Equation-of-Motion Coupled-Cluster Protocol for Calculating Magnetic Properties: Theory and Applications to Single-Molecule Magnets

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We present a new computational protocol for computing macroscopic magnetic properties of transition-metal complexes using equation-of-motion coupled-cluster (EOM-CC) framework. The approach follows a two-step state-interaction scheme: we first compute zero-order states using non-relativistic EOM-CC and then use these states to evaluate matrix elements of the spin-orbit and Zeeman operators. Diagonalization of the resulting Hamiltonian yields spin-orbit- and field-perturbed eigenstates. Temperature- and field-dependent magnetization and susceptibility are computed by numerical differentiation of the partition function. To compare with powder-sample experiments, these quantities are numerically averaged over field orientations. We applied this protocol to several mononuclear Fe(II) and Fe(III) single-molecule magnets (SMMs) trigonal pyramidal, linear, and trigonal bipyramidal coordination environments. The underlying electronic structure was described by the electron-attached (EOM-EA) and spin-flip (EOM-SF) variants of EOM-CC. The computed energy barriers for spin inversion, and macroscopic magnetization and susceptibility agree well with experimental data. Trends of magnetic anisotropy and spin-reversal energy barrier are explained in terms of a molecular orbital picture rigorously distilled from spinless transition density matrices between many-body states. The results illustrate excellent performances of EOM-CC for describing magnetic behavior of mononuclear transition-metal SMMs.

I. INTRODUCTION

Single-molecule magnets (SMMs) are attracting considerable attention owing to their potential applications in information technologies, such as quantum information storage and computing, molecular spintronics, and microelectronics[1, 2]. SMMs are molecules that are able to retain their magnetization upon removal of the magnetic field for an appreciable time below a critical temperature, such that each molecule can act as a data-storage unit. Most often, SMMs are transition-metal complexes.

FIG. 1: Splitting of a doubly degenerate $S = 2$ ground state (red) under spin-orbit (dark blue) and Zeeman (light blue) perturbations. Spin-orbit coupling splits the doubly degenerate multiplet into 10 spin-orbit levels, which are pairwise degenerate. For SMMs (negative D value), the $M_S = \pm S$ levels are the lowest. External magnetic field removes the two-fold degeneracy by virtue of the Zeeman effect.

The relaxation time of the magnetization is controlled by the energy barrier U for spin inversion (as illustrated in Fig. 1 for a doubly degenerate quintet state), which arises due to the zero-field splitting (ZFS) of the $2S + 1$ degenerate components (with spin projection $M_S = S, S - 1, \dots, -S + 1, -S$) of the spin S ground state. This splitting originates from the coupling of the ground state with low-lying excited states through spin-orbit coupling (SOC), and leads to anisotropy of the magnetic properties (i.e., the dependence of the magnetic properties on the field orientation). The magnetization of a magnetically anisotropic system depends on both field orientation and its strength (M_i with $i = x, y, z$), and its magnetic susceptibility is a second-rank tensor (χ_{ij} with $i, j = x, y, z$). Molecules with magnetic anisotropy tend to orient their magnetization along one preferential direction, which is called easy-axis of the magnetization and, by convention, is parallel to the z -axis. Due to the energy barrier for spin inversion from $M_S = +S$ to $M_S = -S$, this energetically most favorable orientation of the magnetization can be maintained after the field is switched off. The

relaxation process (reorientation of the magnetization by climbing up the energy barrier) occurs if the thermal energy ($k_B T$) of the system is larger than U . However, this thermally activated mechanism can be sidestepped by spin-phonon coupling and quantum tunneling of the magnetization under the barrier between the degenerate $\pm M_S$ levels[1, 3]. Tunneling is facilitated by distortions from axial symmetry, which cause mixing of the $\pm M_S$ levels. In the presence of fast tunneling, the effective energy barrier U_{eff} measured from alternating current (ac) susceptibilities is much smaller than the thermal energy barrier U . While SOC is at the origin of ZFS and magnetic anisotropy, Zeeman interactions, which are induced by an external magnetic field, define the energy splittings as a function of the field orientation and its magnitude. Under an applied field, the energy of the $+M_S$ levels increases and that of the $-M_S$ ones decreases (shown in Fig. 1), thus preventing magnetization decay via tunneling.

For systems possessing axial symmetry (i.e., with rotational axis), the ZFS can be related to the axial parameter D , which also quantifies the axial magnetic anisotropy of the system. The magnitude of U depends on this ZFS axial parameter D and on the spin S of the ground state, according to the expression $U = |D|S^2$ for integer spin ($U = |D|(S^2 - 1/4)$ for half-integer spin values). For practical applications, SMMs with higher energy barriers are desirable. Barriers can be increased by either maximizing the spin or the magnetic anisotropy. A higher spin can be obtained by introducing more magnetic centers and imposing ferromagnetic coupling of the spins; however, increasing the total spin is not the most efficient way of obtaining better SMMs because of the proportionality of D to $1/S^2$ [4–6]. Alternatively, magnetic anisotropies can be obtained by enhancing the SOC contribution. By using perturbation theory arguments, one can show that SOC (which arises due to the coupling of the orbital angular momentum L with the spin) leads to large anisotropies in the presence of the unquenched angular momentum[7–9], which, in turn, requires orbital (near-)degeneracies. Following this second strategy, several mononuclear lanthanide complexes with slow magnetic relaxation and large magnetic anisotropy were designed[10, 11]. To date, a metallocene of Dy(III) exhibits the largest ever measured energy barrier of 1,541 cm^{-1} and blocking temperature up to 80 K [12]. In these systems, strong magnetic anisotropy results from nearly-degenerate f -orbitals. When combined with an appropriate number of f -electrons, these degeneracies lead to a large first-order orbital momentum contributing to their anisotropic magnetic behavior. In contrast, in transition-metal complexes, $3d$ elec-

trons are less shielded from ligands than $4f$ electrons of rare earth ions, so that ligand field is stronger than spin-orbit interactions, such that orbital momentum is typically quenched by ligand field and structural distortions that remove the necessary d -orbital degeneracies. Furthermore, structural distortions are also responsible for the tunneling, which accelerates the magnetic relaxation. Hence, the best mononuclear transition-metal SMMs are those with low-coordination number (i.e., weak ligand field) and highly symmetric coordination spheres (i.e., minimal structural distortions). Since the first example of a mononuclear Fe(II) complex exhibiting slow relaxation[13], an increasing number of $3d$ -block transition-metal SMMs has been reported, whose performance is comparable to the outstanding lanthanide SMMs[3, 14, 15]. Their strong magnetic anisotropy arises due to the partially preserved d -orbital degeneracy, leading to degenerate ground states (as in Fig. 1) and unquenched orbital momentum.

Tunneling can be suppressed, leading to improved SMMs, by using half-integer spin ions (Kramer ions), e.g., Co(II) and Fe(I), as magnetic centers[1, 16] and enforcing linear geometries by means of bulky ligands[17]. Among the best examples, a linear and two-coordinate Co(II) complex with a non-Aufbau ground state, and, consequently, maximal orbital momentum, set the record of energy barrier up to 450 cm^{-1} for transition-metal SMMs[18].

Quantum chemistry is a critical instrument for developing better SMMs. Theoretical modeling of magnetic molecules and related materials provides the interpretation of experiments, and inspires novel design strategies. However, for the theory to be useful, it should be able to provide experimentally observable quantities. Spin Hamiltonians, which are commonly used to interpret experimentally observed magnetic behavior, provide the link between ab initio calculations and macroscopic magnetic properties [8, 19]. Spin-Hamiltonian parameters, such as exchange-coupling constant J , magnetic anisotropy parameter D , and g -tensors, can be determined from the computed energies and underlying wave functions, and then can be compared with analogous quantities extracted by fitting experimental magnetization and susceptibility data[8, 19].

Ab initio description of SMMs is challenging because of their multi-configurational wave functions and multiple nearly degenerate electronic states. Standard quantum chemistry methods, such as density functional theory (DFT) or single-reference methods based on coupled-cluster (CC) or perturbation theory (PT), fail when wave functions are dominated

by more than one Slater determinant. A common strategy is to use multi-reference (MR) methods that include both static and dynamical correlation, such as complete active space self-consistent field methods augmented with a posteriori PT corrections. For example, CASPT2[20] and NEVPT2[21] (n-electron valence state PT) are frequently used in studies of magnetic molecules, providing accurate estimates of their magnetic properties, such as J constants, D parameters, and g -tensors.[22, 23] In addition to numerical derivation of these spin-Hamiltonian parameters from ab initio calculations, tools have been developed in combination with MR wave functions for computing macroscopic observables, such as magnetization and susceptibility, which enable direct comparison with experiment, without relying on the spin-Hamiltonian formalism or on the Van-Vleck expression of the susceptibility. Among the most rigorous, the implementation of Neese and co-workers[24] computes magnetization and susceptibility by differentiation of the partition function computed using the energies of the SOC- and field-corrected NEVPT2 states. In addition, the SINGLE_ANISO module[25–27] of the Molcas program affords calculations of macroscopic magnetic properties via Van-Vleck formalism using energies and magnetic moments of the spin-orbit perturbed states obtained using RASSI (restricted active space state interaction)[28].

