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Ab initio calculation of anisotropic magnetic properties of complexes. I. Unique definition of pseudospin Hamiltonians and their derivation

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A methodology for the rigorous nonperturbative derivation of magnetic pseudospin Hamiltonians of mononuclear complexes and fragments based on *ab initio* calculations of their electronic structure is described. It is supposed that the spin-orbit coupling and other relativistic effects are already taken fully into account at the stage of quantum chemistry calculations of complexes. The methodology is based on the establishment of the correspondence between the *ab initio* wave functions of the chosen manifold of multielectronic states and the pseudospin eigenfunctions, which allows to define the pseudospin Hamiltonians in the unique way. Working expressions are derived for the pseudospin Zeeman and zero-field splitting Hamiltonian corresponding to arbitrary pseudospins. The proposed calculation methodology, already implemented in the SINGLE_ANISO module of the MOLCAS-7.6 quantum chemistry package, is applied for a first-principles evaluation of pseudospin Hamiltonians of several complexes exhibiting weak, moderate, and very strong spin-orbit coupling effects. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4739763]

I. INTRODUCTION

Molecular magnetic complexes and materials exhibiting strong magnetic anisotropy attracted wide attention in the last two decades due to new fundamental properties and potential applications.[1] The magnetic anisotropy of the complexes arises from the interplay of spin-orbit coupling at the metal ion and the ligand (crystal) field of its environment,[2] and is manifested in two basic interactions, the Zeeman and the zero-field splitting (ZFS) interactions within a relevant manifold of lowest electronic states.[2] The first interaction defines the splitting of a group of degenerate energy levels in applied magnetic field as function of its direction. The second interaction is responsible for the splitting of the chosen group of energy levels, e.g., corresponding to the manifold of $2S + 1$ states of the ground term S of the complex, in the absence of applied magnetic field. Both these interactions are generally described by effective spin or *pseudospin* ($\tilde{S}$) Hamiltonians acting in the space of the corresponding manifold of $2\tilde{S} + 1$ states.[2] The parameters of these pseudospin Hamiltonians are the Zeeman-splitting and zero-field splitting tensors, respectively. Knowledge of these tensors determine completely the anisotropic properties of paramagnetic complexes,[2–4] such as the EPR spectrum.[5]

The pseudospin Hamiltonians have been introduced phenomenologically by Pryce and Abragam in the beginning of 1950s (Refs. 6 and 7) to describe the splitting of spin multiplets in complexes and since then were widely employed.[8–13] At the early stage, when the theory was not able to provide the parameters of pseudospin Hamiltonians with sufficient accuracy, the latter were efficiently constructed as invariants of given symmetry groups of the complexes[14–19] (see, e.g., Ref. 20 for a review). Indeed, written in a coordinate system related to the symmetry axes of the complex they involve a minimal number of parameters which can in principle be extracted from experiment. To this end, the eigenvalues of pseudospin Hamiltonians are fitted to the observed transition energies, while their eigenfunctions are used to simulate the experimental probabilities of transitions between different energy levels.[2,20] Experimentally, the parameters of the spin Hamiltonians are most often extracted from EPR spectroscopy.[2,3,20]

Recently, the increased power of quantum chemistry methods made the accurate determination of these parameters feasible. Thus it became possible to determine the Zeeman-splitting g tensor by density functional (DFT) calculations either perturbatively[21] or straightforwardly from discrete Fourier transform,[22] Dirac-Fock (four-component)[23,24] and explicitly correlated *ab initio* calculations.[25,26] The parameters of the zero-field splitting D tensor have been extracted from DFT calculations via a direct perturbative approach,[27] by analysing the second-order spin-orbit coupling contributions to the magnetic anisotropy energy,[28,29] via a DFT-based ligand field model,[30] and from explicitly correlated *ab initio* calculations by analysing the zero-field splitting of spin levels.[31–34]

Concerning the quantum chemistry calculations of magnetic properties of complexes one should distinguish two aspects of the problem. The first is related to the calculation of physical quantities themselves, such as magnetization or magnetic susceptibility, which poses no fundamental problems since these are just expectation values for the calculated eigenstates. Thus including the spin-orbit coupling and the magnetic field in the calculations we can obtain the magnetic properties of the complex via matrix elements of magnetic moments operators on the ground and excited states for explicitly correlated methods or as the ground state properties (magnetization, anisotropy energy) in DFT. The second aspect is related to the derivation of the parameters of pseudospin Hamiltonians from quantum chemistry calculations. For this purpose, we should first *put into one-to-one correspondence* the *ab initio* calculated multielectronic wave functions to the eigenfunctions of the pseudospin operators entering the pseudospin Hamiltonian. This condition is tacitly considered fulfilled in the theoretical approaches mentioned above (except for Refs. 25 and 26). This is approximately the case for relatively weak spin-orbit coupling effects, when the pseudospin entering the magnetic Hamiltonians can be associated in a good approximation to the true spin of the complex. However, in the case of strong spin-orbit coupling effects, when the lowest electronic states of the complex are described by the pseudospin rather than the true spin (or true total angular momentum), finding such a correspondence is a nontrivial task which has not been considered yet.

In this paper, we describe a general methodology for the rigorous, nonperturbative derivation of magnetic pseudospin Hamiltonians of mononuclear complexes and fragments based on explicitly correlated (multiconfiguration) *ab initio* calculations of their electronic structure. It is supposed that the spin-orbit coupling and other relativistic effects are already taken fully into account at the stage of quantum chemistry calculations of complexes. The methodology is based on the establishment of the correspondence between the *ab initio* wave functions of the chosen manifold of multielectronic states and the pseudospin eigenfunctions, which allows to define the pseudospin Hamiltonians *in a unique way*. Working expressions are derived for the pseudospin Zeeman and zero-field splitting Hamiltonians corresponding to arbitrary pseudospins. This calculation methodology has been developed and applied several years ago[35–38] and recently implemented as a separate module SINGLE_ANISO in the MOLCAS-7.6 quantum chemistry package,[39] however, the theoretical grounds behind it are described here for the first time. We illustrate this methodology by applying it for a first-principles derivation of pseudospin Hamiltonians of several complexes exhibiting weak, moderate, and very strong spin-orbit coupling effects.

Finally, we note that in the established terminology the term “spin Hamiltonian” is often used for both isotropic and anisotropic magnetic complexes, which appears misleading in many situations. As explained in the book of Abragam and Bleaney (Sec. 3.1 in Ref. 2) the symbol S for pseudospin and the term “spin Hamiltonian” are still often used because the pseudospin Hamiltonian description was initially applied to cases where the pseudospin $\tilde{S}$ was the same as the true electronic spin S of the complex. In order to avoid confusion, we will always use the term “pseudospin Hamiltonian” when the latter is expressed via pseudospin operators.

II. PSEUDOSPIN HAMILTONIANS OF MONONUCLEAR COMPLEXES FROM *AB INITIO* CALCULATIONS

The increased power of *ab initio* methods underlined an important progress manifested in two aspects. First, they allow nowadays to treat large complexes (with more than a hundred atoms) fully *ab initio*. Second, these methods provide accurate solutions for multielectronic eigenstates which often allows to make predictions of different properties of the complexes with an experimental accuracy. A representative quantum chemistry software is the MOLCAS package.[39] Recently, a combination of the scalar-relativistic Douglas-Kroll-Hess Hamiltonian[40,41] with an efficient treatment of spin-orbit coupling via the atomic mean-field integral method[42] has been implemented in this package. In combination with explicitly correlated multiconfiguration description of the multielectronic wave functions this approach generally provides very good solutions for molecular spin-orbit multiplets. The latter can be used in principle for the calculation of magnetic properties of different complexes. Indeed, since these properties are simply a response to a Zeeman interaction induced by an applied homogeneous magnetic field **B**, in order to evaluate them we only need to know the matrix elements of the operator of total magnetic moment of the complex,

$$\hat{\boldsymbol{\mu}} = -\mu_{\mathrm{B}}(g_e\hat{\mathbf{S}} + \hat{\mathbf{L}}), \tag{1}$$

calculated in the basis of multiplet eigenstates. In (1) $g_e = 2.0023$ is the free spin g factor, μ_{B} is the Bohr magneton, $\hat{\mathbf{S}}$ is the operator of the total spin momentum,

$$\hat{\mathbf{S}} = \sum_{i=1}^{N_{\mathrm{el}}} \hat{\mathbf{s}}_i, \tag{2}$$

and $\hat{\mathbf{L}}$ is the operator of the total orbitals momentum,

$$\hat{\mathbf{L}} = \sum_{i=1}^{N_{\mathrm{el}}} \hat{\mathbf{l}}_i. \tag{3}$$

The summation in Eqs. (2) and (3) runs over all electrons of the complex. With Eq. (1), the Zeeman interaction of the complex with homogeneous magnetic field has the form,[2]

$$\hat{\mathrm{H}}_{\mathrm{Zee}} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B}. \tag{4}$$

A. Unique definition of pseudospin Hamiltonians

In the absence of spin-orbit coupling the electronic states of the complex are characterized by the total spin S and are called molecular terms. Each molecular term is degenerate after the spin projection M on some chosen axis, $M = -S, -S + 1, \ldots S$. The Zeeman Hamiltonian of this term in the absence of an additional orbital degeneracy, which is usually the case, is described by the Zeeman Hamiltonian (4) with the magnetic moment,[2]

$$\hat{\boldsymbol{\mu}} = -\mu_{\mathrm{B}} g_e \hat{\mathbf{S}}, \tag{5}$$

which is isotropic, i.e., of invariant form in any coordinate system, and therefore leads to an isotropic Zeeman splitting. Accordingly, all magnetic properties will be also isotropic.

