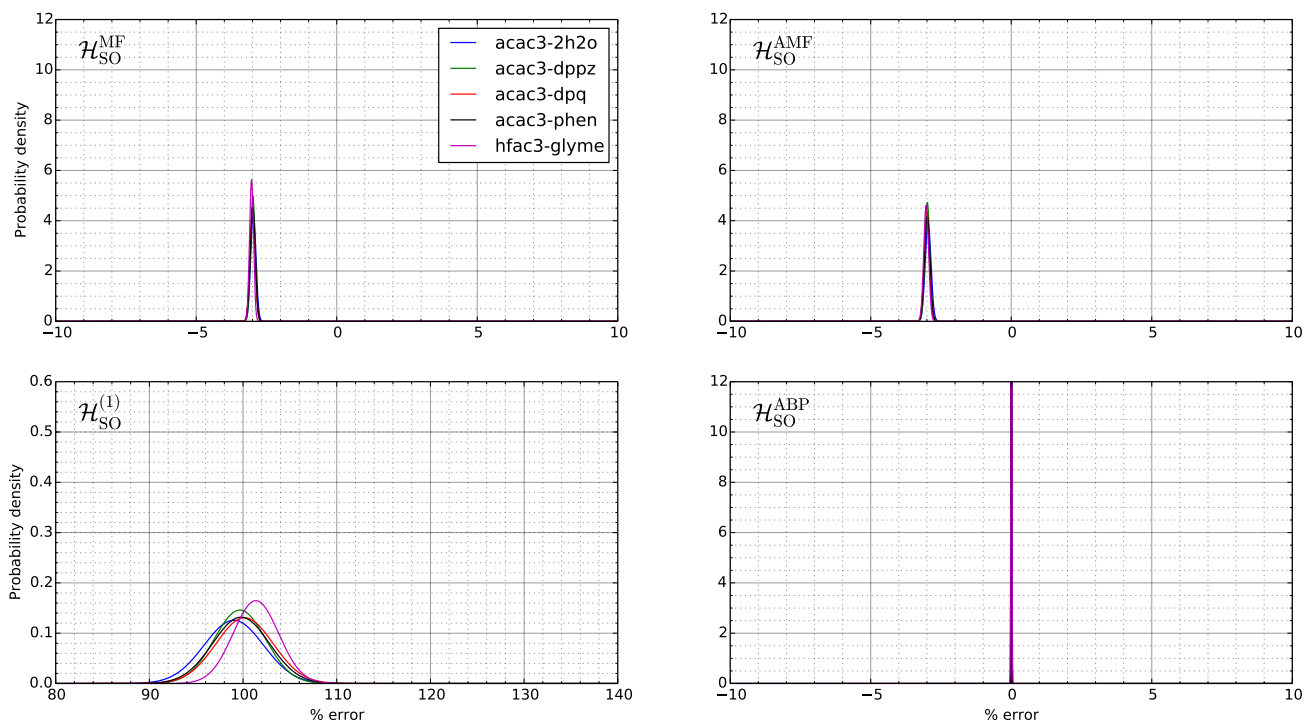
**Fig. 2** Graphical representation (by normal distribution function) of the mean  $\mu$  and standard deviation  $\sigma$  for the %errors affecting the energy gaps within the first excited spin-orbit multiplet for Ln-acac<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> complexes, estimated using different approximations for the SOC interaction with respect to the Breit-Pauli Hamiltonian (see Table S1).



**Fig. 3** Graphical representation (by normal distribution function) of the mean  $\mu$  and standard deviation  $\sigma$  for the %errors affecting the energy gaps within the lowest energy spin-orbit multiplets  ${}^7F_J$ , with  $J = 1, 2, 3, 4, 5, 6$ , for Eu-acac<sub>3</sub>-(H<sub>2</sub>O)<sub>2</sub> complex, estimated using different approximations for the SOC interaction with respect to the Breit-Pauli Hamiltonian (see Table S1).



**Fig. 4** Graphical representation (by normal distribution function) of the mean  $\mu$  and standard deviation  $\sigma$  for the %errors affecting the energy gaps within the ground spin-orbit multiplet  ${}^6H_{15/2}$  for Dy(III) complexes, estimated using different approximations for the SOC interaction with respect to the Breit-Pauli Hamiltonian (see Table S2).



**Fig. 5** Graphical representation (by normal distribution function) of the mean  $\mu$  and standard deviation  $\sigma$  for the % errors affecting the energy gaps within the first excited spin-orbit multiplet  ${}^6H_{13/2}$  for Dy(III) complexes, estimated using different approximations for the SOC interaction with respect to the Breit-Pauli Hamiltonian (see Table S2).

**Table 1**  $g$  tensor values for the first Kramers doublet in Dy(III) complexes estimated using different approximations to SOC Hamiltonian with respect to the results obtained by inclusion of the true Breit-Pauli Hamiltonian contribution.

		$\mathcal{H}_{SO}^{(1)}$	$\mathcal{H}_{SO}^{MF}$	$\mathcal{H}_{SO}^{AMF}$	$\mathcal{H}_{SO}^{ABP}$	$\mathcal{H}_{SO}^{BP}$
acac <sub>3</sub> -(H <sub>2</sub> O) <sub>2</sub>	$g_x$	0.000	0.000	0.000	0.000	0.005
	$g_y$	0.000	0.000	0.000	0.000	0.007
	$g_z$	-0.282	-0.002	-0.001	+0.001	19.441
acac <sub>3</sub> -dppz	$g_x$	-0.001	0.000	0.000	0.000	0.005
	$g_y$	-0.002	0.000	0.000	0.000	0.009
	$g_z$	-0.268	-0.002	+0.001	+0.003	19.363
acac <sub>3</sub> -dpq	$g_x$	0.000	-0.000	0.000	0.000	0.006
	$g_y$	-0.004	-0.000	0.000	0.000	0.014
	$g_z$	-0.260	-0.001	0.000	+0.001	19.219
acac <sub>3</sub> -phen	$g_x$	0.000	0.000	0.000	0.000	0.005
	$g_y$	0.000	0.000	0.000	0.000	0.007
	$g_z$	-0.263	-0.002	+0.002	+0.004	19.340
hfac <sub>3</sub> -glyme	$g_x$	-0.002	0.000	0.000	0.000	0.006
	$g_y$	-0.004	0.000	0.000	0.000	0.010
	$g_z$	-0.255	-0.002	+0.003	+0.005	19.445