We present an alternative strategy based on the equation-of-motion coupled-cluster (EOM-CC) family of methods [29–32]. In EOM formalism, a single-determinant state is used as a reference from which relevant target states are obtained by applying a linear EOM excitation operator. Different EOM-CC models are defined by choosing the reference state and the excitation operator. EOM-CC family of methods provides access to multi-configurational states of radicals, poliradicals and other open-shell species, which makes EOM-CC suitable for applications to SMs[33–37]. To describe d^5 and d^6 patterns, we use the electron-attached (EOM-EA) and spin-flip (EOM-SF) variants and high-spin d^5 references. We treat SOC effects by a state-interaction approach[38–40] in which SOC is computed as matrix elements of the Breit-Pauli spin-orbit Hamiltonian[41, 42] using non-relativistic EOM-CC wave functions, as was recently done by Krylov and co-workers[36, 43, 44]. Trends in SOC can be rationalized in terms of El-Sayed’s rules[45], which predict a large SOC for those transitions that involve a change of orbital orientation. This molecular orbital picture can be extended to correlated wave functions by using reduced quantities such as transition density matrix (TDM) and corresponding natural transition orbitals (NTOs)[46]. By representing the electronic transition between the spin-orbit interacting states in terms of hole-particle

NTO pairs, one can quantify the contribution of each orbital pair into the overall SOC, and the shape and orientation of these orbitals allow one to rationalize El-Sayed’s rules for p - and d -manifolds[43].

In this contribution, we describe a computational protocol for computing macroscopic magnetic properties and their dependence on temperature and applied magnetic field using the EOM-CC framework. We compute SOC- and field-perturbed energy levels through the two-step state-interaction approach described above, and then apply Boltzmann statistics to connect microscopic quantities, such as energies of each magnetic sublevel, to macroscopic magnetic properties. The approach is implemented as a postprocessing tool within the *ezMagnet* module[47] of the *ezSpectra* suite[48]. The script (written in *Python*) takes the raw data (EOM energies, orbital momentum and spin-orbit matrix elements) provided by the *Q-Chem* software[49, 50], and computes temperature- and field-dependent magnetization and susceptibility. We illustrate the capabilities of our approach by applications to a representative set of Fe(II) and Fe(III) SMMs:

- (1) a tris(pyrrolylmethyl)-amine Fe(II) complex, denoted as $[(\text{tpa})\text{Fe}]^-$, whose structural model has been derived by Pokhilko *et al.* [36] from the original one, $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$, [13] by replacing the mesitylene group in the ligand, tpa^{Mes} , by hydrogen,
- (2) a two-coordinate (locally linear) $\text{Fe(II)}[\text{C}(\text{SiMe}_3)_3]_2$ complex[51], where Me stands for CH_3 ,
- (3) and a trigonal bipyramidal $(\text{PMe}_3)\text{Fe(III)}\text{Cl}_3$ complex.[52]

These SMMs feature local trigonal symmetry, which has been utilized to develop compounds with large spin-reversal barriers and slow magnetic relaxation[53]. We assess the performance of our computational protocol for energy barriers and magnetic properties by comparison to the experimental[13, 51, 52, 54, 55] and available theoretical data from NEVPT2 calculations[24, 51, 56]. We complement our calculations by orbital analysis using NTOs. This analysis explains magnetic anisotropies and spin-reversal energy barriers in terms of El-Sayed’s rules.

The structure of the paper is as follows. Section II presents the theory. We begin with a brief introduction of the EOM-CC methods and of the hole-particle picture used to interpret El-Sayed’s rules, followed by the presentation of our formalism for computing spin-orbit and

Zeeman interactions, magnetic properties, and their average quantities. Section III describes model systems. The results are presented and discussed in Section IV. We also report and compare orbital angular momentum and spin-orbit matrix elements for all systems under study, explaining trends in their anisotropic magnetic behavior.

II. THEORY

A. EOM-CC approach

FIG. 2: EOM family of methods. The reference states for EOM-IP/EA are determinants for $N+1/N-1$ electron states, and the excitation operator is ionizing or electron-attaching. DIP and DEA refer to double ionizing or double electron-attaching operators. EOM-SF method employs the high-spin references and spin-flipping operators. Adapted from Ref. [57].

EOM-CC extends the single-reference CC methodology to multi-configurational wave functions and provides an efficient, robust, and accurate framework for computing multiple electronic states. Within the EOM-CC formalism[29–32], target-state wave functions have the following form:

$$|\Psi\rangle = Re^T|\Phi_0\rangle, \quad (1)$$

where $|\Phi_0\rangle$ is the reference Slater determinant, $e^T|\Phi_0\rangle$ is the CC wave function, and R is the linear EOM excitation operator usually truncated at the same excitation level as the cluster

excitation operator T , e.g., up to doubly excited configurations at the EOM-CCSD and EOM-MP2 levels. By using different types of R and of reference states, different manifolds of target states can be accessed, as illustrated in Fig. 2. For example, spin-flip (SF)[57–59] excitation operators access multi-configurational low-spin states in di- and tri-radicals, transition metal complexes, and bond-breaking situations. In SF methods, a single-determinant high-spin state is used as a reference from which lower-spin states with the same orbital occupation can be obtained by single-electron spin-flipping excitations. The SF ansatz can be used with EOM-CC[58] as well as with time-dependent DFT (TD-DFT),[60, 61] PT,[62] and configuration interaction (CI) [63]. The SF approaches provide a balanced treatment of relevant spin states, treat both non-dynamical and dynamical correlation simultaneously, do not require active-space selection, and do not rely on symmetry-broken solutions or on (non-unique) spin projectors. EOM-SF has been used for describing various types of SMMs.[33–35, 37] Other forms of R , such as the electron-ionizing (IP)[64, 65] and electron-attaching (EA)[66] operators, do not conserve the number of electrons and can accurately treat doublet radicals and other open-shell systems. For example, EOM-EA with high-spin d^5 reference has been used to treat ground and excited states of mononuclear Fe(II) SMMs.[36] Following these previous studies, here we employ the EOM-SF and EOM-EA variants with high-spin d^5 references to describe d^5 and d^6 patterns of Fe(III) and Fe(II) single-center SMMs.

B. A molecular orbital picture for many-body wave functions

The ability to assign an orbital character to a particular electronic state provides an insight into molecular properties. Molecular orbital theory can be extended to correlated many-body wave functions through reduced quantities, such as density matrices and NTOs[46, 67–73]. The key quantity, which enables the interpretation of one-electron excitations between initial Ψ^I and final Ψ^F states and the calculations of related transition properties, is the one-particle transition density matrix (1PTDM),

$$\gamma_{pq}^{FI} = \langle \Psi^F | a_p^\dagger a_q | \Psi^I \rangle, \quad (2)$$

where $a_p^\dagger$ and a_q are the creation and annihilation operators associated with the ϕ_p and ϕ_q orbitals. For a one-electron operator $\hat{A} = \sum_{pq} A_{pq} a_p^\dagger a_q$, the corresponding one-electron transition property is computed as contraction of the associated integrals, $A_{pq} = \langle \phi_p | \hat{A} | \phi_q \rangle$, with the 1PTDM,

$$\langle \Psi^F | \hat{A} | \Psi^I \rangle = \sum_{pq} A_{pq} \langle \Psi^F | a_p^\dagger a_q | \Psi^I \rangle = \sum_{pq} A_{pq} \gamma_{pq}^{FI} = \text{Tr}[\gamma^{FI} A], \quad (3)$$

where the sum runs over all orbitals p and q . The expectation value $\langle \Psi^F | \hat{A} | \Psi^I \rangle$ is invariant with respect to the orbital choice, in contrast to the values of the individual integrals A_{pq} and of the matrix elements of the 1PTDM. A unique set of orbitals that represents the 1PTDM in the most compact form is provided by singular value decomposition (SVD)[74, 75] of the 1PTDM,

$$\gamma = \mathbf{V} \Sigma \mathbf{U}^\dagger, \quad (4)$$

where Σ is the diagonal matrix of the singular values σ_k , and $\mathbf{V}$ and $\mathbf{U}$ contain the pairs of singular vectors ψ_k^h and ψ_k^p , which are called hole and particle NTOs. In the basis of these NTOs, the transition property is expressed as a sum of the matrix elements between the hole and particle NTOs, each term being weighted by the corresponding singular value:

$$\langle \Psi^F | \hat{A} | \Psi^I \rangle = \text{Tr}[\gamma A] = \sum_k \langle \psi_k^p | \hat{A} | \psi_k^h \rangle \sigma_k. \quad (5)$$

Often, only one or two singular values are non zero. Thus, a few NTO pairs are sufficient to compute physical observables, providing a way to relate the property to a simple hole-particle picture.

