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ABSTRACT: We present a new computational protocol for computing macroscopic magnetic properties of transition-metal complexes using the equation-of-motion coupled-cluster (EOM-CC) framework. The approach follows a two-step state-interaction scheme: we first compute zero-order states using nonrelativistic 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 single-molecule magnets (SMMs) with Fe(II) and Fe(III) in trigonal pyramidal, linear, and trigonal bipyramidal coordination environments. We described the underlying electronic structure by the electron-attachment (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 in magnetic anisotropy and spin-reversal energy barriers 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 in describing magnetic behavior of mononuclear transition-metal SMMs.

I. INTRODUCTION

Single-molecule magnets (SMMs) are attracting considerable attention due 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.

The relaxation time of the magnetization is controlled by the energy barrier $U$ for spin inversion, which arises due to the zero-field splitting (ZFS) of the $2S + 1$ degenerate components (with spin projection $M_i = S, S-1, ..., -S+1, -S$) of the spin $S$ ground state, as illustrated in Figure 1 for a doubly degenerate quintet state. This splitting originates from the coupling of the ground state with low-lying excited states by 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 ($\chi_{ij}$ with $i, j = x, y, z$). Molecules with magnetic anisotropy tend to orient their magnetization along one preferential direction, which is called the 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 (as the one shown in Figure 1) one step at a time via the Orbach process3,4—occurs if the thermal energy ($k_B T$) is sufficient to overcome $U$. This thermally activated mechanism can be sidestepped by spin-phonon coupling and quantum tunneling under the barrier between the degenerate $\pm M_S$ levels.3,5 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 $U_{\text{eff}}$...
measured from alternating current (ac) susceptibilities is much smaller than the thermal energy barrier $U$. Whereas ZFS and magnetic anisotropy arise due to SOC's, the energy splittings due to an external magnetic field arise due to Zeeman interactions. Under a field applied along the $z$-axis, the energy of the $+M_s$ levels increases and that of the $-M_s$ levels decreases (shown in Figure 1), thus suppressing 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 and $U = D (S^2 - 1/4)$ for half-integer spin values. For practical applications, SMMs with higher energy barriers are desirable. Barriers can be increased by maximizing either 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 $D$ is proportional to $1/S^2$. Alternatively, magnetic anisotropy can be enhanced by increasing 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, 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. To date, a metalloocene of Dy(III) exhibits the largest-ever measured energy barrier of 1541 cm$^{-1}$ and blocking temperature up to 80 K.

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, $3d$ electrons are less shielded from ligands than $4f$ electrons of rare-earth ions. Consequently, the ligand field is stronger than spin–orbit interactions, such that orbital momentum is quenched by the ligand field and structural distortions that remove the necessary $d$-orbital degeneracies. Furthermore, structural distortions also contribute to the tunneling, accelerating 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, an increasing number of $3d$-block transition-metal SMMs have been reported, the performance of which is comparable to the outstanding lanthanide SMMs. Their strong magnetic anisotropy arises due to the partially preserved $d$-orbital degeneracy, leading to degenerate ground states (as in Figure 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 and enforcing linear geometries by means of bulky ligands. 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.

Quantum chemistry is a critical instrument for developing better SMMs. The 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. 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 compared with analogous quantities extracted by fitting experimental magnetization and susceptibility data.

Ab initio description of SMMs is challenging because of their multiconfigurational 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 multireference 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 and NEVPT2 ($n$-electron valence-state PT) are frequently used in studies of magnetic molecules, providing accurate estimates of their magnetic properties.

In addition to numerical derivation of spin-Hamiltonian parameters—such as $J$ constants, $D$ parameters, and $g$-tensors—from ab initio calculations, tools have been developed in combination with multireference 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 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 of the Molcas program affords calculations of macroscopic magnetic properties via the Van-Vleck formalism using the energies and...
magnetic moments of the spin–orbit perturbed states obtained using RASSI (restricted active space state interaction).31

We present an alternative strategy based on the equation-of-motion coupled-cluster (EOM-CC) family of methods32−35 in the 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. The EOM-CC family of methods provides access to multiconfigurational states of radicals, polyradicals, and other open-shell species, which makes EOM-CC suitable for treating SMMs.36−40

To describe d5 and d6 patterns, we use the electron-attachment (EOM-EA) and spin-flip (EOM-SF) variants in combination with high-spin d5 references. We treat SOC effects by a state-interaction approach31−35 in which SOCs are computed as matrix elements of the Breit-Pauli spin−orbit Hamiltonian44,45 using nonrelativistic EOM-CC wave functions, as was recently done by Krylov and co-workers.39,40,41 Trends in SOCs can be rationalized in terms of El-Sayed’s rules,15,54,55,57,58 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).49 As shown by Pokhilko and Krylov,40 transitions between spin−orbit interacting states can be described in terms of hole-particle NTO pairs, allowing one to quantify the contribution of each orbital pair to the overall SOC. Consequently, the shapes and orientation of these orbitals allow one to rationalize El-Sayed’s rules for p- and d-manifolds.46

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 in the ezMagnet module50 of the ezSpectra suite.51 The script (written in Python) takes the raw data (EOM energies, orbital momentum, and spin−orbit matrix elements) provided by the Q-Chem software52,53 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(pyrrrolylmethyl)-amine Fe(II) complex, denoted as [(tpa)Fe]3+, the structural model of which has been derived by Pokhilko et al.39 from the original one, [(tpaMe)Fe]3+ by replacing the mesitylene group in the ligand, tpaMe, by hydrogen;
2. A two-coordinate (locally linear) Fe(II)(C(SiMe3)3)2 complex,54 where Me stands for CH3;
3. A trigonal bipyramidal (PMe3)2Fe(III)Cl3 complex.55

These SMMs feature local trigonal symmetry, which has been utilized to develop compounds with large spin-reversal barriers and slow magnetic relaxation.56 We assess the performance of our computational protocol for energy barriers and magnetic properties by comparison to the experimental15,54,55,57,58 and available theoretical data from NEVPT2 calculations.