In the presence of spin-orbit coupling two main effects arise. First, the degeneracy of the ground state spin is removed for $S > 1/2$, even in the absence of an external magnetic field,[2] resulting in a ZFS of the molecular term. In the case of relatively weak spin-orbit coupling the zero-field splitting can be described in the second order perturbation theory after spin-orbit coupling leading to the following ZFS Hamiltonian in the crystal field approximation:[2,43]

$$\mathrm{H}_{\mathrm{ZFS}} = \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}, \tag{6}$$

where **D** is a 3 × 3 symmetric traceless matrix called ZFS (or *D*) tensor. Second, the operator of magnetic momentum is not of the form (5) anymore but still can be expressed in the lowest order of perturbation theory within the crystal field approximation via the operators of the total spin, the same for the Zeeman Hamiltonian,[2]

$$\begin{aligned} \boldsymbol{\mu} &= -\mu_B \mathbf{g} \cdot \hat{\mathbf{S}}, \\ \mathrm{H}_{\mathrm{Zee}} &= -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_{\mathrm{B}} \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{S}}, \end{aligned} \tag{7}$$

where **g** is a 3 × 3 Zeeman-splitting symmetric matrix (or *g* tensor). The Hamiltonians (6) and (7) are called *spin* Hamiltonians since they are expressed via the operators of true spin S of the corresponding molecular term. They contain all information about the magnetic properties of this term, i.e., are the physical characteristics of the complex. The final goal of rationalization of experimental magnetic data of a complex is the derivation of the parameters (elements of the matrices **D** and **g**) of these Hamiltonians. Going beyond the crystal field approximation, the same lowest order of perturbation theory after spin-orbit coupling will keep the form of ZFS Hamiltonian (6) unchanged[27] but will make the matrix **g** in Eqs. (7) generally non-symmetric.[44] While in this case the ZFS and Zeeman Hamiltonians still remain spin Hamiltonians, the second one does not have anymore a form used to rationalize EPR and other magnetic data because it cannot be brought to diagonal form (see below).

If the spin-orbit coupling on the metal site is comparable with or larger than the separation between the ligand-field terms of the complex, it cannot be accounted for by several lowest orders of perturbation theory (more generally, the perturbation theory with respect to this interaction does not converge). As a consequence, we cannot use the true total spin eigenstates as a model space for the construction of ZFS and Zeeman spin Hamiltonians of the complex, contrary to Eqs. (6) and (7). Also the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$, cannot be used for the construction of J-spin Hamiltonians if a restricted manifold of crystal-field states, not covering the model space of all its $2J + 1$ eigenstates is considered. In all such cases the Zeeman and ZFS Hamiltonians are formulated in terms of *pseudospins* $\tilde{\mathbf{S}}$ which are abstract operators acting in the space of $N = 2\tilde{S} + 1$ lowest (or any chosen) spin-orbit states Ψ_i, $i = 1, \ldots, N$ of the complex.[2,20] The last equation defines the dimension of pseudospin. For instance, the Kramers doublet corresponds to a pseudospin $\tilde{S} = 1/2$.

The pseudospin description is based on the decomposition of $N \times N$ matrices of the operators of magnetic moment components ($\hat{\mu}_\alpha$, $\alpha = x, y, z$), of zero-field splitting and of Zeeman interaction into spin matrices $\tilde{\mathrm{S}}_\alpha$, $\alpha = x, y, z$, and their products and powers.[2,20] We emphasize that although the matrices $\tilde{\mathrm{S}}_\alpha$ look precisely as the conventional spin matrices S_α of the corresponding dimension,[45] they are not related to any physical angular momentum. The matrices of time-odd operators such as $\hat{\mu}_\alpha$ and $\hat{\mathrm{H}}_{\mathrm{Zee}}$, which change the sign under time inversion,[2] will contain only odd powers of $\{\tilde{\mathrm{S}}_\alpha\}$ in this decomposition. By contrary, the matrices corresponding to time-even operators ($\mathrm{H}_{\mathrm{ZFS}}$), which are invariant under time inversion, will contain only even powers of $\{\tilde{\mathrm{S}}_\alpha\}$. In the Secs. III–V we will give several examples of such decompositions.

Contrary to true spin operators $\hat{\mathrm{S}}_\alpha$, the pseudospin operators $\tilde{\mathrm{S}}_\alpha$ can only be defined as matrices with respect to the basis functions Ψ_i, $i = 1, \ldots N$ or any their linear combinations. In the pseudospin formalism the latter correspond to the eigenfunctions $|\tilde{S}M\rangle$, $M = -\tilde{S} \cdots \tilde{S}$ of the pseudospin operator $\tilde{\mathrm{S}}_z$. The major complication with the pseudospin description is that we can put in correspondence to pseudospin eigenfunctions any combination of $\{\Psi_i\}$, which means that the pseudospin eigenfunctions are *a priori* undefined in terms of *ab initio* (exact) wave functions of the complex. For comparison, there is no ambiguity in defining a unique set of eigenstates $\{|SM\rangle\}$ of a true spin operator $\hat{\mathrm{S}}_z$ on the corresponding manifold of states. This is the main difference between the true physical operator $\hat{\mathrm{S}}_z$ and the abstract operator $\tilde{\mathrm{S}}_z$. Putting in correspondence different combinations of $\{\Psi_i\}$ to pseudospin eigenfunctions $|\tilde{S}M\rangle$ will result in different pseudospin Hamiltonians (different decompositions of $\hat{\mu}_\alpha$, $\hat{\mathrm{H}}_{\mathrm{Zee}}$, and $\mathrm{H}_{\mathrm{ZFS}}$ into pseudospin matrices and their products), which all will be equivalent in the sense of predictable quantities. However, the real value of spin/pseudospin Hamiltonians is that they serve as physical characteristics of the complexes by concentrating in several parameters all their magnetic properties. To be suitable for such a purpose, these parameters (**g** tensors, **D** tensors, etc.) and the pseudospin Hamiltonian themselves should be *uniquely* defined with respect to a given coordinate system attached to the complex. This requires a unique pseudospin decomposition of relevant operators in a given coordinate system which, at its turn, requires a unique definition of pseudospin operators $\tilde{\mathrm{S}}_\alpha$ in this coordinate system. The latter is equivalent with indicating a unique combination of *ab initio* wave functions $\{\Psi_i\}$ which should be put in correspondence to the eigenfunctions $\{|\tilde{S}M\rangle\}$ of $\tilde{\mathrm{S}}_z$ in a given coordinate system.

The natural constraints which should be imposed on the linear combinations of $\{\Psi_i\}$ to represent pseudospin eigenfunctions $\{|\tilde{S}M\rangle\}$ are the symmetry ones. Thus each linear combination of $\{\Psi_i\}$, which is put in correspondence to a particular pseudospin eigenfunction $|\tilde{S}M\rangle$ should transform under time reversal operation and point group symmetry operations as a corresponding true spin eigenfunction $|SM\rangle$. As we mentioned in the introduction, the transformation properties under space rotations were especially used for phenomenological constructions of pseudospin Hamiltonians.[20] However, these constraints are not sufficient for a unique definition of pseudospins if the symmetry of the complex is not high enough, which is usually the case. In such situations we can complete the assignment of pseudospin eigenfunctions following the principle that the obtained pseudospin Hamiltonian should be equivalent in form with the phenomenological Hamiltonians used for the rationalization of experimental data.[44] According to this principle, our basic requirement is that the part of Zeeman Hamiltonian which is linear in pseudospin operators (described by the g tensor) should acquire a diagonal form when written in a coordinate system related to the main magnetic axes of the complex. The corresponding phenomenological Zeeman Hamiltonians used, e.g., for the description of the EPR data are of the form[2,20]

$$\mathrm{H_{Zee}} = -\hat{\mu}_i B_i, \quad \hat{\mu}_i = -\mu_B g_i \tilde{\mathrm{S}}_i, \tag{8}$$

where the magnetic field B_i is applied along the main magnetic axes, $i = X, Y, Z$. These are specific directions for which the Zeeman splitting (or the corresponding g_i factor) has an extremum value, i.e., a maximum, a minimum, or a saddle point. The spin Hamiltonians in (8) have a diagonal form, with the magnetic moment operators μ_i "parallel" to the pseudospin components $\mathbf{S}_i$ for each of main magnetic axes. These relations allows to define completely the pseudospin operators in this special coordinate system. Indeed, the relation (8) for $i = Z$ shows that the eigenfunctions of $\hat{\mu}_Z$ are automatically eigenfunctions of $\tilde{\mathrm{S}}_Z$. This means that diagonalizing the matrix of the operator $\hat{\mu}_Z$, written in the basis of $\{\Psi_i\}$ (or their arbitrary combinations)[46] will yield a unique set of *ab initio* wave functions which should be put in *one-to-one correspondence* to pseudospin eigenfunctions $\{|\tilde{S}M\rangle\}$, M being the projection of pseudospin on the axis Z. Equations (8) relate the subscripts of pseudospin operators to Cartesian axes of the real space, i.e., fix the pseudospin coordinate system, in which the components $\tilde{\mathrm{S}}_i$ of the pseudospin vector $\tilde{\mathbf{S}}$ are defined, with respect to the real space coordinate system in which μ_i are defined. One can say that although the orientation of pseudospin coordinate system with respect to the real space coordinate system is *a priori* undefined, in the special case (8) these two coordinate systems coincide.