C. Macroscopic magnetic properties

Magnetic properties originate from magnetic field and spin-orbit relativistic interactions. For molecules composed of light atoms and under weak magnetic fields, one can accurately account for these effects following a two-step state-interaction procedure[38–40]. Fig. 3 shows a flowchart of the computational protocol. Starting from a zero-order non-relativistic Hamiltonian (the Born-Oppenheimer Hamiltonian, H^0), SOC and field interactions are incorporated by augmenting H^0 by the spin-orbit (H^{SO}) and Zeeman (H^{Z}) operators. SOC-

FIG. 3: Flowchart of the computational protocol. E^0 and Ψ^0 are the zero-order energies and eigenstates derived from an EOM-CC calculation. $\langle L \rangle$ and SOCs are matrix elements of the orbital momentum and spin-orbit operators, respectively, computed using a zero-order basis of non-relativistic EOM-CC states. H is a perturbed Hamiltonian, which includes: the zero-order Born-Oppenheimer Hamiltonian H^0 , the spin-orbit H^{SO} operator, and the Zeeman operator H^Z . E and Ψ are the SOC- and field-corrected energies and eigenstates. Magnetization $\mathbf{M}$ and susceptibility χ are computed via numerical differentiation of the partition function Z constructed using eigenstates of H .

and field-corrected eigenstates and their energies are then computed by diagonalizing the matrix representation of the resulting perturbed Hamiltonian ($H = H^0 + H^{\text{SO}} + H^Z$) in the basis of zero-order non-relativistic eigenfunctions ($\Psi_I^{SM_S}$) [22, 24]:

$$\langle \Psi_I^{SM_S} | H^0 + H^{\text{SO}} + H^Z | \Psi_{I'}^{S'M'_S} \rangle = E_I^S \delta_{II'} \delta_{SS'} \delta_{M_S M'_S} + \langle \Psi_I^{SM_S} | H^{\text{SO}} + H^Z | \Psi_{I'}^{S'M'_S} \rangle, \quad (6)$$

where indices I , S , and M_S denote the multiplet components of the state I of spin angular momentum S and spin projection M_S . Hence, our initial quantities are matrix elements of the spin-orbit and Zeeman operators between the non-relativistic EOM wave functions of a few interacting states. The spin-orbit and Zeeman terms are computed using the transition property suite of the *Q-Chem* program.[49, 50] Via Boltzmann statistics, we then derive macroscopic properties (e.g., total energy of a system, magnetization, and susceptibility) at a given temperature and under an applied field as mean values of microscopic quantities (e.g., SOC- and field-corrected energy levels and their derivatives with respect to the field), weighted with their probability factors. This procedure can be combined with numerical averaging over molecular/field orientations for isotropic (i.e., powder) samples. Our approach for computing temperature- and field-dependent magnetization and susceptibility closely follows the one of Neese and co-workers[24], but uses EOM-CC instead of multi-reference perturbation theory (MRPT), such as CASPT2 and NEVPT2. As pointed out by Neese and co-workers[24], such procedure does not require extraction of spin-Hamiltonian parameters via effective Hamiltonian theory, nor rely on the Van-Vleck expression of the magnetic

susceptibility. Additionally, the benefits of the current implementation is that it explicitly computes macroscopic magnetic properties at all temperatures and at various magnetic field strengths, allowing direct comparison with experiments. The comparisons with experimental data and Neese's calculations allow us to assess the performances of the EOM methods for magnetic properties.

1. Spin-orbit and Zeeman interactions

The interaction of the electrons with an external magnetic field $\mathbf{H}$ is given by the Zeeman operator,

$$H^Z = \mu_B \mathbf{H} (\mathbf{L} + g_e \mathbf{S}), \quad (7)$$

where $g_e = 2.0023$ is the free spin g -factor, μ_B is the Bohr magneton, and $\mathbf{S}$ and $\mathbf{L}$ are the spin and orbital angular momentum operators, respectively. For a field of magnitude H in the direction given by the vector (n_x, n_y, n_z) , Eq. (7) becomes:

$$H^Z = \mu_B H [n_x (L_x + g_e S_x) + n_y (L_y + g_e S_y) + n_z (L_z + g_e S_z)], \quad (8)$$

where we have introduced the Cartesian operators S_i and L_i with $i = x, y, z$. The evaluation of matrix elements of the Zeeman operator reduces to computing matrix elements of these Cartesian components of the spin and orbital momentum operators. To derive matrix elements for the Cartesian components of the spin operator, it is useful to introduce the rising and lowering operators, S_+ and S_- , respectively. Then, S_x , S_y , and S_z operators can be written in terms of the spherical ones (S_+ , S_- , and S_0) as:

$$S_x = \frac{1}{2} (S_+ + S_-) \quad (9)$$

$$S_y = \frac{1}{2i} (S_+ - S_-) \quad (10)$$

$$S_z = S_0 \quad (11)$$

Spin operators act only on S and M_S spin variables. From $S_z |S, M_S\rangle = M_S |S, M_S\rangle$ and $S_{\pm} |S, M_S\rangle = \sqrt{S(S+1) - M_S(M_S \pm 1)} |S, M_S \pm 1\rangle$, and using Eq. (9)–(11), matrix ele-

ments of the spin Cartesian components are given by[76]:

$$\begin{aligned}\langle S_x \rangle = \langle S', M'_S | S_x | S, M_S \rangle &= \frac{1}{2} \sqrt{S(S+1) - M_S(M_S+1)} \delta_{S'S} \delta_{M'_S M_S+1} \\ &+ \frac{1}{2} \sqrt{S(S+1) - M_S(M_S-1)} \delta_{S'S} \delta_{M'_S M_S-1}\end{aligned}\quad (12)$$

$$\begin{aligned}\langle S_y \rangle = \langle S', M'_S | S_y | S, M_S \rangle &= \frac{1}{2i} \sqrt{S(S+1) - M_S(M_S+1)} \delta_{S'S} \delta_{M'_S M_S+1} \\ &- \frac{1}{2i} \sqrt{S(S+1) - M_S(M_S-1)} \delta_{S'S} \delta_{M'_S M_S-1}\end{aligned}\quad (13)$$

$$\langle S_z \rangle = \langle S', M'_S | S_z | S, M_S \rangle = M_S \delta_{S'S} \delta_{M'_S M_S} \quad (14)$$

Once the matrix elements of the x , y , and z components of the orbital momentum operator computed between many-body correlated wave functions are evaluated (using 1PTDM), L_+ and L_- matrix representations can be obtained from the L_x and L_y matrices through $L_{\pm} = L_x \pm iL_y$.

Spin-orbit interactions arise due to the coupling between the angular momentum of an electron and its spin. As spin-orbit operator H^{SO} , we use the one-electron operator derived from the Breit-Pauli spin-orbit Hamiltonian[41, 42] within the spin-orbit mean-field (SOMF) approximation[40, 77] of the the two-electron part, as was described in Ref. [36, 43, 44]:

$$\langle \Psi_I^{S, M_S} | H^{\text{SOMF}} | \Psi_{I'}^{S', M'_S} \rangle = \sum_{pq} H_{pq}^{\text{SOMF}} \gamma_{pq}, \quad (15)$$

$$H_{pq}^{\text{SOMF}} = I_{pq} + \frac{1}{2} \sum_{rs} \rho_{rs} [J_{prqs} - J_{prsq} - J_{r pqs}], \quad (16)$$

where γ_{pq} is the 1PTDM (see Eq. (2)), ρ_{rs} is the density matrix of the reference determinant (usually, the Hartree-Fock determinant), and I_{pq} and J_{prqs} are the one- and two-electron spin-orbit integrals, respectively. Full details for calculating these spin-orbit integrals can be found in Ref. [36]. As one can see, when the SOMF approximation is applied, the two-particle TDM is not needed, which considerably reduces the cost of the two-electron contribution to the total SOC. An additional benefit of this approach is that, by applying the Wigner-Eckart's theorem,[78, 79] one computes all requisite SOC's between the two multiplets through only one spinless (or reduced) TDM (denoted by u_{pq}) that does not depend on the spin projection of the states, which greatly simplifies the SOC calculation. Details for the construction of this spinless TDM and for the calculation of the associated

reduced matrix elements are given in Ref. [36]. The SVD of u_{pq} yields an analogue of Eq. (5), introducing a new set of spinless NTOs (particle, ζ_k^p ; hole, ζ_k^h) suitable for the analysis of SOC and related weights (singular values ω_k of the spinless TDM). Within this new basis, spin-orbit reduced matrix elements can be written as:

$$\langle \Psi_I^S || H_{L_i}^{\text{SOMF}} || \Psi_{I'}^{S'} \rangle = N_i \sum_{pq} h_{L_i,pq}^{\text{SOMF}} u_{pq} = N_i \sum_k \langle \zeta_k^p | h_{L_i}^{\text{SOMF}} | \zeta_k^h \rangle \omega_k, \quad (17)$$

where i indicates the spherical components $H_{L_+}^{\text{SOMF}}$, $H_{L_-}^{\text{SOMF}}$, and $H_{L_0}^{\text{SOMF}}$ of the effective spin-orbit operator H^{SOMF} , each term being multiplied by the appropriate factor N_i (i.e., $\frac{1}{2}$, $-\frac{1}{2}$, and $\frac{\sqrt{2}}{2}$, respectively). The SVD of the reduced TDM gives only a few ω_k that are dominant (typically just one or two), which allows us to interpret SOC in terms of a few matrix elements between hole and particle NTOs, providing a compact orbital representation of the corresponding electronic transition.