We complement our calculations by orbital analysis36 using spin–orbit NTOs, explaining 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. EOM-CC extends the single-reference CC methodology to multiconfigurational wave functions and provides an efficient, robust, and accurate framework for computing multiple electronic states. Within the EOM-CC formalism,32−35 target-state wave functions have the following form:

$$|\Psi\rangle = Re^{|\Phi_0\rangle}$$

(1)

where $|\Phi_0\rangle$ is the reference Slater determinant, $e^{|\Phi_0\rangle}$ 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, for example, up to doubly excited configurations at the EOM-CCSD and EOM-MP2 levels. In EOM-CCSD,61 the amplitudes of $T$ are determined by solving the coupled-cluster equations for the reference state whereas in EOM-MP2 (originally called EOM-CCSD(2))62,63 the amplitudes are computed using MP2. By using different types of R and of reference states, different manifolds of target states can be accessed, as illustrated in Figure 2. For example, spin-flip (SF)60,64,65 excitation operators access multiconfigurational low-spin states in di- and triradicals, 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-CC64 as well as with time-dependent DFT (TD-DFT)66,67 PT,58 and configuration interaction (CI).69 The SF approaches provide a balanced treatment of relevant spin states, treat both nondynamical and dynamical correlation simultaneously, do not require active-space selection, and do not rely on symmetry-broken solutions or on (nonunique) spin-projectors. EOM-SF has been used for describing various types of SMMs.36−38,40 Other forms of R, such as the electron-ionicizing (IP)70,71 and electron-attaching (EA)72 operators, do not conserve the number of electrons and can accurately treat doublet radicals and other open-shell systems. For example, the EOM-EA with a high-spin d5 reference has been used to treat ground and excited states of mononuclear Fe(II) SMMs.59 Following these previous studies, here we employ the EOM-SF and EOM-EA variants with high-spin d5 references to describe d5 and d6 patterns of Fe(III) and Fe(II) single-center SMMs.

B. A Molecular Orbital Picture for Many-Body Wave Functions. The ability to assign 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 Dyson orbitals, density matrices, and NTOs. The key quantity, which enables the interpretation of one-electron excitations between initial $\Psi^I$ and final $\Psi^F$ states and the calculations of related transition properties, is the one-electron transition density matrix (1PTDM),

$$\gamma^F_{pq} = \langle \Psi^F | a_p^\dagger a_q | \Psi^I \rangle$$

(2)

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

$$\langle \Psi^F | \hat{A} | \Psi^I \rangle = \sum_{pq} A_{pq} \langle \Psi^F | a_p^\dagger a_q | \Psi^I \rangle = \sum_{pq} A_{pq} \gamma^F_{pq} = \text{Tr}[\gamma^F A]$$

(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) of the 1PTDM,

$$\gamma = V \Sigma U^\dagger$$

(4)

where $\Sigma$ is the diagonal matrix of the singular values $\sigma_k$ and $V$ and $U$ contain the pairs of singular vectors $\psi_k^F$ and $\psi_k^I$, which are called hole and particle NTOs. On 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:

$$\langle \Psi^F | \hat{A} | \Psi^I \rangle = \text{Tr}[\gamma A] = \sum_k \langle \psi_k^F | \hat{A} | \psi_k^I \rangle \sigma_k$$

(5)

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

Unlike Hermitian theories in which $\gamma^F$ and $\gamma^I$ are Hermitian conjugates of each other, in EOM-CC they are not, giving rise to slightly different values of the $A_{FI}$ and $A_{IF}$ matrix elements. Consequently, state and transition properties are computed as averages. However, the deviations from the Hermitian behavior are small and the NTOs derived from $\gamma^F$ and $\gamma^I$ are nearly indistinguishable, so that we can use only one set for the analysis, as in previous studies.

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. Figure 3 shows a flowchart of the computational protocol. Starting from a zero-order nonrelativistic 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- and field-corrected eigenstates and their energies are then computed by diagonalizing the matrix representation of the resulting perturbed Hamiltonian ($H = H^0 + H^{SO} + H^{Z}$) in the basis of zero-order nonrelativistic eigenfunctions ($\Psi^I_{SM}$):}

$$\langle \Psi^F | \hat{A} | \Psi^I \rangle = \text{Tr}[\gamma A] = \sum_k \langle \psi_k^F | \hat{A} | \psi_k^I \rangle \sigma_k$$