The validity of described general rules for unique definition of pseudospins (and pseudospin Hamiltonians) is proven by recovering the expected form of pseudospin Hamiltonians in the limiting cases of vanishing spin-orbit coupling ($\tilde{\mathbf{S}} \to \mathbf{S}$), vanishing crystal-field splitting of atomic J-multiplets in, e.g., lanthanide complexes ($\tilde{\mathbf{S}} \to \mathbf{J}$) and in complexes with high enough symmetry.[44] Besides, it can be shown that the pseudospins defined according to these rules transform under the rotations of pseudospin coordinate system as true vectors.[44] This means that the parameters of pseudospin Hamiltonians will transform as true tensors under the rotations of common coordinate system (for both $\hat{\boldsymbol{\mu}}$ and $\tilde{\mathbf{S}}$), therefore, these Hamiltonians can be defined for *any* coordinate system in full analogy with true spin Hamiltonians.

B. Explicitly correlated *ab initio* calculations of mononuclear complexes

We consider complexes with arbitrary strength of spin-orbit coupling effects which, generally, should be treated in a non-perturbative way. Therefore, as a starting point we solve a complete electronic Schrödinger equation of the complex with spin-orbit coupling included in the full Hamiltonian $\hat{\mathrm{H}}$,

$$\hat{\mathrm{H}}\Psi_i = E_i \Psi_i, \tag{9}$$

where i is a common index which numerates both different multiplets (levels having different energies) and the degenerate components within one multiplet. The latter can be degenerate either due to high point symmetry of the molecules or in complexes with odd number of electrons, where all multiplets are at least twofold degenerate in virtue of Kramers' theorem.[2]

In practice, we find the solutions Ψ_i in (9) in two steps. First, we find the eigenfunctions of the Hamiltonian without spin-orbit coupling (but with all scalar-relativistic terms included), which are characterized by the total spin S and its projection M. In the MOLCAS package[39] this spin-free wave functions are obtained in the complete active space self-consistent field approach (CASSCF) and are denoted as $\Psi^{\mathrm{CASSCF}}_{rSM}$, where r numerates solutions with the same S (or roots[39]). In the second step, spin-orbit interaction is taken into account within the restricted active space state interaction (RASSI) method, which uses the spin-free multiconfigurational wave functions as input states. This gives the multiplet eigenstates Ψ_i in (9) in the following form:

$$\Psi_i = \sum_{rSM} c^{\mathrm{RASSI}}_{i,rSM} \Psi^{\mathrm{CASSCF}}_{rSM}, \tag{10}$$

where the admixture coefficients $c^{\mathrm{RASSI}}_{i,rSM}$ are obtained via the diagonalization of spin-orbit coupling matrix within RASSI. We would like to emphasize that this approach allows to treat the spin-orbit coupling effects in an essentially exact way, irrespective of the nature of the multielectronic wave functions $\Psi^{\mathrm{CASSCF}}_{rSM}$ which can be, in particular, of strongly multiconfigurational character. This distinguishes the present approach from traditional derivations of magnetic Hamiltonians based on orbitally non-degenerate ground state molecular term and second-order perturbational treatment of spin-orbit coupling. The latter is only valid for complexes with weak spin orbit-coupling effects.

For the description of magnetic properties of complexes we will need the matrix elements of $\hat{\boldsymbol{\mu}}$ between multiplet wave functions, which reduce, according to Eq. (1), to the matrix elements of $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$. These are expressed via the solutions (10) as follows:

$$\begin{aligned}
\langle\Psi_i|\hat{\mathrm{S}}_\alpha|\Psi_j\rangle &= \sum_{rS}\sum_{MM'} \left(c^{\mathrm{RASSI}}_{i,rSM}\right)^* c^{\mathrm{RASSI}}_{j,rSM'} (\hat{\mathrm{S}}_\alpha)_{MM'}, \\
\langle\Psi_i|\hat{\mathrm{L}}_\alpha|\Psi_j\rangle &= \sum_{rr'}\sum_{SM} \left(c^{\mathrm{RASSI}}_{i,rSM}\right)^* c^{\mathrm{RASSI}}_{j,r'SM} \left\langle\Psi^{\mathrm{CASSCF}}_{rSM}\middle|\hat{\mathrm{L}}_\alpha\middle|\Psi^{\mathrm{CASSCF}}_{r'SM}\right\rangle,
\end{aligned} \tag{11}$$

where α denotes the Cartesian components. In the first equation, the matrix elements of the total spin are given by conventional expressions,[45]

$$\begin{aligned}
(\hat{\mathrm{S}}_z)_{MM'} &= M\delta_{MM'}, \\
(\hat{\mathrm{S}}_x)_{MM'} &= \frac{1}{2}\sqrt{(S+M)(S-M+1)}\,\delta_{M',M-1} \\
&\quad + \frac{1}{2}\sqrt{(S-M)(S+M+1)}\,\delta_{M',M+1}, \\
(\hat{\mathrm{S}}_y)_{MM'} &= -\frac{i}{2}\sqrt{(S+M)(S-M+1)}\,\delta_{M',M-1} \\
&\quad + \frac{i}{2}\sqrt{(S-M)(S+M+1)}\,\delta_{M',M+1}.
\end{aligned} \tag{12}$$

In the second equation of (11), the matrix elements $\langle\Psi^{\mathrm{CASSCF}}_{rSM}|\hat{\mathrm{L}}_\alpha|\Psi^{\mathrm{CASSCF}}_{r'SM}\rangle$ do not depend on M and are provided by the output of the MOLCAS calculation.

III. THE PSEUDOSPIN $\tilde{S} = 1/2$

This pseudospin corresponds to a Kramers doublet which, according to the Kramers theorem, is always degenerate in the absence of applied magnetic field,[2] i.e., there is no zero-filed splitting for $\tilde{S} = 1/2$. The quantum chemistry calculations give two wave function components of the Kramers doublet Ψ_1 and Ψ_2 which are always Kramers conjugated up to a common phase, $\hat{\theta}\Psi_1 \equiv \bar{\Psi}_1 = e^{i\varphi}\Psi_2$, where $\hat{\theta}$ is the operator of the time inversion.[2] The $S = 1/2$ eigenfunctions $|SM\rangle$ transform under time inversion as follows: $\hat{\theta}|S1/2\rangle = |S-1/2\rangle$, $\hat{\theta}|S-1/2\rangle = -|S1/2\rangle$. We require that the pseudospin eigenfunctions $|\tilde{S}M\rangle$ obey the same time reversal constraints. This fixes the phase in the relation between $\bar{\Psi}_1$ and Ψ_2 to $\varphi = 0$. Then the allowed unitary transformations of the functions Ψ_1 and Ψ_2 are described by the group SU(2). Since this special unitary group is generated by three independent parameters, the general form of the unitary transformation in this case is isomorphic to the one corresponding to rotations of pseudospin coordinate system. Therefore, we can say that the wave functions Ψ_1 and $\bar{\Psi}_1$ are already the two eigenfunctions of the z-projection of the pseudospin $\tilde{S} = 1/2$ in a pseudospin coordinate system with unknown orientation. As discussed in Sec. II A, in order to relate this coordinate system to the real space coordinate system we should find first the main magnetic axes of the complex, where their axes coincide.