2. El-Sayed's rules

Calculation of SOC based on TDM and hole-particle NTO pairs provides a way to rationalize El-Sayed's rules in terms of correlated molecular orbitals.[43] The nature of the spin-orbit operator is revealed by the form of its one-electron term:

$$\mathbf{h}^{\text{so}}(i) = \sum_K \frac{Z_K(\mathbf{r}_i - \mathbf{R}_K) \times \mathbf{p}_i}{|\mathbf{r}_i - \mathbf{R}_K|^3} = \sum_K \frac{Z_K}{r_{iK}^3}(\mathbf{r}_{iK} \times \mathbf{p}_i), \quad (18)$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the coordinate and momentum operators of the i th electron and $\mathbf{R}_K$ and Z_K denote the coordinates and the charge of the K th nucleus. As evident from Eq. (18), $\mathbf{h}^{\text{so}}$ is proportional to the orbital momentum operator $\mathbf{L}$ through the cross products between $\mathbf{r}_i$ and $\mathbf{p}_i$; thus, matrix elements of the spin-orbit and orbital momentum operators are expected to follow similar trends. Matrix representations of the Cartesian components of the orbital momentum operator (L_i , $i = x, y, z$) can be written in the basis of real harmonics Y_{L,M_L} , where L and M_L are the orbital quantum numbers associated with $\mathbf{L}^2$ and L_z operators. In the case of transition-metal ions ($L = 2$), $Y_{2,-2} = d_{xy}$, $Y_{2,-1} = d_{yz}$, $Y_{2,0} = d_{z^2}$, $Y_{2,+1} = d_{xz}$, and $Y_{2,2} = d_{x^2-y^2}$. The resulting matrices are given in the Supplementary Information (SI). Consider, for example, transition-metal complexes whose

transition between two electronic states has non-zero average value $\langle L_i \rangle$ of the L_z component of the orbital momentum operator, as in the Fe systems under study. In this case, the orbital momentum couples with the spin momentum, and the corresponding SOC is expected to be large. From the form of the L_z matrix in the basis of real harmonics,

$$\langle L_z \rangle = \begin{matrix} & |Y_{2,-2}\rangle & |Y_{2,-1}\rangle & |Y_{2,0}\rangle & |Y_{2,1}\rangle & |Y_{2,2}\rangle \\ \begin{matrix} \langle Y_{2,-2}| \\ \langle Y_{2,-1}| \\ \langle Y_{2,0}| \\ \langle Y_{2,1}| \\ \langle Y_{2,2}| \end{matrix} & \begin{pmatrix} 0 & 0 & 0 & 0 & 2i \\ 0 & 0 & 0 & i & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & -i & 0 & 0 & 0 \\ -2i & 0 & 0 & 0 & 0 \end{pmatrix} \end{matrix},$$

one can analyze the conditions for $\langle L_z \rangle$ and SOC to be non-zero in terms of orbitals. The L_z matrix has zero elements on the main diagonal, which shows that SOC between the states that have same orbital character are small. In contrast, the off-diagonal elements of L_z are non zero, which shows that SOC are large between states that have different orbital orientation. This is the essence of El-Sayed's rules. The results can be verified by considering the magnitude of the reduced matrix element of the spin-orbit operator $H_{L_0}^{\text{SOMF}}$ of Eq. (17). Its value is large when leading hole and particle NTOs, resembling d -orbital shapes, have different orientations.[43] Similar conclusions can be derived when the electronic transition is allowed through the L_+ and L_- operators.[43] For a free transition-metal ion, the L_i matrix derived from the TDM and the one written in the basis of real harmonics, are equivalent, which corroborates our quantitative analysis of orbital momentum and SOC in terms of NTOs. Small discrepancies for transition-metal complexes are expected due to deviation of the computed NTOs from ideal d -orbitals.

The NTO representation allows us to connect many-body wave functions with El-Sayed's rules formulated in terms of orbitals. In this way, the analysis of magnetic anisotropies by Ruiz and co-workers,[80] which was based on a qualitative molecular orbital picture, can be cast in a quantitative fashion within many-body formalism. See also discussion in Section IV D and Table S1 in the SI, in which the magnitude of orbital momentum and spin-orbit matrix elements is correlated to the height of the spin-reversal energy barrier.

3. Magnetization vector and magnetic susceptibility tensor

When the sample is perturbed by an external magnetic field $\mathbf{H}$, its magnetization vector $\mathbf{M}$ is defined as a derivative of the total energy of the system at a finite temperature T with respect to the magnetic field:

$$\mathbf{M}(T, \mathbf{H}) = -\frac{\partial E(T, \mathbf{H})}{\partial \mathbf{H}}, \quad (19)$$

and the susceptibility χ is

$$\chi(T, \mathbf{H}) = \frac{\partial \mathbf{M}(T, \mathbf{H})}{\partial \mathbf{H}}. \quad (20)$$

The total energy of the system is given as a sum over all SOC- and field-perturbed state energies, $E(T, \mathbf{H}) = \sum_n E_n(\mathbf{H})p_n$, each weighted by the Boltzmann factor, $p_n = e^{E_n(\mathbf{H})/kT}/Z$, where k is the Boltzmann constant and Z is the partition function:

$$Z = \sum_n e^{-E_n(\mathbf{H})/kT}. \quad (21)$$

The magnetization is then obtained by summing over all energy first derivatives along the field, $\frac{\partial E_n(\mathbf{H})}{\partial \mathbf{H}}$, each weighted by p_n , which leads to

$$\mathbf{M}(T, \mathbf{H}) = N \sum_n \left(-\frac{\partial E_n(\mathbf{H})}{\partial \mathbf{H}} \right) p_n. \quad (22)$$

Finally, from the expression of the first derivative of the partition function with respect to the field,

$$\frac{\partial \ln Z(T, \mathbf{H})}{\partial \mathbf{H}} = \frac{1}{kT} \sum_n \left(-\frac{\partial E_n(\mathbf{H})}{\partial \mathbf{H}} \right) p_n, \quad (23)$$

we obtain working equations for computing magnetization

$$\mathbf{M}(T, \mathbf{H}) = NkT \frac{\partial \ln Z(T, \mathbf{H})}{\partial \mathbf{H}} \quad (24)$$

and susceptibility

$$\chi(T, \mathbf{H}) = NkT \frac{\partial^2 \ln Z(T, \mathbf{H})}{\partial \mathbf{H}^2}. \quad (25)$$

We evaluate these derivatives numerically. One can perform numerical differentiation with respect to each Cartesian component of the field, which gives the magnetization vector and susceptibility tensor components, M_i and χ_{ij} , respectively. Alternatively, one can compute these derivatives with respect to the field magnitude, which is useful for powder averaging. Diagonalization of the χ tensor yields the main susceptibility values (χ_{x_m} , χ_{y_m} , and χ_{z_m}) and main magnetic axes (X_m , Y_m , and Z_m). For systems with axial symmetry and axial magnetic anisotropy, as the ones investigated here, there is one easy magnetic axis (one preferential spin direction) that is collinear with the rotational axis, whereas the other two are equivalent and perpendicular to it. The response of such a system to an applied field is sensitive to both magnitude and orientation of the field.

4. Powder averaging

To compare with experimental powder spectra, the computed properties need to be averaged over randomly distributed crystallite orientations. This can be replaced by fixing the molecule orientation and performing a numerical averaging over a large set of field orientations, ideally uniformly distributed over a unit sphere. The average of a function can be computed by:

$$F_{av} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi F(\theta, \varphi) \sin(\theta) d\theta d\varphi. \quad (26)$$

This integral is then approximated by a sum of weighted function values,

$$F_{av} = \sum_i \sum_j F(\theta_{ij}, \varphi_{ij}) w_{ij}, \quad (27)$$

where the subscript ij indicates that polar angles θ and φ may not be selected independently. We follow the REPULSION integration scheme,[81] which provides a uniform distribution of 150 crystallites (field orientations) over the surface of a unit sphere, leading to an efficient powder averaging. For any pair of θ_{ij} and φ_{ij} , the direction of an applied magnetic field is given by the vector components $n_x = \sin(\theta_{ij})\cos(\varphi_{ij})$, $n_y = \sin(\theta_{ij})\sin(\varphi_{ij})$, and $n_z = \cos(\theta_{ij})$. Using these equations allows derivation of angular dependent magnetization $M(H, \theta_{ij}, \varphi_{ij})$ and susceptibility $\chi(H, \theta_{ij}, \varphi_{ij})$, which are computed by numerical differentiation of $\ln Z(H, \theta_{ij}, \varphi_{ij})$ with respect to the field magnitude H , as per Eq. (24) and (25). Average magnetization and susceptibility are then obtained by substituting $M(H, \theta_{ij}, \varphi_{ij})$

and $\chi(H, \theta_{ij}, \varphi_{ij})$ values into Eq. (27).