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The rising and lowering operators, \( S_+ \) and \( S_- \), respectively. For a spherical one (e.g., the magnetic moment operator), it is useful to introduce the orbital momentum operator computed between many-body correlated wave functions. The matrix elements of the spin–orbit operator \( \gamma_{pq} \) are obtained from the Breit-Pauli spin–orbit Hamiltonian, by solving the Schrödinger equation with an added spin–orbit potential. The evaluation of matrix elements of the Zeeman operator, \( \mathbf{H} \), acting on the spinless TDM (denoted by \( \rho_{pq} \)), is given by

\[
\langle \Psi_{\downarrow} | \mathbf{H} | \Psi_{\uparrow} \rangle = \sum_{pq} \rho_{pq} \gamma_{pq},
\]

where \( \gamma_{pq} \) is the IPDTM (see eq 2), \( \rho_{pq} \) is the density matrix of the reference determinant (usually, the Hartree–Fock determinant), and \( I_{pq} \) and \( J_{pq} \) are the one- and two-electron spin–orbit integrals, respectively. Full details for calculating these spin–orbit integrals can be found in ref 39. As one can see, when the SOMF approximation is applied, the two-particle TDM is not needed, which considerably reduces the cost of evaluating the two-electron contribution to the total SOC. An additional benefit of this approach is that, by applying the Wigner-Eckart theorem, one can compute all requisite SOCs 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 39. The SVD of \( u_{pq} \) yields an analogue of eq \( S \), introducing a new set of spinless NTOs (particle, hole, and \( c_l^0 \)) suitable for the analysis of SOCs and related weights (singular values \( \omega_k \) of the spinless TDM). Within this new basis, spin–orbit reduced matrix elements can be written as
The SVD of the reduced TDM gives only a few matrix elements that are reported in ref 46 are also given in the Supporting Information (SI) for convenience. Consider, \( \langle \psi | H^{\text{SOMF}} | \psi \rangle \), resulting in the basis of real harmonics \( d_{xy} \) for convenience. The nature of the spin–orbit operator is revealed by the form of its one-electron term:

\[
\hat{h}^{\text{so}}(i) = \sum_k Z_k(r_i - R_k) \times p_i = \sum_k Z_k(r_i - R_k) \cdot p_i
\]

where \( r_i \) and \( p_i \) are the coordinate and momentum operators of the \( i \)th electron and \( R_k \) and \( Z_k \) denote the coordinates and the charge of the \( k \)th nucleus. As evident from eq 18, \( \hat{h}^{\text{so}} \) is proportional to the orbital momentum operator \( L \) through the cross products between \( r_i \) and \( p_i \); 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 \( (L_y, L_z) \) can be written in the basis of real harmonics \( Y_{LM} \), where \( L \) and \( M \) are the orbital quantum numbers associated with \( L^2 \) and \( L_z \) operators. In the case of transition-metal ions \( (L = 2) \), \( Y_{2,0} = d_{xy}, Y_{2,-1} = d_{yz}, Y_{2,-2} = d_{zx} \), and \( Y_{2,2} = d_{z^2} \). The resulting matrices, which were reported in ref 46 are also given in the Supporting Information (SI) for convenience. Consider, \( \langle L_z | Y_{2,-2} | Y_{2,-1} \rangle = \delta_{i1} \delta_{ii} \), \( \langle L_z | Y_{2,0} | Y_{2,0} \rangle = \delta_{i1} \delta_{ii} \), \( \langle L_z | Y_{2,1} | Y_{2,1} \rangle = \delta_{i1} \delta_{ii} \), and \( \langle L_z | Y_{2,2} | Y_{2,2} \rangle = \delta_{i1} \delta_{ii} \), providing the conditions for \( (L_z) \) and SOC to be nonzero in terms of orbitals. The \( L_z \) matrix has zero elements on the main diagonal, which means that SOCs between the states that have the same orbital character are small. The off-diagonal elements of \( L_z \) are nonzero, which means that SOCs are large between states that have different orbital orientation. This is the essence of El-Sayed’s rules. \(^{30,36} \) The results can be verified by considering the magnitude of the reduced matrix element of the spin–orbit operator \( H^{\text{SOMF}} \) of eq 17. Its value is large when leading hole and particle NTOs, resembling \( d \)-orbital shapes, have different orientations. \(^{46} \) Similar conclusions can be derived when the electronic transition is allowed through the \( L_z \) and \( L_y \) operators. \(^{46} \) For a free transition-metal ion, the \( L_z \) 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 SOCs 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, \(^{30} \) which was based on a qualitative molecular orbital picture, can be cast in a quantitative fashion within many-body formalism. By using this quantitative analysis, we show that the magnitude of orbital momentum and spin–orbit matrix elements correlates with the height of the spin-reversal energy barrier (see section IVD and also Table S1 in the SI).
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 $\chi_{ij}$, respectively. Alternatively, one can compute these derivatives with respect to the field magnitude, which is useful for powder averaging. Diagonalization of the $\chi$ tensor yields the main susceptibility values ($\chi_{x'}$, $\chi_{y'}$, and $\chi_{z'}$) 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 random 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,

$$F_n = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi F(\theta, \varphi) \sin(\theta) \, d\theta \, d\varphi$$

(26)

can be approximated by a sum of weighted function values,

$$F_n = \sum_{i} \sum_{j} F(\theta_i, \varphi_j) w_{ij}$$

(27)

where the subscript $ij$ indicates that polar angles $\theta$ and $\varphi$ may not be selected independently. We follow the REPULSION integration scheme, which provides a uniform distribution of 150 crystallites (field orientations) over the surface of a unit sphere, leading to an efficient powder averaging. For a pair of $\theta_i$ and $\varphi_j$, the direction of an applied magnetic field is given by the vector components $n_x = \sin(\theta_i) \cos(\varphi_j)$, $n_y = \sin(\theta_i) \sin(\varphi_j)$, and $n_z = \cos(\theta_i)$. From these equations we derive angular-dependent magnetization $M(\theta, \varphi, \phi)$ and susceptibility $\chi(\theta, \phi, \phi')$, which are computed by numerical differentiation of $\ln Z(\theta, \phi, \phi')$ with respect to the field magnitude, as per eqs 24 and 25. Average magnetization and susceptibility are then obtained by substituting $M(\theta, \phi, \phi')$ and $\chi(\theta, \phi, \phi')$ values into eq 27.