A. Zeeman pseudospin Hamiltonian

Practically, the magnetic axes can be found as follows. We write the matrix of microscopic Zeeman Hamiltonian (4) in an arbitrary basis (Ψ_1, Ψ_2) and diagonalize it for an arbitrary orientation of magnetic field, $\mathbf{B} = (\xi_x, \xi_y, \xi_z)B$, where ξ_α are directional cosines in the real space coordinate system where $\hat{\mu}$ is defined ($\xi_x^2 + \xi_y^2 + \xi_z^2 = 1$). The obtained eigenvalues look as follows:

$$E_{\mathrm{Zee}} = -\lambda B, \quad \lambda_\pm = \pm\left(\sum_{\alpha\beta}\xi_\alpha A_{\alpha\beta}\xi_\beta\right)^{1/2}, \tag{13}$$

where the new tensor $\mathbf{A}$ is defined as

$$A_{\alpha\beta} = -\frac{1}{2}(|\mu_\alpha\mu_\beta| + |\mu_\beta\mu_\alpha|),$$
$$|\mu_\alpha\mu_\beta| \equiv \begin{vmatrix} (\mu_\alpha)_{11} & (\mu_\alpha)_{12} \\ (\mu_\beta)_{21} & (\mu_\beta)_{22} \end{vmatrix}. \tag{14}$$

We can infer from above equations that all elements of this tensor are real, while the diagonal matrix elements are always positive. Besides, both indices in this tensor denote the Cartesian coordinates of the same real space coordinate system, i.e., it is a true tensor. Moreover, each $A_{\alpha\beta}$ is invariant with respect to unitary transformations of the basis set. Indeed, substituting the second equation of (14) into the first one and comparing the result with the trace of the product $\mu_\alpha\mu_\beta$ written in the basis of Ψ_1 and Ψ_2, we conclude

$$A_{\alpha\beta} = \frac{1}{2}\mathrm{Sp}\{\mu_\alpha\mu_\beta\} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(\mu_\alpha)_{ij}(\mu_\beta)_{ji}, \tag{15}$$

where $N = 2$ in the present case. The trace of any operator is known to be invariant with respect to unitary transformations of the basis set,[47] so is $\mathbf{A}$, which is to be expected because this tensor defines the Zeeman splitting of the Kramers doublet, Eq. (13). Via an appropriate rotation of the real space coordinate system,

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \mathbf{R}_r \cdot \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \tag{16}$$

the tensor $\mathbf{A}$ can be diagonalized,

$$\mathbf{R}_r{}^{-1}\mathbf{A}\mathbf{R}_r = \tilde{\mathbf{A}}_{\mathrm{diag}} \equiv \{\tilde{A}_{XX}, \tilde{A}_{YY}, \tilde{A}_{ZZ}\}, \tag{17}$$

which brings the quadratic form under square root in Eq. (13) into $\tilde{A}_{XX}\xi_X^2 + \tilde{A}_{YY}\xi_Y^2 + \tilde{A}_{ZZ}\xi_Z^2$. Mathematically, this transformation renders the equation for a three-dimensional ellipsoid to its main axes, along which the above function has extremal values: a maximum, a minimum, and a saddle point.[48] Since this function defines the Zeeman splitting via Eq. (13), the latter will have extremal values along the axes X, Y, Z too. Therefore, these are the main magnetic axes of the complex.

Remarkably, we were able to derive the orientations of main magnetic axes only using the matrix elements of the magnetic moment components supplied by quantum chemistry. The pseudospin Zeeman Hamiltonian will only include terms linear in pseudospin,

$$\boldsymbol{\mu} = -\mu_B\mathbf{g}\cdot\tilde{\mathbf{S}},$$
$$\mathrm{H}_{\mathrm{Zee}} = \mu_{\mathrm{B}}\mathbf{H}\cdot\mathbf{g}\cdot\tilde{\mathbf{S}}. \tag{18}$$

Indeed, since $\hat{\mu}_\alpha$ are given by 2 × 2 matrices they can be decomposed in the basis of Pauli matrices, σ_0 and σ_β, $\beta = x, y, z$.[47] $\hat{\mu}_\alpha$ is a time-odd operator and therefore traceless, then only the last three matrices can enter its decomposition, which are employed in the form of $s = 1/2$ matrices: $\mathrm{S}_\beta = \frac{1}{2}\sigma_\beta$.[47] Furthermore, the coefficients in this decomposition should be real because S_β are Hermitean matrices. The three real numbers of the decomposition of a given μ_α ($g_{\alpha\beta}$ in Eq. (18)) vary independently under unitary transformations of the basis set $(\Psi_1, \bar{\Psi}_1)$. On the other hand, diagonalizing (18) the eigenvalues of pseudospin Zeeman Hamiltonian can be expressed via $g_{\alpha\beta}$,[2]

$$\lambda_\pm = \pm\frac{\mu_{\mathrm{B}}}{2}\left(\sum_{\alpha\beta}\xi_\alpha G_{\alpha\beta}\xi_\beta\right)^{1/2}, \tag{19}$$

where $G_{\alpha\beta}$ are the components of the Abragam-Bleaney tensor,[2]

$$\mathbf{G} = \mathbf{g}\mathbf{g}^T, \tag{20}$$

where T in the superscript means transponation. According to the definition (20), both indices of $G_{\alpha\beta}$ refer to the same real space coordinate system, therefore $\mathbf{G}$ is a true tensor. Comparing the above equations with Eq. (13) we obtain

$$\frac{\mu_{\mathrm{B}}^2}{4}\mathbf{G} = \mathbf{A}. \tag{21}$$

Equation (21) is equivalent with Gerloch-McMeeking relation.[49] It implies that both $\mathbf{G}$ and $\mathbf{A}$ can be brought simultaneously to the diagonal form by the rotation of the real space coordinate system to the main magnetic axes (16). This yields immediately the expression for the main components of the g tensor,

$$g_i = \pm \frac{2}{\mu_{\mathrm{B}}}\sqrt{\tilde{A}_{ii}}, \quad i = X, Y, Z, \tag{22}$$

where we have in mind that, according to Eq. (15), $\tilde{A}_{ii}$ are always positive. Apart from the sign, the above scheme allows for nonperturbative calculations of the main g factors of a Kramers doublet and has been implemented in two schemes (i) by calculating the matrix elements $(\mu_\alpha)_{ij}$ directly[26] or (ii) by parametrizing first a ligand-field model.[25,50] In both cases the *ab initio* calculations have been done within the SO-RASSI-CASPT2 approach by using the MOLCAS package.[39]

Having found the main values g_i, the whole g tensor in the initial coordinate system can be obtained by an inverse rotation,

$$\mathbf{g} = \mathbf{R}_r \mathbf{g}_{\mathrm{diag}} \mathbf{R}_r^{-1}, \quad \mathbf{g}_{\mathrm{diag}} \equiv \{g_X, g_Y, g_Z\}. \tag{23}$$

We note that the above derivation is completely general, i.e., does not involve any additional conditions like the symmetry of the complex and the strength of spin-orbit coupling. This allowed for an accurate determination of the direction of magnetic axes (16) and the main values of the g tensors (22) for the Kramers doublets of strongly anisotropic complexes containing cobalt and lanthanide metal ions.[36–38] When the symmetry is present, the determination of (part of) magnetic axes can be done straightforwardly. For instance, if the complex is characterized by one single twofold symmetry axis, this will coincide with one of the main magnetic axes. Any additional symmetry operation (higher order of the rotational axis, another rotational axis or mirror plane) will allow to resolve for all three magnetic axes. For instance, in the case of orthorhombic symmetry D_2, the main magnetic axes lie along the three twofold rotational axes, while in the case of C_{2v} symmetry they lie along the twofold axis and in two perpendicular mirror planes, respectively. In complexes with axial symmetry, containing a main rotational axis of third order or higher, the magnetic axes in the perpendicular plane will be degenerate, i.e., characterized by the same g_i factors, because these axes pass into each other under the symmetry rotations around the main rotational axis. Finally, in the case of cubic symmetry all three magnetic axes pass into each other under the symmetry operations, therefore, they are all degenerate, $g_i = g$.

B. The sign of the main values of the *g* tensor

The two signs in (22) formally appear as two possible solutions of the quadratic equation with respect to g_i. The choice of the sign is not a matter of convention,[51] however, it is not trivial and requires additional analysis as discussed elsewhere.[52]

The indeterminacy of the signs of g_i encountered above is related to the fact that knowledge of magnetic axes alone is not sufficient to assign unambiguously the two wave functions Ψ_1 and Ψ_2 to pseudospin eigenfunctions. Indeed, diagonalizing the Zeeman Hamiltonian for a field applied along the main magnetic axis Z we obtain two eigenfunctions Ψ_- and Ψ_+, corresponding to the lowest and highest eigenvalue, respectively, which due to the form of the pseudospin Hamiltonian for this field, $\mathrm{H}_{\mathrm{Zee}} = g_Z \tilde{\mathrm{S}}_Z B_Z$, should be simultaneously eigenfunctions of the pseudospin operator $\tilde{\mathrm{S}}_Z$. However, we do not know how (in what order and with which phases) Ψ_- and Ψ_+ should be assigned to $|\tilde{S}\ \frac{1}{2}\rangle$ and $|\tilde{S} - \frac{1}{2}\rangle$. The time inversion cannot help here because the behaviour of the wave functions under time inversion can be easily reversed by changing their phases. For instance, if we have $\Psi_- = \hat{\theta}\Psi_+$ and $\Psi_+ = -\hat{\theta}\Psi_-$ then for $\Psi'_\pm = i\Psi_\pm$ we will have the opposite behaviour: $\Psi'_- = -\hat{\theta}\Psi'_+$ and $\Psi'_+ = \hat{\theta}\Psi'_-$. Taking $|\tilde{S}\ \frac{1}{2}\rangle = \Psi_-$ and $|\tilde{S} - \frac{1}{2}\rangle = \Psi_+$ with the phases of $\Psi_\pm$ adjusted to obey conventional time-reversal relations for $|S \mp \frac{1}{2}\rangle$,[2] the unitary transformations of these wave two wave functions corresponding to a rotation of pseudospin coordinate system provide several other equivalent solutions. Note that all these solutions should remain eigenfunctions of the same operator $\tilde{\mathrm{S}}_Z$, i.e., be proportional to Ψ_+ and Ψ_-, and the pseudospin axes corresponding to them should remain aligned to the main magnetic axes of the complex. Then the only unitary transformations allowed by these constraints are those induced by rotations of the pseudospin coordinate system which change the directions of some axes in opposite at most. Thus we are left with only three transformations corresponding to π-rotations of the coordinate system around one of its axes, which always reverses the directions of two other axes. We stress that we are speaking about the rotation of pseudospin coordinate system which can thus have four parallel alignments with respect to the real space coordinate system. Each of new alignments corresponds to the change of the sign of two of the g_i factors, so that their product remains unchanged.