III. MODEL SYSTEMS AND COMPUTATIONAL SETUP

FIG. 4: Left: Structures of the considered complexes: (1) trigonal pyramidal $[(\text{tpa})\text{Fe}(\text{II})]^-$, (2) linear and two-coordinate $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$, and (3) trigonal bipyramidal $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$. Color code: Fe — orange, Cl — green, P — purple, Si — yellow, N — blue, C — gray, and H — white. Right: Electronic configurations of the reference and the doubly degenerate ground states, called states 1 and 2. For $[(\text{tpa})\text{Fe}(\text{II})]^-$ and $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$, target states (quintet d^6 configurations of Fe^{2+}) are obtained by attachment of a β -electron (in red) to the high-spin reference state (hextet d^5 configuration of Fe^{3+}). For $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$, target states (quartet d^5 configurations of Fe^{3+}) are obtained by single spin-flip excitations from the high-spin hextet reference state of Fe^{3+} . Matrix elements of L_z operator are reported in Section IV D and Table S1 of the SI. Higher electronic states are described in the SI.

To assess the performance of the presented computational protocol, we compute magnetic properties of three Fe-based SMMs (structures are shown in Fig. 4) with a three-fold symmetry, for which reliable experimental and theoretical data exist. These are: (1) a trigonal pyramidal $[(\text{tpa})\text{Fe}(\text{II})]^-$, (2) a linear and two-coordinate $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$, and (3) a trigonal bipyramidal $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$. Due to the presence of three electrons in $d_{x^2-y^2}, d_{xy}$ and d_{xz}, d_{yz} orbitals and of degenerate ground states, both the experiments[13, 51, 52, 54, 55] and the theoretical studies[24, 51, 56] suggested a certain degree of unquenched orbital momentum, and, consequently, the potential for strong axial magnetic anisotropy. X-ray structures reveal that these compounds undergo Jahn-Teller distortions of the trigonal site,

resulting in fast quantum tunneling pathways for magnetic relaxation. Consequently, the measured energy barriers (U_{eff}) are smaller than the ones expected for a spin-only system that follows a thermally activated relaxation mechanism. The magnitude of U_{eff} is typically determined from temperature-dependent ac susceptibility experiments by construction of Arrhenius plots of the magnetic relaxation times. Because of the presence of efficient quantum tunneling in the investigated Fe-based systems, slow magnetic relaxation could not be observed with ac-susceptibility measurements at zero applied direct current (dc) field, and, hence, small dc fields were required to suppress tunneling and probe SMM behavior. In addition to ac-susceptibility studies, Mössbauer spectroscopy enables determination of magnetic relaxation times and energy barriers when relaxation times are much shorter than those measurable with the ac magnetometer. For Fe(II)[C(SiMe₃)₃]₂, Mössbauer spectra at zero field yielded temperature-dependence of the magnetic relaxation times from which its spin-reversal barrier was extracted in the high-temperature regime[55].

Fig. 4 summarizes electronic structure of the three complexes under study and illustrates which EOM-CC methods were used to access their doubly degenerate ground states. Higher excited states were also considered to check the convergence of the results with respect to the number of electronic states (see the SI). To treat relevant electronic states of [(tpa)Fe(II)]⁻ and Fe(II)[C(SiMe₃)₃]₂, we carried out EOM-EA-MP2 calculations with high-spin d^5 hextet references, which allows a balanced treatment of the quintet d^6 electronic configurations. For the quartet d^5 configurations of (PMe₃)Fe(III)Cl₃, we used EOM-SF-CCSD approach with a d^5 high-spin hextet reference. All calculations were performed using the *Q-Chem* software[49, 50]. For [(tpa)Fe(II)]⁻, we used the same structure and followed the same protocol as in Ref. [36]. Calculations on Fe(II)[C(SiMe₃)₃]₂ and (PMe₃)Fe(III)Cl₃ were performed at the experimental structures taken from Ref. [82] and Ref. [52], respectively. We used Dunning’s cc-pVDZ basis sets[83–85]. Open-shell reference states were computed using unrestricted Hartree-Fock (HF). For these Fe(II) and Fe(III) SMMs, spin contamination was small: the corresponding $\langle S^2 \rangle$ values are between 6.03 and 6.11 for $S = 2$ states of Fe(II) and between 3.81 and 3.83 for $S = 3/2$ states of Fe(III). The core electrons were frozen in all EOM calculations. To speed up the calculations, we applied: (i) Cholesky decomposition[86] with a threshold of 10^{-2} for two-electron integral calculations, (ii) open-shell frozen natural orbital (OSFNO)[87] truncation of the virtual space with the total population threshold of 99%, and (iii) single precision execution.[88]

IV. RESULTS AND DISCUSSION

A. Trigonal pyramidal $[(\text{tpa})\text{Fe}(\text{II})]^-$ complex

The family of trigonal pyramidal Fe(II) complexes with different variants of the tpa^{R} ligand is the first reported example of mononuclear transition-metal complexes exhibiting slow magnetic relaxation[13, 54]. We use a simplified model system, i.e., $[(\text{tpa})\text{Fe}]^-$ [36], which closely resembles the original $[(\text{tpa}^{\text{R}})\text{Fe}]^-$ with $\text{R} = \text{tert-butyl (Tbu)}$ and mesityl (Mes) , and compare results of this work with experiments[13, 54] and NEVPT2 calculations[24] available for both $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ and $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$. Susceptibility measurements under a dc magnetic field confirmed the $S = 2$ ground-state spin of these complexes[13, 54]. To probe magnetic anisotropy, low-temperature magnetization data were collected under various applied dc fields (from 1 to 7 T) by changing temperature (from 2 to 5 K). Resulting isofield magnetization curves are well separated and not-superimposed upon the Brillouin function, which indicates strong magnetic anisotropy[13, 54]. Indeed, fitting of these magnetizations to a spin Hamiltonian yielded large and negative axial ZFS parameters of $D = -48$ and $-44 \pm 4 \text{ cm}^{-1}$ for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ and $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$, respectively.[54] The sign and magnitude of D together with the spin S provide a spin-reversal barrier of $U = 192 \text{ cm}^{-1}$ for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ and $176 \pm 16 \text{ cm}^{-1}$ for $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$, suggesting the possibility of SMM behavior. Moreover, ac susceptibility measurements in the presence of a small dc field probed relaxation barriers of $U_{\text{eff}} = 65 \text{ cm}^{-1}$ [54] for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ and 42 cm^{-1} [13, 54] for $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$, demonstrating slow magnetic relaxation. In these systems, small geometrical distortions from the three-fold symmetry lead to tunneling, which explains the much faster spin inversion than would be expected by spin and magnetic anisotropy (i.e, $U_{\text{eff}} < U = |D|S^2$). Fig. 4 shows electronic configurations of the two lowest (degenerate) quintet states of $[(\text{tpa})\text{Fe}]^-$, namely, states 1 and 2 (see the SI for higher quintet states). These states are near-degenerate with a small energy difference in between of 9 cm^{-1} due to small geometric distortion. To reduce the impact of this artifact on the magnitude of the spin-orbit splitting, we follow Ref. [36] and average the energies of states 1 and 2. From the natural orbital occupancies, n , an effective number of unpaired electrons, $n_{n,nl}$, is computed by Head-Gordon's formula.[89] For the quintet states, $n_{n,nl}$ is exactly 4. $\langle S^2 \rangle$ is between 6.03 and 6.11: showing negligible spin-contamination. For all transitions between the computed target states, there is only

one non-zero singular value ω of the spinless transition density matrix, i.e., only one hole-particle NTO pair is needed to describe each transition. Fig. 5 shows the leading NTO pair of the spinless transition density matrix computed between states 1 and 2. As one can see,

FIG. 5: Hole and particle NTOs of the spinless density matrix giving rise to SOC within the states 1 and 2 of $[(\text{tpa})\text{Fe}(\text{II})]^-$. Singular value ω is 0.88. $\langle L_z \rangle \approx \pm i$. Red, green, and blue axes indicate x , y , and z coordinates axes, respectively.

the transition between the two states can be described as transition between nearly perfect d_{yz} and d_{xz} orbitals—this is the reason of unquenched orbital momentum of $\langle L_z \rangle \approx \pm i$ and large SOC (see also Section IV D and Table S1 in the SI).