III. MODEL SYSTEMS AND COMPUTATIONAL SETUP

To assess the performance of the presented computational protocol, we compute magnetic properties of three Fe-based SMMs (structures are shown in Figure 4) with a 3-fold symmetry, for which reliable experimental and theoretical data exist. There are (1) a trigonal pyramidal [((tpa)Fe(II))]$^-$, (2) a linear and two-coordinate Fe(II)C(SiMe$_3$)$_3$$_2$ and (3) trigonal bipyramidal (PMe$_3$)$_2$Fe(III)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 [((tpa)Fe(II))]$^-$ and Fe(II)C(SiMe$_3$)$_3$, target states (quartet $d^6$ configurations of Fe$^{3+}$) are obtained by attachment of a $\beta$-electron (in red) to the high-spin reference state (hextet $d^5$ configuration of Fe$^{3+}$). For (PMe$_3$)$_2$Fe(III)Cl$_3$, target states (quartet $d^6$ configurations of Fe$^{3+}$) are obtained by single spin-flip excitations from the high-spin hextet reference state of Fe$^{3+}$. Higher electronic states are described in the SI.

Figure 4 summarizes the 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(SiMe$_3$)$_3$, we carried out EOM-EE-MP2 calculations with high-spin $d^5$ hextet references, which affords a balanced treatment of the quintet $d^6$ electronic configurations. For the quartet $d^6$ configurations of (PMe$_3$)$_2$Fe(III)Cl$_3$, we used the EOM-SF-CCSD approach with a $d^5$ high-spin hextet reference. All calculations were performed using the Q-Chem software. For [((tpa)Fe(II))]$^-$, 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 the 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(SiMe$_3$)$_3$, Mössbauer spectra at zero field yielded the temperature dependence of the magnetic relaxation times from which its spin-reversal barrier was extracted in the high-temperature regime.58

![Figure 4](https://example.com/figure4.png)
we used the same structure and followed the same protocol as in ref 39. Calculations on Fe(II)\([\text{C(SiMe}_3\text{)}_2]_2\) and (PMe\(_3\))\(_2\)Fe- (III)Cl\(_2\) were performed using the experimental structures taken from ref 92 and ref 55, respectively. We used Dunning’s cc-pVDZ basis set.\(^{93-95}\) For (PMe\(_3\))\(_2\)Fe(III)Cl\(_2\), EOM-SF-CCSD and SOC calculations were also carried out with the cc-pVTZ basis. Open-shell reference states were computed using unrestricted Hartree–Fock (HF). For these Fe(II) and Fe(III) SMMs, spin-contamination of the reference and EOM-CCSD/MP2 states was small; the corresponding \((S^2)\) 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); hence, in contrast to other cases,\(^{36}\) no special treatment\(^{37}\) to mitigate spin-contamination was necessary. To properly handle the construction of SOMF operators for open-shell references, we follow the procedure described in ref 39. The core electrons were frozen in all EOM calculations. To speed up the calculations, we applied (i) Cholesky decomposition\(^{38}\) with a threshold of \(10^{-2}\) for two-electron integral calculations, (ii) open-shell frozen natural orbital\(^{85}\) truncation of the virtual space with the total population threshold of 99%, and (iii) single precision execution.\(^{39}\)

IV. RESULTS AND DISCUSSION

A. Trigonal Pyramidal \([\text{tptaFe(II)}]^−\) Complex. The family of trigonal pyramidal Fe(II) complexes with different variants of the tpa\(^8\) ligand is the first reported example of mononuclear transition-metal complexes exhibiting slow magnetic relaxation.\(^{15,57}\) We used a simplified model system, that is, \([\text{(tpta)}\text{Fe}]^−\),\(^{39}\) which closely resembles the original \([\text{(tpta)}^8\text{Fe}]^−\) with \(R = \text{tert}-\text{butyl} (\text{Tbu})\) and mesityl (Mes), and compare the results of this work with experiments\(^{15,57}\) and NEVPT2 calculations\(^{27}\) available for both \([\text{(tptaTbu)}\text{Fe}]^−\) and \([\text{(tptaMes)}\text{Fe}]^−\). Susceptibility measurements under a dc magnetic field confirmed the \(S = 2\) ground-state spin of these complexes.\(^{15,57}\) 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-superoimposed upon the Brillouin function, which indicates strong magnetic anisotropy.\(^{15,57}\) Indeed, fitting these magnetization data to a spin Hamiltonian yielded large and negative axial ZFS parameters \(D = -48\) and \(-44 ± 4\) cm\(^{-1}\) for \([\text{tptaTbu})\text{Fe}]^−\) and \([\text{tptaMes})\text{Fe}]^−\), respectively.\(^{39}\) The sign and magnitude of \(D\), together with the spin \(S\), yield a spin-reversal barrier of \(U = 192\) cm\(^{-1}\) for \([\text{tptaTbu})\text{Fe}]^−\) and \(176 ± 16\) cm\(^{-1}\) for \([\text{tptaMes})\text{Fe}]^−\), suggesting the possibility of SMM behavior. Moreover, ac susceptibility measurements in the presence of a small dc field yielded relaxation barriers of \(U_{\text{eff}} = 65\) cm\(^{-1}\) for \([\text{tptaTbu})\text{Fe}]^−\) and \(42\) cm\(^{-1}\)\(^{115,57}\) for \([\text{tptaMes})\text{Fe}]^−\), demonstrating slow magnetic relaxation. In these systems, small geometrical distortions from the 3-fold symmetry lead to tunneling, which explains the much faster spin inversion than would be expected by spin and magnetic anisotropy (i.e., \(U_{\text{eff}} < U = \text{IDS}^2\)). Figure 4 shows electronic configurations of the two lowest (degenerate) quintet states of \([\text{tpta})\text{Fe}]^−\), called states 1 and 2 (see the SI for higher quintet states). These states are nearly-degenerate with a small energy difference of 9 cm\(^{-1}\) due to a small geometric distortion. To reduce the impact of this artifact on the magnitude of the spin–orbit splitting, we followed ref 39 and averaged the energies of states 1 and 2. From the natural orbital occupancies, \(n\), the number of effectively unpaired electrons, \(n_{\text{eff}}\), is computed by Head-Gordon’s formula.\(^{100}\) For the quintet states, \(n_{\text{eff}}\) is exactly 4. \((S^2)\) is between 6.03 and 6.11, showing small spin-contamination. For all transitions between the computed target states, there is only one nonzero singular value \(\omega\) of the spinless transition density matrix, that is, only one hole–particle NTO pair is needed to describe each transition. Figure 5 shows the leading NTO pair of the spinless transition density matrix computed between states 1 and 2.