The invariance of the sign of $g_X g_Y g_Z$ with respect to redefinition of pseudospin induced by the rotations of the pseudospin coordinate system actually is not accidental because it defines the direction of precession of magnetic moment in magnetic field.[51] The direction of this precession can be probed directly in resonance experiments with circularly polarized radiation (Sec. II, Chap. III in Ref. 2). This was first demonstrated for NpF_6 in experiments using circularly polarized light,[53] where it was found $g_X g_Y g_Z < 0$. The sign of this product was also deduced relative to the sign of the hyperfine coupling,[51] in which way it was also found negative for PaCl_6^{2-}.[54] Later negative product of the g_i factors was found for UF_6^- in different environments by using circularly polarized EPR.[55] In all these examples the investigated complexes were of cubic symmetry, in which case the sign of the product of g_i is equal to the sign of the common g factor. Therefore, in this particular case not only the sign of the product of three g_i factors but also the sign of each of them has a physical meaning.

The "measurability" of the sign of $g_X g_Y g_Z$ also means that it can be extracted directly from quantum chemistry calculations like other observables for the complex. Indeed, the following relation for the main values of the g tensor can be proven:[56]

$$\frac{g_X g_Z}{g_Y} = -\frac{i}{\mu_{\mathrm{B}}}\frac{\mu_X\mu_Z - \mu_Z\mu_X}{\mu_Y}, \tag{24}$$

where μ_I are 2×2 matrices of magnetic moments along the main magnetic axes of the complex, calculated in the basis of *ab initio* multielectronic wave functions of the Kramers doublet, and it is understood that the commutator in the numerator, after performing the matrix multiplications, will give a matrix $\sim i\mu_Y$, so that the whole ratio in the right hand side is a real number. Moreover, it does not matter in what basis of Ψ_1 and Ψ_2 the matrices μ_i are written, the result of the evaluation of the right hand side (including the sign) will be invariant with respect to the used basis set. In practice, we only need to evaluate one off-diagonal matrix element in the numerator and denominator of (24). In the following examples we will see that $g_X g_Y g_Z < 0$ is a usual feature of lanthanide complexes.

If the symmetry of the complex is high enough, also the sign of individual g_I factors can be established, by using the equivalence of the symmetry transformations of the wave functions of the Kramers doublet and of a true spin $S = 1/2$.[52] It was shown that this approach can be extended to a unique definition of the signs of g_I factors in complexes without symmetry by using the principle of adiabatic connection.[52]

TABLE I. Energies of the lowest spin-free states originating from the ^{6}H multiplet and the energies of the lowest Kramers doublets of the $DyZn_3$ complex.

Atomic multiplet	Spin free states	*J* multiplet	Kramers doublets
^{6}H	0.000	$^6H_{\frac{15}{2}}$	0.000
	29.141		41.656
	88.324		75.414
	95.610		217.659
	173.780		273.593
	192.913		298.865
	365.422		343.111
	387.092		391.886
	497.258		
	538.556		
	581.656		

Main values of the *g* tensor in the ground Kramers doublet

g_X	0.105
g_Y	0.255
g_Z	18.148
Sign of $g_X g_Y g_Z$	+

C. Example: *g* tensors of Dy(III) complexes

A good example of pseudospin $\tilde{S} = 1/2$ is, e.g., the ground Kramers doublet of a Dy^{3+} ion in some arbitrary ligand-field environment. The Dy^{3+} ion has the $4f^9$ electronic configuration with the ground state multiplet $^6H_{15/2}$ of multiplicity $2 \times (\frac{15}{2}) + 1 = 16$. In the presence of low symmetry ligand field this multiplet splits into eight Kramers doublets. The ground and excited Kramers doublets are described by pseudospins $\tilde{S} = 1/2$, each defined in the space of corresponding wave functions Ψ_1 and Ψ_2.

As a first example we consider the recently investigated $DyZn_3$ complex (Fig. 1).[57] Due to diamagnetic Zn^{2+} ions, the $DyZn_3$ complex is similar in respect to magnetic properties to a mononuclear Dy complex, because its lowest energy spectrum reflects the lowest energy states on the central Dy^{3+} ion. *Ab initio* calculations using MOLCAS program package[39] were performed for the experimental molecular structure (Fig. 1) in order to determine the low-lying energy states and to investigate the magnetic properties. The details of calculations are presented in the Appendix B 2. Table I shows the lowest calculated energies, the *g* tensor of the lowest Kramers doublet and the sign of the $g_X g_Y g_Z$ product. Figure 1 shows the orientation of the main anisotropy axis *Z* with respect to the molecular frame. On the basis of obtained energy spectrum, the magnetization at low temperature and molar magnetic susceptibility were computed entirely *ab initio* and showed a very good agreement with the experimental magnetic measurements (Fig. 2 in Ref. 57), which proves the high accuracy of the calculated low-lying states and their magnetic moments. Substituting the latter into Eq. (24) gives the sign of the $g_X g_Y g_Z$ product for the ground Kramers doublet of $DyZn_3$, which turns out to be positive. One should mention that the orientation of the main magnetic axis of the $DyZn_3$ complex (dashed red line in Fig. 1(a)) does not lie perpendicularly to the Zn_3 plane, which one could expect at a first glance due to pseudo-trigonal symmetry of $DyZn_3$ complex.

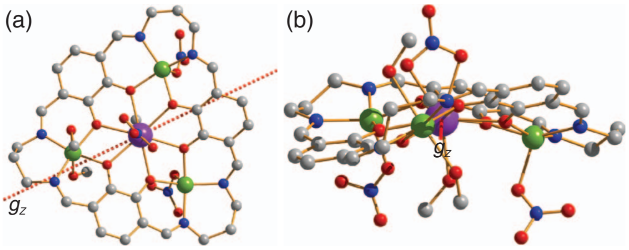

FIG. 1. Orientation of the main magnetic axis *Z* (dashed line) in the ground Kramers doublet of the $DyZn_3$ complex with respect to the molecular frame. Color scheme: Dy-violet, Zn-green, O-red, N-blue, C-grey. Hydrogens were omitted for clarity.

The sign of the product of the main values of *g* tensor for Dy(III) complexes is not always positive. Thus, a recently investigated[58] mononuclear $[Dy(H_2DABPH)_2]^{3+}$ complex, considered here as a second example, shows a negative sign of $g_X g_Y g_Z$ in the ground state. The details of calculations are presented in the Appendix B 2, Figs. 2 and 9. Table II shows the lowest calculated energies, the *g* tensor of the lowest Kramers doublet and the obtained sign of the $g_X g_Y g_Z$ product. Figure 2 shows the orientation of the main anisotropy axis g_Z with respect to the molecular frame of $[Dy(H_2DABPH)_2]^{3+}$ complex. We can see from Tables I and II that the splitting patterns of the ground atomic multiplet $J = 15/2$ are similar for both compounds. At the same time the different sign of $g_X g_Y g_Z$ product in their ground states cannot be foreseen. These examples show that in realistic low-symmetric lanthanide complexes it is impossible to predict the magnetic properties of multiplets with sufficient accuracy without applying high-level *ab initio* calculations.

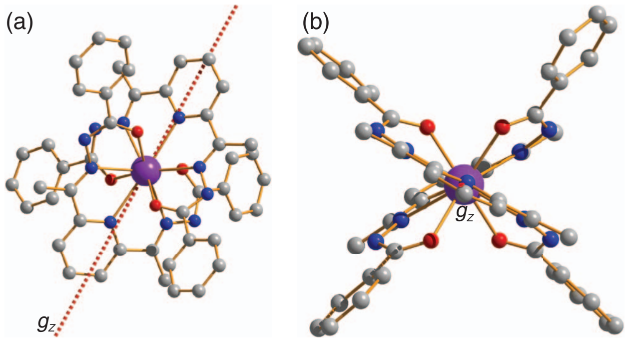

FIG. 2. Orientation of the main magnetic axis Z (dashed line) in the ground Kramers doublet of the $Dy(H_2DABPH)_2]^{3+}$ complex[58] with respect to the molecular frame. Color scheme: Dy-violet, O-red, N-blue, C-grey. Hydrogens were omitted for clarity.