For states 1 and 2, Fig. 1 shows spin-orbit splittings alone and compares them with the combined SOC-Zeeman effect (energies are reported in the SI). This manifold of 10 spin-orbit levels is located within an interval of 400 cm^{-1} and is well separated from higher states by 3000 cm^{-1} . Therefore, these sublevels are the only ones expected to be populated at temperatures up to 300 K (Table S4 in the SI), and the mixing due to SOC with high-lying excited states is small. Considering these 10 sublevels, Pokhilko *et al.* reported an energy barrier of $U = 173 \text{ cm}^{-1}$.^[36] This barrier lowers and converges to 158 cm^{-1} when an additional quintet excited state (for a total of 15 spin-orbit levels) is included in the SOC calculation. Table I reports calculated energy barriers of this work, which agree with previous calculations^[36] and with experimental values for both $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ and $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$.

TABLE I: Convergence of the energy barrier U (cm^{-1}) with the number of multiplets.

N. of states	System	U	U_{eff}
2	$[(\text{tpa})\text{Fe}]^-$	173	
3	$[(\text{tpa})\text{Fe}]^-$	158	
5	$[(\text{tpa})\text{Fe}]^-$	157	
Exp. ^{a,b}	$[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$	192	65
Exp. ^{a,b}	$[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$	176 ± 16	42
Exp. ^{a,c}	$[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$	158	42

^a Energy barrier ($U = |D|S^2$) from D parameter and spin S . Effective energy barrier (U_{eff}) from ac susceptibility measurements. ^b Ref. [54]. ^c Ref. [13].

FIG. 6: (a) Calculated field-dependent magnetizations of $[(\text{tpa})\text{Fe}(\text{II})]^-$ at low temperature ($T = 1.8$ K). Magnetization is in Bohr magneton (μ_B) units. Color code: this work (EOM-EA-MP2) — black curves; Ref. [24] (NEVPT2) for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ — yellow, green, and blue curves; experiment of Ref. [54] for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ — red curves. (b) Calculated $\chi_{Z_m} T$, $\chi_{X_m} T$ ($\chi_{Y_m} T$), and $\chi_{\text{av}} T$ of $[(\text{tpa})\text{Fe}(\text{II})]^-$ in the temperature range from 5 to 300 K and under an applied field of 1000 Oe (0.1 T). Experimental susceptibility data for $[(\text{tpa}^{\text{Tbu}})\text{Fe}(\text{II})]^-$ (red curve) and $[(\text{tpa}^{\text{Mes}})\text{Fe}(\text{II})]^-$ (black curve) are taken from Ref. [54] and Ref. [13], respectively. “av” stands for isotropic powder averaging.

Using these 10 SOC- and field-corrected sublevels of the ground state, we computed field-dependent magnetizations for a magnetic field oriented either parallel or perpendicular to the C_3 rotational axis, as well as powder magnetizations M_{av} (numerical averaging). Fig. 6 compares calculated magnetizations for $[(\text{tpa})\text{Fe}]^-$ with results for $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ from the experiment[54] and the NEVPT2 calculations of Neese and co-workers.[24] Our computed curves agree perfectly with the theoretical curves obtained from NEVPT2 calculations. The computed average values in this work and in Ref. [24] are higher than the experimental ones. At 1.8 K and 7 T, we compute a saturation value of the magnetization of $2.68 \mu_B$, which is lower than the $4 \mu_B$ expected for a spin-only $S = 2$ ion, suggesting prominent magnetic anisotropy of this complex. Our calculations also predict a separation between magnetization isofield curves, as was observed experimentally for both $[(\text{tpa}^{\text{Tbu}})\text{Fe}]^-$ [54] and $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$ [13] (Fig. S4 and S5 in the SI). We also computed susceptibility main values, i.e., χ_{Z_m} and χ_{X_m} (χ_{Y_m}), by diagonalization of the χ tensor. The direction of the easy magnetic axis Z_m is found to be collinear with the rotational C_3 axis. Powder susceptibilities χ_{av} are then computed by numerical averaging. Fig. 6 shows the temperature dependence

(from 5 to 300 K) of the product of the susceptibility and temperature (χT) under an applied field of 1000 Oe (0.1 T) parallel to the z -axis. Calculated $\chi_{Z_m} T$ increases on cooling and tends to a finite value when T approaches zero. $\chi_{X_m} T$ and $\chi_{Y_m} T$, on the other hand, converge to zero. In the low-temperature regime, the temperature dependence of the susceptibility deviates from the Curie law, which can be attributed to the magnetic anisotropy of the system. At 300 K, the calculated $\chi_{av} T$ is 3.48 cm³K/mol, which is in between the saturation values for [(tpa^{Tbu})Fe][−] (3.55 cm³K/mol)[54] and [(tpa^{Mes})Fe][−] (3.32 cm³K/mol),[13] and close to the expected value of 3 cm³K/mol for an isotropic $S = 2$ ion. Finally, we verified the convergence of the magnetization and susceptibility with respect to the number of multiplets (2-5) included in the calculations, and found that taking into account the two lowest states is sufficient for accurate description of their average quantities (Fig. S8 in the SI).

B. Two-coordinate and linear Fe(II)[C(SiMe₃)₃]₂ complex

We consider a two-coordinate and linear Fe(II) complex, Fe(II)[C(SiMe₃)₃]₂, which was shown to exhibit slow magnetic relaxation with an effective energy barrier of $U_{\text{eff}} = 146$ cm^{−1}, which is the highest value reported to date for Fe(II) complexes[51]. This strong magnetic anisotropy was ascribed to the unquenched orbital momentum of the ground state of Fe(II)[C(SiMe₃)₃]₂, about twice as large as that of [(tpa)Fe(II)][−] (see discussion in Section IV D and Table S1 in the SI). Determination of the axial ZFS parameter D by fitting the magnetization data to a spin Hamiltonian did not provide satisfactory results[51]. This is expected for systems with more substantial orbital angular momentum, whose magnetic behavior cannot be rationalized by conventional spin-only models[90]. Furthermore, high-temperature Mössbauer spectra at zero field yielded a barrier height of $U_{\text{eff}} = 178 \pm 9$ cm^{−1},[55] somewhat larger than the value of 146 cm^{−1} determined by ac-susceptibilities at non-zero dc field[51], but closer to the ab initio value of 196 cm^{−1} derived by Neese and co-workers from NEVPT2 calculations[56]. We follow the same strategy as in Ref. [56], in which the spin-reversal barrier was found to correspond to the energy separation between the ground and first-excited states, assuming that relaxation occurs mainly via the Orbach mechanism.

Fig. 4 shows electronic configurations of the doubly degenerate ground state of Fe(II)[C(SiMe₃)₃]₂, called states 1 and 2 (see the SI for a description of additional quin-

FIG. 7: Hole and particle NTOs of the spinless density matrix giving rise to SOC within the states 1 and 2 of Fe(II)[C(SiMe₃)₃]₂. Singular value ω is 0.85. $\langle L_z \rangle \approx \pm 2i$. Red, green, and blue axes indicate x , y , and z coordinates axes, respectively.

tet states). Due to symmetry lowering from $D_{\infty h}$ to C_3 , we observe energy splitting between states 1 and 2 of 195 cm⁻¹, as also reported by Neese and co-workers[56]. For these states, spin contamination is negligible ($n_{n,nl} = 4$ and $\langle S^2 \rangle = 6.03$ -6.06). A single hole-particle NTO pair (Fig. 7) fully describes the transition between states 1 and 2. This transition involves $d_{x^2-y^2}$ and d_{xy} orbitals, leading to the largest orbital momentum of $\langle L_z \rangle \approx \pm 2i$ for the Fe systems under study, and therefore, to the largest SOC (Section IV D and Table S1 in the SI).

TABLE II: Convergence of the energy barrier U (cm⁻¹) with the number of multiplets.

N. of states	U_{eff}
2^a	160
3^a	161
Exp. ^{b,c}	146
Exp. ^{d,e}	178 ± 9
NEVPT2 ^{a,f}	196

^a Energy barrier computed as energy difference between the ground and the first excited states. ^b Effective energy barrier (U_{eff}) from ac susceptibility measurements. ^c Ref. [51]. ^d Effective energy barrier (U_{eff}) from Mössbauer spectroscopy. ^e Ref. [55]. ^f Ref. [56].

Diagonalization of the SOC-augmented Hamiltonian (i.e, $H^0 + H^{\text{SO}}$) for states 1 and 2 yields the splitting of the ground state into 10 spin-orbit sublevels, as shown in Fig. 1. Corresponding energies are reported in the SI. These first 10 sublevels of the ground state are relatively well-isolated from higher excited states, and are the only energy levels populated in the temperature range from 5 to 300 K (Table S4 in the SI). Additionally, there is no SOC mixing with higher states. Using these first 10 spin-orbit levels, we compute the energy separation between the ground and first-excited states of 160 cm⁻¹, which is in

agreement with both Mössbauer[55] and ac-susceptibility[51] experiments, and also with similarly derived energy difference from NEVP2 energy levels[56] (Table II). In contrast to $[(\text{tpa})\text{Fe}(\text{II})]^-$, we note that the spin-reversal energy barrier for $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$ is not sensitive to the number of multiplets included in the SOC calculation. This can be ascribed to the smaller SOC of states 1 and 2 with state 3 than the corresponding ones computed for the trigonal pyramidal $\text{Fe}(\text{II})$ complex.