![Figure 5. Hole and particle NTOs of the spinless density matrix giving rise to SOC within states 1 and 2 of \([\text{tptaFe(II)})]^−\).](image)

As one can see, the transition between the two states can be described as a transition between nearly perfect \(dx_z\) and \(dz^2\) orbitals—this is the reason for unquenched orbital momentum of \((\mathcal{L}_z) \approx ±i\) and large SOC (see also section IVD and Table S1 in the SI).

<table>
<thead>
<tr>
<th>Table 1. Convergence of the Energy Barrier ((U)) (cm(^{-1})) with the Number of Multiplets</th>
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<tbody>
<tr>
<td>no. of states</td>
</tr>
<tr>
<td>2</td>
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<td>5</td>
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<td>(\text{exp}^{a,b})</td>
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<td>(\text{exp}^{a,v})</td>
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<td>(\text{exp}^{a,v})</td>
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\(^{a}\) Energy barrier \((U = \text{IDS}^2)\) from \(D\) parameter and spin \(S\). Effective energy barrier \((U_{\text{eff}})\) from ac susceptibility measurements.\(^{37}\) Reference 57. \(^{b}\) Reference 15.

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 \(M_{\text{av}}\) (numerical averaging). Figure 6 compares the calculated magnetizations for \([\text{tpta})\text{Fe}]^−\) with the results for \([\text{tptaTbu})\text{Fe}]^−\) from the experiment\(^{39}\) and from the NEVPT2
calculations of Neese and co-workers.\textsuperscript{27} Our computed curves agree perfectly with the theoretical curves obtained from the NEVPT2 calculations. The computed average values in this work and in ref \textsuperscript{27} are slightly higher than the experimental ones. At 1.8 K and 7 T, we obtain a saturation value of the magnetization of 2.68 μβ, which is lower than the 4 μβ expected for a spin-only \( S = 2 \) ion, suggesting prominent magnetic anisotropy of this complex. Our calculations also predict a separation between magnetization isofields, as was observed experimentally for both \([(tpa^{Th})Fe]\)\textsuperscript{27} and \([(tpa^{Me})Fe]\)\textsuperscript{33} (Figures S4 and S5 in the SI). We also computed susceptibility main values, that is, \( \chi_{z} \) and \( \chi_{x} - \langle Y_{m} T \rangle \), by diagonalization of the \( \chi \) tensor. The direction of the easy magnetic axis \( Z_{m} \) is found to be collinear with the rotational \( C_{3} \) axis. Powder susceptibilities \( \chi_{av} \) are then computed by numerical averaging. Figure 6 shows the temperature dependence (from 5 to 300 K) of the product of the susceptibility and temperature (\( \chi T \)) under an applied field of 1000 Oe (0.1 T) parallel to the \( z \)-axis. Calculated \( \chi_{z} T \) increases upon cooling and approaches a finite value when \( T \) approaches zero. \( \chi_{x} T \) and \( \chi_{y} T \), 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 \( \chi_{z} T \) is 3.48 cm\(^3\) K/mol, which is in between the saturation values for \([(tpa^{Th})Fe]\)\textsuperscript{27} (3.55 cm\(^3\) K/mol)\textsuperscript{35} and \([(tpa^{Me})Fe]\)\textsuperscript{33} (3.32 cm\(^3\) K/mol)\textsuperscript{15} and close to the expected value of 3 cm\(^3\) K/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 magnetic properties (Figure S8 in the SI).