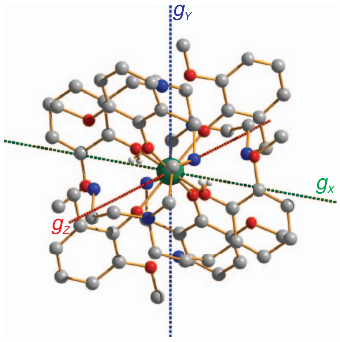

FIG. 3. Orientation of the main magnetic axes X, Y, and Z (dashed lines) in the ground Kramers doublet of the Yb(III) complex[59] with respect to the molecular frame. Color scheme: Yb-sea green, O-red, N-blue, C-grey, H-white. Distant hydrogens of the ligand were omitted for clarity.

D. Example: *g* tensor of Yb(III) complex

Consider now a mononuclear Yb(III) complex (Fig. 3).[59] The electronic configuration of the Yb(III) free ion is $4f^{13}$, while the ground ionic multiplet is $^2F_{\frac{7}{2}}$, and the first excited ionic multiplet $^2F_{\frac{5}{2}}$ lies higher than 10 000 cm^{-1}. In the presence of ligand field the ground multiplet $J = \frac{7}{2}$ splits into four Kramers doublets. Although the spin of Yb(III) is $S = 1/2$, its use for the description of resulting Kramers doublets would not be correct because of strong (first-order) coupling of spin and orbital angular momenta in the ground ionic term. Then each Kramers doublet should be described by the pseudospin $\tilde{S} = 1/2$, as in the case of Dy(III) complexes. The results of *ab initio* calculations performed for the slightly reduced fragment (A) (Fig. 10) and for the molecular structure taken from experiment (B) are given in Table III (see Appendix B 3 for computational details). Figure 3 shows the orientation of the main magnetic axes of the Yb(III) with respect to the molecular frame.

As we can see from Table III, the ground ionic multiplet $^2F_{\frac{7}{2}}$ is strongly split by the ligand field, and therefore the magnetic behaviour of this Yb(III) complex at low temperature is entirely defined by the magnetic anisotropy of the lowest Kramers doublet. The comparison between the calculated and experimental molar magnetization at low temperature is excellent,[59] which allows us to conclude that the ground Kramers doublet is well reproduced by the calculations. Table III shows that in contrast to Dy(III) complexes considered above, the ground Kramers doublet is of easy-plane type. The second remarkable feature is a unexpectedly strong dependence of the hard axis g-factor on the details of the two structural models, which only differ in the distant part of the ligand surrounding Yb(III). Clearly such a sensitivity will not be adequately described by any crystal/ligand field approach.

TABLE II. Energies of the lowest spin-free states originating from the ^6H multiplet and the energies of the lowest Kramers doublets of the $[Dy(H_2DABPH)_2]^{3+}$ complex,[58] obtained in two computational approximations (A and B).

	Spin free states			Kramers doublets	
Atomic multiplet	A	B	J multiplet	A	B
^6H	0.000	0.000	$^6H_{\frac{15}{2}}$	0.000	0.000
	7.301	6.529		64.260	24.797
	95.452	61.366		86.449	56.448
	126.993	106.179		101.357	79.022
	167.608	139.779		147.846	147.235
	246.595	260.620		184.127	179.535
	271.443	285.356		282.633	253.169
	320.089	317.569		439.944	404.120
	378.706	359.937			
	600.803	578.172			
	641.538	616.895			
Main values of the g tensor in the ground Kramers doublet					
g_X				0.032	0.155
g_Y				0.080	0.240
g_Z				17.084	16.592
Sign of $g_X g_Y g_Z$				−	−

TABLE III. Energies of the lowest spin-free states originating from the ^2F atomic multiplet and the energies of the lowest Kramers doublets of the studied Yb(III) complex,[59] obtained in two computational approximations (A and B).

	Spin free states			Kramers doublets	
Atomic multiplet	A	B	J multiplet	A	B
^2F	0.000	0.000	$^2F_{\frac{7}{2}}$	0.000	0.000
	88.581	49.774		157.456	187.935
	135.820	87.714		356.766	300.026
	315.396	346.043		550.950	485.034
	573.690	477.403	$^2F_{\frac{5}{2}}$	10 396.169	10 420.549
	622.436	524.851		10 522.190	10 484.847
	656.668	572.017		10 832.461	10 768.123
Main values of the g tensor in the ground Kramers doublet					
g_X				3.599	3.209
g_Y				2.884	2.694
g_Z				0.449	1.763
Sign of $g_X g_Y g_Z$				−	−

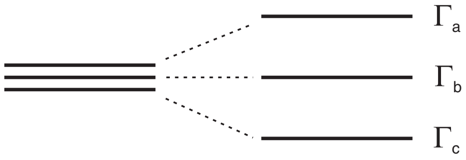

FIG. 4. Zero-field splitting of the energy levels belonging to the pseudospin $\tilde{S} = 1$.

IV. THE PSEUDOSPIN $\tilde{S} = 1$

This is the smallest (non-zero) pseudospin which arises in systems with even number of electrons. Since in this case the Kramers theorem[2] does not apply, the $N = 2\tilde{S} + 1 = 3$ states of this pseudospin split in the presence of spin-orbit coupling into free separate energy levels, if the symmetry of the complex is not high enough (Fig. 4). The quantum chemistry calculations give three wave functions, Ψ_a, Ψ_b, and Ψ_c corresponding to three energy levels in Fig. 4. Our goal is to construct from these functions three pseudospin eigenfunctions in a general case, without making use of the symmetry of the complex. Since the three wave functions Ψ_a, Ψ_b, and Ψ_c belong to non-degenerate energy levels, they are essentially real, and therefore cannot obey the time inversion relations expected for pseudospin eigenfunctions. Nevertheless it is easy to construct from them three linear combinations, Ψ_1, Ψ_2, and Ψ_3 which fulfill the time inversion relations expected for $|S\ -\ 1\rangle$, $|S0\rangle$, and $|S1\rangle$ of a true $S = 1$, respectively. These are $\Psi_3 = \hat{\theta}\Psi_1 \equiv \bar{\Psi}_1$, $\Psi_1 = \hat{\theta}\Psi_3$, and $\hat{\theta}\Psi_2 = -\Psi_2$ (Ψ_2 is real). It can be shown that these relations impose $N_\theta = 6$ constraints on the possible unitary transformations of the three wave functions.[44] Given the total number $N^2 = 9$ of independent parameters describing general unitary transformations of three wave functions, with time reversal constraints we are left with $N^2 - N_\theta = 3$ free real parameters to represent the possible unitary transformation of the pseudospin wave functions. As a result the general form of the unitary transformation is again isomorphic to the one induced by the rotations of pseudospin coordinate system. Therefore, as for $\tilde{S} = 1/2$, we can say in this case too that the wave functions Ψ_1, Ψ_2, and Ψ_3 are already the three eigenfunctions of the z-projection of the pseudospin $\tilde{S} = 1$ in a pseudospin coordinate system with unknown orientation. As discussed in Sec. II A, in order to relate this coordinate system to the real space coordinate system we should find first the main magnetic axes of the complex.

A. Zeeman pseudospin Hamiltonian

To find the magnetic axes, as in the previous case of $\tilde{S} = 1/2$, we write the matrix of microscopic Zeeman Hamiltonian (4) in an arbitrary basis (Ψ_1, Ψ_2, Ψ_3) and diagonalize it for an arbitrary orientation of magnetic field, $\mathbf{B} = (\xi_x, \xi_y, \xi_z)B$. The obtained eigenvalues look as follows:

$$E_{\mathrm{Zee}} = -\lambda B, \qquad \lambda_{\pm} = \pm\left(\sum_{\alpha\beta} \xi_\alpha A_{\alpha\beta}\xi_\beta\right)^{1/2}, \quad \lambda_0 = 0, \tag{25}$$

where the tensor $\mathbf{A}$ is defined in Eq. (15), in which the trace is supposed to be taken now over the three states of the $\tilde{S} = 1$ manifold. It results from Eq. (25) that the amplitude of the Zeeman splitting, λ_+, is determined by the tensor $\mathbf{A}$. Therefore, the extremal values of this splitting will occur, as in the case of $\tilde{S} = 1/2$, along the main axes of this tensor. Thus the main magnetic axes are obtained, in this case too, via the diagonalization of $\mathbf{A}$, Eq. (17).