FIG. 8: Calculated field-dependent magnetizations of $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$ at low temperature ($T = 1.8$ K). Magnetization is in Bohr magneton (μ_b) units. Color code: this work (EOM-EA-MP2) — black curves; Ref. [56] (NEVP2) — yellow, green, and blue curves; experiment of Ref. [51] — red curves. “av” stands for isotropic powder averaging.

Fig. 8 and 9 show temperature- and field-dependent magnetizations (M vs H/T) and susceptibilities (χT vs T). The calculated curves of this work are in excellent agreement with experiment[51] and with curves obtained from NEVP2 calculations by Neese and co-workers[56]. From experiments at 1.8 K and 7 T [51], the saturation magnetization is $3.24 \mu_b$, which is close to our computed value of $3.04 \mu_b$, but much lower than the expected value ($4 \mu_b$) for spin-only magnetic behavior. Both experiment and our calculations report separation between isofield curves of the magnetization (Fig. S6 in the SI), which is also indicative of strong magnetic anisotropy. At 300 K, the computed $\chi_{\text{av}}T$ of this work is $4.59 \text{ cm}^3\text{K/mol}$, which agrees well with both the experimental ($4.78 \text{ cm}^3\text{K/mol}$)[51] and NEVP2 ($4.82 \text{ cm}^3\text{K/mol}$)[56] results, but is by far exceeding the spin-only χT value of $3 \text{ cm}^3\text{K/mol}$ expected for an $S = 2$ ion. Such larger χT value is typical of transition-metal complexes with a sizable contribution of orbital momentum to their magnetic behavior. Finally, we

FIG. 9: Calculated $\chi_{Z_m}T$, $\chi_{X_m}T$ ($\chi_{Y_m}T$), and $\chi_{av}T$, of Fe(II)[C(SiMe₃)₃]₂ in the temperature range from 5 to 300 K and under an applied field of 1000 Oe (0.1 T). Experimental powder spectra (top, black curve) from Ref. [51]. Average susceptibilities from this work (green curve) and from NEVPT2 calculations[56] (bottom, red curve).

observe that neither energy barriers nor magnetic properties are influenced by the number of multiplets (2 or 3) taken into account (Table II and Fig. S9 in the SI).

C. Trigonal bipyramidal (PMe₃)Fe(III)Cl₃ complex

We compute magnetic properties of a mononuclear $S = 3/2$ Fe(III) complex, (PMe₃)Fe(III)Cl₃, whose three-fold symmetry is key to designing Fe(III) SMMs with large magnetic anisotropy [52]. Magnetization measurements revealed a large and negative axial ZFS parameter of $D = -50 \text{ cm}^{-1}$ [52]. Moreover, ac-susceptibility experiments observed slow magnetic relaxation under the presence of a small applied dc field with an effective energy barrier of $U_{\text{eff}} = 81 \text{ cm}^{-1}$, which is the highest relaxation barrier yet observed for a mononuclear Fe(III) SMM [52].

FIG. 10: Hole and particle NTOs of the spinless density matrix giving rise to SOC within the states 1 and 2 of (PMe₃)Fe(III)Cl₃. Singular value ω is 0.87. $\langle L_z \rangle \approx \pm i$. Red, green, and blue axes indicate x , y , and z coordinates axes, respectively.

Fig. 4 shows electronic configurations of the doubly degenerate ground state, called states 1 and 2 (see the SI for a description of additional states higher in energy). Small deviations from a perfect three-fold symmetry lead to an artificial energy splitting of about 92 cm^{-1} between states 1 and 2. The number of unpaired electron, $n_{u,nl}$, is estimated as 3. $\langle S^2 \rangle$ is 3.81, showing low spin-contamination (the exact value is 3.75). Hole and particle NTOs (Fig. 10) for the transition between states 1 and 2 involve nearly perfect d_{yz} and d_{xz} orbitals, which yields non-zero orbital momentum of $\langle L_z \rangle \approx \pm i$ and large SOC (Section IV D and Table S1 in the SI).

Due to SOC, the ground-state multiplet splits into eight (doubly degenerate) sublevels (Fig. 11). These first eight sublevels are about 2000 cm^{-1} below the next excited hextet state. Therefore, these sublevels are the only ones that are occupied in the temperature range 5-300 K (Table S4 in the SI). Additionally, there is no SOC mixing of this manifold with higher excited states. Considering these spin-orbit levels, we derived an energy barrier

of $U = 103 \text{ cm}^{-1}$, which increases up to 128 cm^{-1} when 5 multiplets (corresponding to 22 spin-orbit levels) are included in the SOC calculation. There is a reasonable agreement of the calculated barriers from this study with the predicted experimental value of $U = 100 \text{ cm}^{-1}$ for $S = 3/2$ and $D = -50 \text{ cm}^{-1}$ (Table III).

FIG. 11: Splitting of the quartet ground state of $(\text{PMe}_3)\text{Fe(III)Cl}_3$ under the SOC (computed using states 1 and 2) effects.

TABLE III: Convergence of the energy barrier U (in cm^{-1}) with the number of multiplets.

N. of states	U	U_{eff}
2	103	
3	130	
5	128	
Exp. ^{a,b}	100	81

^a Energy barrier ($U = D(S^2 - 1/4)$) from experimental D parameter and S spin. Effective energy barriers (U_{eff}) from ac susceptibility measurements. ^b Ref. [52].

We computed temperature- and field-dependent magnetizations (panel (a) of Fig. 12) and susceptibilities (panel (b) of Fig. 12) using the lowest in energy manifold of eight SOC- and field-corrected sublevels. The saturation magnetization is $1.94 \mu_b$, as determined from magnetization data measured at 7 T in Ref. [52], which is in agreement with the calculated value of $2.04 \mu_b$ and much smaller than the expected value of $3 \mu_b$ for a spin-only $S = 3/2$ system. This deviation arises from substantial orbital momentum contributions to the magnetic behavior of the Fe(III) compound. Fig. 13 illustrate isofield magnetization curves that are obtained for a fixed field (H from 1 to 7 T) by varying the temperature (from 2 to

FIG. 12: (a) Calculated field-dependent magnetizations of $(\text{PMe}_3)\text{Fe(III)Cl}_3$ at low temperature ($T = 1.8$ K). Experimental curves are not available. (b) Calculated $\chi_{Z_m}^*T$, $\chi_{X_m}^*T$ ($\chi_{Y_m}^*T$), and χ_{av}^*T , of $(\text{PMe}_3)\text{Fe(III)Cl}_3$ in the temperature range from 5 to 300 K and under an applied field of 5000 Oe (0.5 T). Experimental susceptibility data (black curve) are taken from Ref. [52]. “av” stands for isotropic powder averaging.

20 K). Both experimental (black curves) and calculated data of this work exhibit separation between these curves, indicative of magnetic anisotropy. Moreover, computed χ_{av}^*T values (green curve in panel (b) of Fig. 12) agree reasonably well with experiment (black curve in panel (b) of Fig. 12). At 300 K, the calculated χ_{av}^*T is $1.91 \text{ cm}^3\text{K/mol}$, while experiment yields $2.29 \text{ cm}^3\text{K/mol}$, confirming a $S = 3/2$ spin ground state of the system ($S = 3/2$, $\chi T = 1.876 \text{ cm}^3\text{K/mol}$). Finally, we investigated the convergence of magnetization and susceptibility data with respect to the number of states and verified that results already converge by including the two lowest multiplets only (Fig. S10 in the SI).

FIG. 13: Calculated (this work) and experimental (black curves, Ref. [52]) isofield magnetization curves (M versus H/T) of $(\text{PMe}_3)\text{Fe(III)Cl}_3$. Magnetization is in Bohr magneton (μ_B) units. For each field (H from 1 to 7 T) the temperature is increased from 2 to 20 K.