B. Two-Coordinate and Linear Fe(II)[C(SiMe\(_3\))]\(_2\) Complex. We consider a two-coordinate and linear Fe(II) complex, Fe(II)[C(SiMe\(_3\))]\(_2\), which was shown to exhibit slow magnetic relaxation with an effective energy barrier of \( U_{\text{eff}} = 146 \text{ cm}^{-1} \), which is the highest value reported to date for Fe(II) complexes.\textsuperscript{24} This strong magnetic anisotropy was ascribed to the unquenched orbital momentum of the ground state of Fe(II)[C(SiMe\(_3\))]\(_2\), about twice as large as that of \([(tpa^{Me})Fe]\)\textsuperscript{27} (see discussion in Section IVD 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.\textsuperscript{54} This is expected for systems with more substantial orbital angular momentum, whose magnetic behavior cannot be rationalized by conventional spin-only models.\textsuperscript{201} Furthermore, high-temperature Mössbauer spectra at zero field yielded a barrier height of \( U_{\text{eff}} = 178 \pm 9 \text{ cm}^{-1} \), somewhat larger than the value of 146 cm\(^{-1}\) determined by ac-susceptibilities at nonzero dc field,\textsuperscript{54} but closer to the ab initio value of 196 cm\(^{-1}\) derived by Neese and co-workers from NEVPT2 calculations.\textsuperscript{28} We follow the same strategy as in ref S9, in which the spin-reversal barrier was found to correspond to the energy separation between the ground and the lowest excited states, assuming that relaxation occurs by a combination of the Orbach mechanism\textsuperscript{34} and quantum tunneling from the first excited state.

Figure 4 shows electronic configurations of the doubly degenerate ground state of Fe(II)[C(SiMe\(_3\))]\(_2\), called states 1 and 2 (see the SI for a description of additional quintet states). Due to symmetry lowering from \( D_{\text{oh}} \) to \( C_{3v} \), we observe energy splitting between states 1 and 2 of 195 cm\(^{-1}\), as also reported by Neese and co-workers.\textsuperscript{59} For these states, spin contamination is negligible (\( n_{\text{sd}} \approx 4 \) and \( \langle S^{2} \rangle = 6.03–6.06 \)). A single hole–particle NTO pair (Figure 7) fully describes the transition between states 1 and 2. This transition involves \( d_{x^{2}−r^{2}} \) and \( d_{xy} \) orbitals, leading to the largest orbital momentum of \( (L_{y}) \approx ±2i \) for the Fe systems under study, and therefore, to the largest SOC (Section IVD and Table S1 in the SI).

Diagonalization of the SOC-augmented Hamiltonian (i.e., \( H^{\text{SOC}} + H^{\text{SO}} \)) for states 1 and 2 yields the splitting of the ground state into 10 spin–orbit sublevels, as shown in Figure 1. The 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 mixing with higher states through SOC. 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\textsuperscript{58} and

Figure 6. (a) Calculated field-dependent magnetizations of \([(tpa)Fe(II)]^{−} \) at low temperature (\( T = 1.8 \text{ K} \)). Magnetization is in Bohr magneton (\( \mu_{\beta} \)) units. Color code: this work (EOM-EA-MP2), black curves; ref \textsuperscript{27} (NEVPT2) for \([(tpa^{Th})Fe]^{−} \), yellow, green, and blue curves; experiment of ref \textsuperscript{57} for \([(tpa^{Me})Fe]^{−} \), red curves. (b) Calculated \( \chi_{x} T, \chi_{y} T (\langle X_{m} T \rangle \), and \( \chi_{y} T \) of \([(tpa)Fe(II)]^{−} \) in the temperature range from 5 to 300 K and under an applied field of 1000 Oe (0.1 T). Experimental susceptibility data for \([(tpa^{Th})Fe(II)]^{−} \) (red curve) and \([(tpa^{Me})Fe(II)]^{−} \) (black curve) are taken from ref \textsuperscript{57} and ref 15, respectively. “av” stands for isotropic powder averaging.
ac-susceptibility\textsuperscript{54} experiments, and also with similarly derived energy difference from the NEVPT2 energy levels\textsuperscript{59} (Table 2). In contrast to \{(tpa)Fe(II)\}\textsuperscript{−}, we note that the spin-reversal energy barrier for Fe(II)[C(SiMe\textsubscript{3})\textsubscript{3}]\textsubscript{2} is not sensitive to the number of multiplets included in the SOC calculation. This can be ascribed to the smaller SOCs of states 1 and 2 with state 3 than the corresponding ones computed for the trigonal pyramidal Fe(II) complex.

Figures 8 and 9 show temperature- and field-dependent magnetizations (\(M \text{ vs } H/T\)) and susceptibilities (\(\chi \text{ vs } T\)). Our calculated curves are in excellent agreement with the experiment\textsuperscript{54} and with the curves obtained from the NEVPT2 calculations by Neese and co-workers\textsuperscript{59}. From the experiments at 1.8 K and 7 T,\textsuperscript{54} the saturation magnetization is 3.24 \(\mu_B\), which is close to our computed value of 3.04 \(\mu_B\), but is much lower than the expected value (4 \(\mu_B\)) for spin-only magnetic behavior. Both the experiment and our calculations find separation between isofield curves of the magnetization (Figure S6 in the SI), which is also indicative of strong magnetic anisotropy. At 300 K, the computed \(\chi_{\text{av,T}}\) is 4.59 cm\textsuperscript{3}·K/mol, which agrees well with both the experimental (4.78 cm\textsuperscript{3}·K/mol)\textsuperscript{55} and NEVPT2 (4.82 cm\textsuperscript{3}·K/mol)\textsuperscript{59} results, but is by far exceeding the spin-only \(\chi T\) value of 3 cm\textsuperscript{3}·K/mol expected for an \(S = 2\) ion. Such larger \(\chi T\) value is typical of transition-metal complexes with a sizable contribution of orbital momentum to their magnetic behavior. Finally, we observe that neither energy barriers nor magnetic properties are influenced by the number of multiplets (2 or 3) taken into account (Table 2 and Figure S1 in the SI).