In order to derive the Zeeman pseudospin Hamiltonian appropriate to $\tilde{S} = 1$ we should find the general form of magnetic moment matrix μ_α written in an arbitrary basis $\{\Psi_i\}$ obeying proper time inversion relations. As stated above, the functions Ψ_1 and Ψ_3 are Kramers conjugated, therefore, for them the following relations are valid:[2] $\langle\Psi_3|\hat{\mu}_\alpha|\Psi_3\rangle = -\langle\Psi_1|\hat{\mu}_\alpha|\Psi_1\rangle \equiv c$, where c is a real parameter. Again, due to the Kramers conjugation of these function we have:[2] $\langle\Psi_1|\hat{\mu}_\alpha|\Psi_3\rangle = 0$. On the other hand, Ψ_2 is a real function for which we have: $\langle\Psi_2|\hat{\mu}_\alpha|\Psi_2\rangle = 0$. The remaining matrix elements between $\Psi_{1,3}$ and Ψ_2 obey the relation: $\langle\Psi_3|\hat{\mu}_\alpha|\Psi_2\rangle = \langle\Psi_2|\hat{\mu}_\alpha|\Psi_1\rangle$, which holds true because $\hat{\mu}_\alpha$ is a time-odd operator. These matrix elements are of general form, $\langle\Psi_3|\hat{\mu}_\alpha|\Psi_2\rangle \equiv (a - ib)/\sqrt{2}$, i.e., are parametrized by two real parameters, a and b. Then the matrix μ_α, written in the basis Ψ_3, Ψ_2, Ψ_1, is generally parametrized as follows:

$$\begin{aligned} \mu_\alpha &= \begin{pmatrix} c & (a - ib)\sqrt{2} & 0 \\ (a + ib)\sqrt{2} & 0 & (a - ib)\sqrt{2} \\ 0 & (a + ib)\sqrt{2} & -c \end{pmatrix} \\ &= a\tilde{\mathrm{S}}_x + b\tilde{\mathrm{S}}_y + c\tilde{\mathrm{S}}_z, \end{aligned} \tag{26}$$

where $\tilde{\mathrm{S}}_x$, $\tilde{\mathrm{S}}_y$ and $\tilde{\mathrm{S}}_z$ in the right hand side are conventional $S = 1$ matrices written in the usual order of eigenfunctions of $\hat{\mathrm{S}}_z$, $|1, 1\rangle$, $|1, 0\rangle$, $|1, -1\rangle$.[45,47] We may conclude that for $\tilde{S} = 1$ the magnetic moment and the Zeeman Hamiltonian are operators linear in pseudospin, Eq. (18). The three real numbers of the decomposition (26) of a given μ_α vary independently under unitary transformations of the basis, as was also the case for $\tilde{S} = 1/2$.

Diagonalizing (18) for $\tilde{S} = 1$ we obtain the eigenvalues of the pseudospin Zeeman Hamiltonian as function of $g_{\alpha\beta}$,

$$\lambda_{\pm} = \pm\mu_{\mathrm{B}}\left(\sum_{\alpha\beta} \xi_\alpha G_{\alpha\beta}\xi_\beta\right)^{1/2}, \quad \lambda_0 = 0, \tag{27}$$

where $\mathbf{G}$ is again the Abragam-Bleaney tensor (20). Comparing (27) with Eq. (25) we obtain the relation

$$\mu_{\mathrm{B}}^2\mathbf{G} = \mathbf{A}, \tag{28}$$

which, being written in the coordinate system of main magnetic axes, gives the main components of the g tensor,

$$g_i = \pm\frac{1}{\mu_{\mathrm{B}}}\sqrt{\tilde{A}_{ii}}, \quad i = X, Y, Z, \tag{29}$$

which are again, as in the case of $\tilde{S} = 1/2$, defined up to the sign.

This approach has been applied for the nonperturbative calculations of the main g_i values of the ground triplet in a Ni(II) complex[35] using the SO-RASSI-CASPT2 *ab initio* results obtained with the MOLCAS package[39] (see Sec. IV C). With the main values g_i we can reconstruct the whole g tensor in the intial coordinate system, Eq. (23).

The symmetry of the complex can help finding the main magnetic axes directly, as in the case of Kramers doublet. Again, $g_i = g$ for cubic symmetry groups, while in the case of axial symmetry, i.e., in the presence of a symmetry axis of order higher than two, the main values are $g_\parallel$ along this axis and $g_\perp$ along each of the two perpendicular directions. For a lower symmetry, even when the main magnetic axes are completely resolved by it (see Sec. III A), all g_i are generally different.

The indeterminacy of the sign in (29) has the same origin as in the case of $\tilde{S} = 1/2$ pseudospin, so the conclusions of Sec. III B are entirely applicable for the pseudospin $\tilde{S} = 1$ as well (one should replace there $|\tilde{S} \pm 1/2\rangle$ by $|\tilde{S} \pm 1\rangle$). In particular, Eq. (24) for the sign of the product of the main values of g tensor is also valid, if we understand now by μ_I the 3×3 matrices of magnetic moment components along the main magnetic axes of the complex.

B. ZFS pseudospin Hamiltonian

Since the spin-orbit interaction is included already in the *ab initio* calculation, the zero-field splitting of the pseudospin triplet emerges simply as the relative energies $E'_i = E_i - E_0$ of three *ab initio* eigenstates $i = a, b, c$ in Fig. 1 measured from their center of gravity $E_0 = (E_a + E_b + E_c)/3$. The corresponding ZFS Hamiltonian is written as follows:

$$\hat{\mathrm{H}}_{\mathrm{ZFS}} = E'_a|\Psi_a\rangle\langle\Psi_a| + E'_b|\Psi_b\rangle\langle\Psi_b| + E'_c|\Psi_c\rangle\langle\Psi_c|, \tag{30}$$

i.e., it is of diagonal form in the basis of these states.

Having assigned the (combinations of) *ab initio* wave functions to pseudospin eigenfunctions $|\tilde{S}M\rangle$, $M = -1, 0, 1$, in some coordinate system, e.g., related to main magnetic axes with the quantization axis Z, we can make the inverse unitary transformation,

$$|\Psi_i\rangle = \sum_M c_{iM}|\tilde{S}M\rangle, \quad i = a, b, c \tag{31}$$

and write the ZFS Hamiltonian (30) as a 3×3 matrix in the basis of $\{|\tilde{S}M\rangle\}$,

$$(\mathrm{H}_{\mathrm{ZFS}})_{MM'} = \sum_i E'_i c^*_{iM} c_{iM'}. \tag{32}$$

This matrix is defined by five independent parameters: two of three energies E'_i (their sum is bound to zero) and three parameters which induce the unitary transformation (31) (see the beginning of this section).

The Hermitean matrix (32) can be decomposed in a bilinear combination of pseudospin matrices corresponding to $\tilde{S} = 1$, in a form similar to (6),

$$\mathrm{H}_{\mathrm{ZFS}} = \tilde{\mathbf{S}} \cdot \mathbf{D} \cdot \tilde{\mathbf{S}}. \tag{33}$$

Indeed, since $\hat{\mathrm{H}}_{\mathrm{ZFS}}$ is a time-even operator, as any other Hamiltonian in the absence of external magnetic field, it can include only even powers of pseudospin operators because the latter are time-odd[2] (the constant term will not enter this decomposition since it corresponds to the center of gravity of ZFS levels which was set to zero). On the other hand, the matrix $\mathbf{D}$ should be real and symmetric,[44] and also traceless since the center of gravity of E'_i is zero. Therefore, it is defined by five independent parameters: two of three diagonal elements and three off-diagonal elements from the upper triangle. These parameters match the five degrees of freedom contained in the definition of matrix (32) which proves the form (33) of pseudospin ZFS Hamiltonian for $\tilde{S} = 1$. Writing the matrix of (33) in the basis of pseudospin eigenstates $|\tilde{S}M\rangle$ and equating the obtained matrix elements to the corresponding $(\mathrm{H}_{\mathrm{ZFS}})_{MM'}$ from (32), provided by *ab initio* calculations, we can express through them the elements $D_{\alpha\beta}$ of ZFS tensor,

$$\begin{aligned} D_{ZZ} &= -(\mathrm{H}_{\mathrm{ZFS}})_{00}, \\ D_{XX} - D_{YY} &= (\mathrm{H}_{\mathrm{ZFS}})_{1-1} + (\mathrm{H}_{\mathrm{ZFS}})_{-11}, \\ D_{XY} &= \frac{i}{2}[(\mathrm{H}_{\mathrm{ZFS}})_{1-1} - (\mathrm{H}_{\mathrm{ZFS}})_{-11}], \\ D_{XZ} &= \frac{1}{\sqrt{2}}[(\mathrm{H}_{\mathrm{ZFS}})_{01} + (\mathrm{H}_{\mathrm{ZFS}})_{10}], \\ D_{YZ} &= \frac{i}{\sqrt{2}}[-(\mathrm{H}_{\mathrm{ZFS}})_{01} + (\mathrm{H}_{\mathrm{ZFS}})_{10}], \end{aligned} \tag{34}$$

where the Cartesian indices correspond to main magnetic axes (note again, $D_{XX} + D_{YY} + D_{ZZ} = 0$).