D. Analysis of orbital angular momentum and spin-orbit matrix elements

To rationalize the trends in magnetic anisotropy, we compare orbital momentum and spin-orbit matrix elements for the transitions between states 1 and 2 of the three SMMs under study. According to El-Sayed's rules,[45] SOC matrix elements are large if the transition involves a change of orbital character. For the SMMs studied here, transitions between states 1 and 2 are allowed through the L_z operator and one pair only of hole-particle NTOs contributes to the electronic transition. Matrix elements of L_z are then computed via the density matrix formalism presented in Section II B. These calculated values slightly deviate from the ones obtained in the basis of d -orbitals (real harmonics) with differences less than 10% (Table S1 in the SI), which has to be ascribed to the non-perfect d -orbital shape of the computed NTOs. For $[(\text{tpa})\text{Fe}(\text{II})]^-$ and $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$, the transition is between d_{yz} and d_{xz} orbitals, corresponding to matrix elements of $\langle L_z \rangle \approx \pm i$. Whereas, the transition for $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$ involves the $d_{x^2-y^2}, d_{xy}$ orbital set, whose computed $\langle L_z \rangle$ matrix elements are larger and about $\pm 2i$. From the relative magnitude of these L_z matrix elements, SOC matrix elements for $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$ are expected to be larger than the ones for $[(\text{tpa})\text{Fe}(\text{II})]^-$ and $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$ that is also the reason of a more pronounced SMM behavior for $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$. This is confirmed by the magnitude of the reduced matrix element of the spin-orbit operator $H_{L_0}^{\text{SOMF}}$ presented in Eq. (17). For $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$, this value is twice as large as that computed for $[(\text{tpa})\text{Fe}(\text{II})]^-$ and $(\text{PMe}_3)\text{Fe}(\text{III})\text{Cl}_3$ (Table S1 in the SI). From molecular orbital theory, slow magnetic relaxation for these systems is attributed to the presence of three electrons in near-degenerate d_{xz}, d_{yz} and $d_{x^2-y^2}, d_{xy}$ orbital sets with orbital projection values of $M_L = \pm 1$ and ± 2 , respectively, which results in non-zero orbital momentum contributions to the magnetic anisotropy.[80] More rigorously, we obtain M_L by diagonalization of the L_z matrix. For instance, from the L_z matrix elements of $\text{Fe}(\text{II})[\text{C}(\text{SiMe}_3)_3]_2$:

$$\langle L_z \rangle = \begin{array}{c} \langle 1| \\ \langle 2| \end{array} \begin{array}{cc} |1\rangle & |2\rangle \\ \begin{pmatrix} 0.01i & 1.94i \\ -1.94i & 0.01i \end{pmatrix} \end{array}, \quad (28)$$

we obtain eigenvalues

$$M_L = \begin{pmatrix} 1.94 & 0.00 \\ 0.00 & -1.94 \end{pmatrix} \quad (29)$$

and corresponding eigenvectors

$$v = \begin{pmatrix} 0.71i & -0.71i \\ 0.71 & 0.71 \end{pmatrix} \quad (30)$$

Similarly, we compute $M_L = \pm 0.95$ for $[(\text{tpa})\text{Fe(II)}]^-$ and $M_L = \pm 0.90$ for $(\text{PMe}_3)\text{Fe(III)Cl}_3$ (corresponding L_z matrices, eigenvalues, and eigenvectors are given in the SI). The doubly degenerate ground state of $\text{Fe(II)[C(SiMe}_3)_3]_2$ has the largest orbital projection of $M_L = \pm 1.94$ among the Fe SMMs investigated in this work, and hence the largest SOC and spin-reversal energy barrier. See Table S1 in the SI for a full comparison between orbital angular momentum and spin-orbit matrix elements with measured relaxation barriers. These results explain the height of the barrier in terms of El-Sayed’s rules: the leading pair of hole-particle NTOs resulting in a larger expectation value of the orbital momentum operator leads to a greater SOC and thus to a slower relaxation of the magnetization. This analysis tool of the magnetic anisotropy in terms of NTOs puts the treatment by Ruiz and co-workers[80] based on a molecular orbital picture on a quantitative footing.

V. CONCLUSIONS

We have presented a protocol for computing macroscopic magnetic properties of mononuclear transition-metal complexes (single-ion magnets) within the EOM-CC framework. Magnetic field and SOC effects are incorporated using a two-step state-interaction scheme in which the perturbed Hamiltonian matrix $H^0 + H^{\text{SO}} + H^{\text{Z}}$ is constructed and diagonalized in the basis of non-relativistic EOM-CC states. Direct comparison with experiments is made possible by the numerical averaging of the computed properties over a large and uniform set of field orientations. Macroscopic magnetic properties, i.e., temperature dependence of the susceptibility in the form χT versus T , and low-temperature magnetization under various applied dc fields, are reproduced well by the calculations. The results are also in excellent agreement with the previous theoretical work using NEVPT2. This indicates that electronic structures of the mononuclear Fe(II) and Fe(III) SMMs investigated in this study are treated reliably by EOM-CC, and that our computational approach for magnetic properties is accurate. Furthermore, we derived energy barriers between the spin-up and spin-down orientations from the spin-orbit splittings of each ground state into the corresponding mag-

netic sublevels. Resulting energy barriers agree well with both experimental values derived from the spin S and the axial ZFS parameter D , and with results from NEVPT2 energy levels, which further strengthens our conclusion.

For the three Fe complexes under study, both experiments and magnetic data of this work report a considerable separation between the isofield magnetization curves together with a non-linear temperature dependence of the average susceptibility $\chi_{\text{av}}T$ curves, which are indicative of anisotropic magnetic behavior. Moreover, our work demonstrates, purely from first principles, the impact of orbital angular momentum and SOC on the magnetic anisotropy and spin-reversal energy barrier. Among the three Fe systems of interest, the doubly degenerate ground state of $\text{Fe(II)[C(SiMe}_3)_3]_2$, whose transition between states 1 and 2 involves just one hole-particle NTO pair of $d_{x^2-y^2}, d_{xy}$ shape, displays the largest orbital projection of $M_L \approx \pm 2$, and thus the largest SOC, followed by complexes $[(\text{tpa})\text{Fe(II)}]^-$ and $(\text{PMe}_3)\text{Fe(III)Cl}_3$, in which the leading NTO pair has a d_{xz}, d_{yz} nature and the computed orbital projection is about ± 1 only. Thus, this trend in orbital momentum and SOC magnitude is in accordance with what expected from both molecular orbital theory and El-Sayed's rules for a system with an odd number of electrons in near-degenerate d -orbitals of different orientation. Furthermore, $\text{Fe(II)[C(SiMe}_3)_3]_2$ exhibits a susceptibility value at room temperature of $\chi_{\text{av}}T = 4.59 \text{ cm}^3\text{K/mol}$, which largely deviates from the expected value of $3 \text{ cm}^3\text{K/mol}$ for a $S = 2$ ground state with spin-only magnetic behavior. Clearly, this deviation of the average susceptibility from the Curie law at even high temperature is due to a significant orbital momentum contribution to the ground-state magnetic behavior of $\text{Fe(II)[C(SiMe}_3)_3]_2$, which is at the origin of its strong magnetic anisotropy. In contrast, complexes $[(\text{tpa})\text{Fe(II)}]^-$ and $(\text{PMe}_3)\text{Fe(III)Cl}_3$, for which the orbital momentum contributions are smaller than the one computed for $\text{Fe(II)[C(SiMe}_3)_3]_2$, display $\chi_{\text{av}}T$ values at 300 K that are close to the predicted values for a spin $S = 2$ and $3/2$ ground state, respectively, which results in a less pronounced magnetic anisotropy. These observations are consistent with the slow relaxation of the magnetization observed from ac susceptibility measurements and relative effective energy barriers extracted from Arrhenius plots. The linear and two-coordinate $\text{Fe(II)[C(SiMe}_3)_3]_2$, which we proved from ab initio calculations to possess the largest SOC and strongest magnetic anisotropy, also shows the highest effective energy barrier of $U_{\text{eff}} = 146 \text{ cm}^{-1}$ [51] against much smaller values of 42 [13] and 81 cm^{-1} [52] for $[(\text{tpa})\text{Fe(II)}]^-$ and $(\text{PMe}_3)\text{Fe(III)Cl}_3$, respectively.

This study validates our computational protocol for magnetization and susceptibility of transition-metal SMMs and introduces quantitative tools for the analysis of magnetic anisotropy in terms of NTOs. This is the first application of the EOM-CC methods to describe magnetic behavior of transition metal complexes, providing an alternative to traditional multi-reference calculations. Future research will focus on extending the methodology to additional electronic structure patterns, e.g., d^7 and d^8 , and other transition metals, e.g., Fe(I), Co(II), and Ni(II), which can be described by different variants of EOM-CC including the double electron-attachment (DEA) and double ionization-potential (DIP) ansätze. Furthermore, the presented methodology is general enough to be applied together with SF-TDDFT and restricted active space CI (RASCI), and it can also be extended to the study of other SMMs with multiple magnetic centers by additional treatment of exchange interactions, which makes it a useful post-processing tool for tuning magnetic behavior of different types of transition-metal complexes.

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Supplementary material

Matrix representations of orbital momentum operators in the basis of spherical harmonics (d block), orbital angular momentum and spin-orbit matrix elements, wave function analysis, spin-orbit and Zeeman splitting, variable-field magnetization data, convergence of magnetization and susceptibility data with number of states; relevant Cartesian coordinates.

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