C. Trigonal Bipyramidal (PMe\textsubscript{3})\textsubscript{2}Fe(III)Cl\textsubscript{3} Complex.

We compute magnetic properties of a mononuclear \(S = 3/2\) Fe(III) complex, (PMe\textsubscript{3})\textsubscript{2}Fe(III)Cl\textsubscript{3}, the 3-fold symmetry of which is the key to designing Fe(III) SMMs with large magnetic anisotropy.\textsuperscript{55} Magnetization measurements revealed a large and negative value of the axial ZFS parameter \(D = -50\) cm\textsuperscript{-1}.\textsuperscript{55} Moreover, ac-susceptibility experiments observed slow magnetic relaxation under the presence of a small applied dc field with an effective energy barrier of \(U_{\text{eff}} = 81\) cm\textsuperscript{-1}, which is the highest relaxation barrier yet observed for a mononuclear Fe(III) SMM.\textsuperscript{55}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
no. of states & \(U_{\text{eff}}\) (cm\textsuperscript{-1}) \\
\hline
2\textsuperscript{a} & 160 \\
3\textsuperscript{a} & 161 \\
exp.\textsuperscript{b,c} & 146 \\
exp.\textsuperscript{d} & 178 \pm 9 \\
NEVPT2\textsuperscript{f} & 196 \\
\hline
\end{tabular}
\caption{Convergence of the Energy Barrier \(U\) (cm\textsuperscript{-1}) with the Number of Multiplets}
\end{table}

\textsuperscript{a}Energy barrier computed as energy difference between the ground and the first excited states. \textsuperscript{b}Effective energy barrier (\(U_{\text{eff}}\)) from ac susceptibility measurements. \textsuperscript{c}Reference 54. \textsuperscript{d}Effective energy barrier (\(U_{\text{eff}}\)) from Mössbauer spectroscopy. \textsuperscript{e}Reference 58. \textsuperscript{f}Reference 59.
transition between states 1 and 2 involve nearly perfect eight sublevels are about 2000 cm\(^{-1}\). These (doubly degenerate) sublevels (Figure 11). These

Because of the SOC, the ground-state multiplet splits into eight (doubly degenerate) sublevels (Figure 11). These first

splitting of the quartet ground state of \((\text{PMe}_3)_2\text{Fe(III)}\text{Cl}_3\) yielding a non-zero orbital momentum of \(\langle L_z \rangle \approx \pm 1\) and a large SOC (section IVD and Table S1 in the SI).

Because of the SOC, the ground-state multiplet splits into eight (doubly degenerate) sublevels (Figure 11). These first

\[ D = -50 \text{ cm}^{-1} \] (Table 3). The discrepancy between the experimentally derived \(U_{\text{eff}}\) and the computed value might reflect the effect of tunneling, which is neglected in the present theoretical treatment.

Table 3. Convergence of the Energy Barrier \(U\) (in cm\(^{-1}\)) with the Number of Multiplets

<table>
<thead>
<tr>
<th>no. of states</th>
<th>(U)</th>
<th>(U_{\text{eff}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>103</td>
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<tr>
<td>3</td>
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</tr>
<tr>
<td>5</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>exp.(^{ab})</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

\(^{ab}\) Energy barrier \((U = D(S^2 - 1/4))\) from experimental \(D\) parameter and \(S\) spin. Effective energy barriers \((U_{\text{eff}})\) from ac susceptibility measurements. \(^{c}\) Reference 55.

We computed temperature- and field-dependent magnetizations (panel a of Figure 12) and susceptibilities (panel b of Figure 12) using the lowest 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 55, 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. Figure 13 illustrates isofield magnetization curves that are obtained for a fixed field \((\text{HI from 1 to 7 T})\) by varying the temperature (from 2 to 20 K). Both experimental (black curves) and calculated data of this work exhibit separation between these curves, indicative of magnetic anisotropy. Moreover, computed \(\chi_{\text{eff}} T\) values (green curve in panel b of Figure 12) agree reasonably well with the experiment (black curve in panel b of Figure 12). At 300 K, the calculated \(\chi_{\text{eff}} T\) is 1.91 cm\(^3\)-K/mol, while the experiment yields 2.29 cm\(^3\)-K/mol, confirming a \(S = 3/2\) spin ground state of the system (for \(S = 3/2\), \(T = 1.876\) cm\(^3\)-K/mol). We also investigated the convergence of the magnetization and susceptibility data with respect to the number of states and verified that results already converge by including the two lowest multiplets only (Figure S10 in the SI). Finally, we determined that using a larger basis set, that is, cc-pVTZ, has a very small effect on the energy barrier \(U\) and on the computed magnetization and susceptibility data (deviations are about 10 cm\(^{-1}\) for \(U\) and within 1% for the average magnetization and susceptibility, see Figure S11 and Table S5 in the SI). This almost negligible dependence on the size of the basis set is in line with the previous results for bicopper compounds and copper oxalate chains.\(^{S,102}\)

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, following the approach of ref 46. According to El-Sayed’s rules,\(^{48}\) 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 only one NTO pair contributes to the electronic transition. Matrix elements of \(L_z\) are then computed via the density matrix formalism presented in section IIB. 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 we
1.94 0.00

\[ H \equiv C_3 \]

\[ H \perp C_3 \]

\[ L_z \]

\[ M_{\text{av}} \]

\[ M_L \]

\[ \nu \]

\[ \langle L_z \rangle \]

\[ \{1\} \begin{pmatrix} 0.01i \\ 1.94i \end{pmatrix} \]

\[ \{2\} \begin{pmatrix} -1.94i \\ 0.01i \end{pmatrix} \]

\[ M_L = \begin{pmatrix} 1.94 & 0.00 \\ 0.00 & -1.94 \end{pmatrix} \]

\[ \nu = \begin{pmatrix} 0.71i & -0.71i \\ 0.71 & 0.71 \end{pmatrix} \]

Figure 12. (a) Calculated field-dependent magnetizations of (PMe$_3$)$_2$Fe(III)Cl$_3$ at low temperature (\( T = 1.8 \) K). Experimental curves are not available. (b) Calculated \( x_{H}, T, x_{X}, T \) and \( x_{M}, T \) of (PMe$_3$)$_2$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 55. 

“av” stands for isotropic powder averaging.

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 \( H^0 + HH^0 + H^2 \) is constructed and diagonalized in the basis of nonrelativistic EOM-CC states, using a previously reported implementation. Direct comparison with experiments is made possible by the numerical averaging of the computed properties over a large and uniform set of field orientations. The calculations accurately reproduce macroscopic magnetic properties, that is, temperature dependence of the susceptibility in the form \( \chi T \) versus \( T \), and low-temperature magnetization under various applied dc fields. The results are also in excellent agreement with previous theoretical work using NEVPT2. This indicates that the electronic structure of the mononuclear Fe(II) and Fe(III) 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 NTO pair 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 based on a molecular orbital picture on quantitative footing.
susceptibility $\chi_{av}T$ curves, which are indicative of anisotropic magnetic behavior. Moreover, our work demonstrates, 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, the doubly degenerate ground state of Fe(II)$[\text{C(SiMe}_3\text{)}_3]$$_2$, the transition of which between states 1 and 2 involves just one NTO pair of the $d_{z^2}^2/d_{xy}$ type, displays the largest orbital projection of $M_l \approx \pm 2\mu_B$ and thus the largest SOC, followed by complexes [(tpa)Fe(II)$]^{-}$ and (PMe$_3$)$_2$Fe(III)$\text{Cl}_3$ in which the leading NTO pair is of the $d_{xz}/d_{yz}$ type and the computed orbital projection is only about $\pm 1$. Thus, this trend in orbital
momentum and SOC magnitude is in accordance with that expected from both molecular orbital theory and El-Sayed’s rules for a system with an odd number of electrons in nearly degenerate d-orbitals of different orientation. Furthermore, Fe(II)[C(SiMe3)3]2 exhibits a susceptibility value at room temperature of $\chi_s T = 4.59 \text{ cm}^3/\text{K mol}$, which significantly deviates from the expected value of 3 cm$^3$/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 magnetic contribution to the ground-state magnetic behavior of Fe(II)[C(SiMe3)3]2, which is at the origin of its strong magnetic anisotropy. In contrast, complexes [(tpa)Fe(II)]$^+$ and (PMe$_3$)$_2$Fe(III)Cl$_3$, for which the orbital momentum contributions are smaller than the one computed for Fe(II)[C(SiMe3)3]2, display $\chi_s T$ 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 the Arrhenius plots. Our ab initio calculations showed that the linear and two-coordinate Fe(II)[C(SiMe3)3]2 has the largest SOC and the strongest magnetic anisotropy, and also shows the highest effective energy barrier of $U_{\text{eff}} = 146 \text{ cm}^{-1}$ to be compared with much smaller values of 42 and 81 cm$^{-1}$54 for [(tpa)Fe(II)]$^+$ and (PMe$_3$)$_2$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 EOM-CC methods to describe magnetic behavior of transition metal complexes, providing an alternative to traditional multireference calculations. Future research will focus on extending the methodology to other electronic structure patterns (e.g., d$^2$ and d$^5$) 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. The presented methodology is general enough to be applied together with SF-TDDFT and restricted active space CI (RASCI), and it can be extended to the study of other SMMs with multiple magnetic centers by additional treatment of exchange interactions, which makes it a useful postprocessing tool for tuning magnetic behavior of different types of transition-metal complexes.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.1c00430.

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; basis-set effects; relevant Cartesian coordinates (PDF)

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**Notes**

The authors declare the following competing financial interest(s): A.I.K. is the president and a part-owner of Q-Chem, Inc.

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(8) de Graaf, C.; Broer, R. Magnetic interactions in molecules and solids; Springer, 2016.
(10) The presence of an external potential, such as the ligand field in a transition-metal complex, removes the orbital degeneracy. When this occurs, the resulting angular momentum of the $\Gamma^{2S+1} \Lambda$ ground state is zero. This means that all the matrix elements $\langle \Psi_{\Lambda^i\Lambda^j}\rangle$ are zero, for which $\Psi$ is the wave function describing the ground state. This effect is called quenching of the orbital momentum. The general condition for $L_z$ to be zero is that the direct product $\Gamma \times \Gamma$ does not contain the irreducible representation of the orbital momentum operators $L_{x,y,z}$ (rotation operators $R_{x,y,z}$). This condition is fulfilled in the absence of orbital degeneracy, as first described in the crystal field theory by Van Vleck (1932). In contrast, when the orbital momentum is not quenched or is only partially quenched, it couples with the spin, contributing to the magnetic anisotropy of the ground state.


The ezMagnet module collects a set of postprocessing tools for the extraction of spin-Hamiltonian parameters from EOM-CC energies/eigenstates and calculation of macroscopic magnetic properties.