Diagonalizing the tensor $\mathbf{D}$ with the elements (34) by rotating the coordinate system to main anisotropy axes X', $Y'Z'$, we obtain for the ZFS Hamiltonian (33) the well-known expression[3,4]

$$\begin{aligned} \mathrm{H}_{\mathrm{ZFS}} &= D\tilde{S}^2_{Z'} + E\left(\tilde{S}^2_{X'} - \tilde{S}^2_{Y'}\right), \\ D &\equiv \frac{3}{2}D_{Z'Z'}, \quad E \equiv \frac{1}{2}(D_{X'X'} - D_{Y'Y'}). \end{aligned} \tag{35}$$

Diagonalizing further $\mathrm{H}_{\mathrm{ZFS}}$ given by Eq. (35) we obtain

$$\begin{aligned} \hat{\mathrm{H}}_{\mathrm{ZFS}} = &-\frac{2}{3}D|\Psi_1\rangle\langle\Psi_1| + \left(\frac{1}{3}D + E\right)|\Psi_2\rangle\langle\Psi_2| \\ &+ \left(\frac{1}{3}D - E\right)|\Psi_3\rangle\langle\Psi_3|, \end{aligned} \tag{36}$$

which coincides with the *ab initio* ZFS Hamiltonian (30) albeit it is not known *a priori* in what order one should assign Ψ_1, Ψ_2, and Ψ_3 in the above equation to Ψ_a, Ψ_b, and Ψ_c in Eq. (30). The six possibilities of such an assignment correspond to six ways of labeling the main anisotropy axes by X', Y', and Z'. The procedure described by Eqs. (31)–(35) not only allows to find the main anisotropy axes but also fixes their labels in a unique way (the X', $Y'Z'$ axes are the closest to the X, YZ, respectively).

Note that in contrast to the main values of the g tensor, the signs of the main values of $\mathrm{H}_{\mathrm{ZFS}}$, D, and E, are firmly defined. Note also that although in the Λ-tensor approximation[2] the main magnetic axes (XYZ) coincide with the main anisotropy axes ($X'Y'Z'$), this is actually not the case even for complexes which are in the weak spin-orbit coupling regime. This is exemplified in Subsection IV C.

Finally, we would like to emphasize that the basis for the above derivation of pseudospin ZFS Hamiltonian was the preliminary assignment of combination of RASSI-SO wave functions Ψ_i, $i = a, b, c$ to pseudospin eigenfunctions $|\tilde{S}M\rangle$, which was done in Sec. IV A. This approach differs drastically from the theory of effective Hamiltonian.[60,61] The latter involves as a crucial step the projection of the chosen eigenstates of the exact Hamiltonian onto a model space, corresponding to eigenstates of some model (zeroth order) Hamiltonian. Such an approach was recently applied to the derivation of ZFS spin Hamiltonians by using eigenfunctions of total spin and its projection as a model space.[32] We note that such a derivation is only adequate for complexes with weak spin-orbit coupling effects (e.g., those of Ni(II)), when the pseudospin can be approximately associated with the total true spin of the complex. As a counterexample, in Sec. IV we derive the pseudospin Hamiltonians for U(IV) complexes characterized by the pseudospin $\tilde{S} = 1$ which cannot be associated at any rate with the total true spin due to very strong spin-orbit mixing of the low-lying terms on this metal ion. Such examples of complexes with strong and intermediate spin-orbit coupling effects show that the philosophy of effective Hamiltonian theory[60,61] cannot be applied for the derivation of magnetic pseudospin Hamiltonians in principle. At variance with the true spin, the pseudospin is an abstract operator and one cannot indicate *a priori* a model space characterized by a definite projection of pseudospin.

C. Example: *g* and *D* tensors of a Ni(II) complex

We consider here a previously investigated[35] complex [Ni-(HIM$_2$-py)$_2$NO$_3$]NO$_3$ (Ref. 62) (Fig. 5), which exhibits a largest axial ZFS ($E \ll |D|$ in Eq. (35)) of the ground $S = 1$ term among the known hexacoordinated Ni^{2+} complexes. In order to investigate the magnetic anisotropy in this complex we have performed *ab initio* calculations using the MOLCAS-7.6 package. Computational details are given in the Appendix B 4.

Table IV gives the energy of low-lying terms calculated at CASSCF and more advanced multistate (MS) CASPT2 levels. We can see from the table that the first excited term lies at >8000 cm^{-1} above the ground one, which is one order of magnitude larger than the spin-orbit coupling constant for the Ni^{2+} ion.[72] Given that the ground term is orbitally nondegenerate we may conclude that the complex is in the weak spin-orbit coupling regime. The multiplets arising from the spin-orbit mixing of the MS CASPT2 states are listed in the last column of Table IV. We can see that the calculations predict an almost axial ZFS of the ground $S = 1$ term of easy plane type in full accord with experiment.[62] Moreover, the energy of the axial splitting is closely reproduced.

TABLE IV. Energies of molecular terms and multiplets (E <20 000 cm^{-1}) of the Ni(II) complex.

Spin mult.	CASSCF[a]	MS CASPT2[a]	RASSI-SO[a]
3	0.0	0.0	0.0
			0.8
			10.7
3	6952	8076	7989
			8138
			8150
3	9073	10 255	10 087
			10 287
			10 344
3	9394	10 612	10 646
			10 692
			10 702
1	18 082	14 050	13 879
1	18 356	14 320	14 137
3	14 069	15 138	14 873
			15 063
			15 315
3	14 359	15 744	15 770
			16 133
			16 314
3	15 145	16 543	16 853
			16 972
			17 043

[a] In cm^{-1}.

In order to get more quantitative insight we derive the Zeeman and ZFS pseudospin Hamiltonians for this complex[35] using the program SINGLE_ANISO. As discussed in Sec. IV B, for $\tilde{S} = 1$ $H_{\rm Zee}$ is linear in $\tilde{\mathbf{S}}$ and is described by the tensor $\mathbf{g}$, while $H_{\rm ZFS}$ is bilinear in $\tilde{\mathbf{S}}$ and is described by the tensor $\mathbf{D}$. We obtain for the main values of the g tensor $g_X = 2.21$, $g_Y = 2.22$, and $g_Z = 2.29$. This gives the average value $g_{\rm iso} = 2.24$ which compares well with the measured value $g_{\rm exp} = 2.20$.[62] The corresponding magnetic axes X_m, Y_m, Z_m (Fig. (5)) are given in Table V with respect to the initial coordinate system x, y, z (Fig. 5). The parameters describing the main values of $\mathbf{D}$, Eq. (35), are calculated as $D = -10.3$ cm^{-1} and $E = 0.4$ cm^{-1}, which compare very well with the experimental values $D_{\rm exp} = -10.1$ cm^{-1} and $E_{\rm exp} = 0.3$ cm^{-1}.[62] The corresponding anisotropy axes X_a, Y_a, Z_a, for which $\mathbf{D}$ is diagonal, are given in the last three lines of Table V. As was mentioned in Sec. IV B the labeling of the main anisotropy axes should be chosen in a way that X_a, Y_a, Z_a are kept as close as possible to X_m, Y_m, Z_m, respectively. Following this convention, the anisotropy axes obtained in the output of SINGLE_ANISO have been rotated around Z_a by $-90°$.

The obtained near axiality of the g and D tensors is rather accidental, since it is not supported by an axial symmetry of the complex. Indeed, the planes of the two HIM$_2$-py ligands make a dihedral angle of 82°, which means that the coordination sphere of the Ni(II) center contains at most one approximate C_2 symmetry axis that bisects the O–Ni–O angle, which is not sufficient to claim axiality on the symmetry grounds. As a result the direction of the main magnetic Z_m (Fig. 5) is arbitrarily oriented, the same for the main anisotropy axis Z_a. As

TABLE V. Main magnetic and anisotropy axes of the Ni(II) complex.

	x	y	z
X_m	−0.02	−0.48	0.87
Y_m	0.47	0.77	0.44
Z_m	−0.88	0.42	0.21
X_a	0.29	0.41	0.86
Y_a	0.25	0.84	−0.48
Z_a	−0.92	0.35	0.15

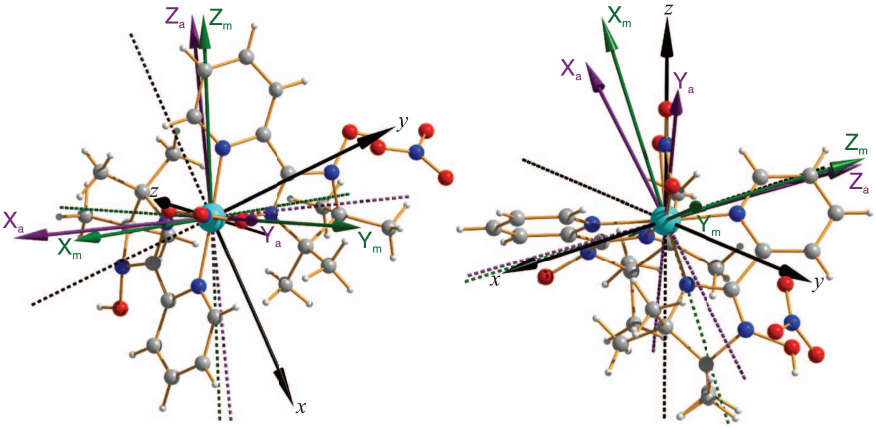

FIG. 5. Two views on the molecular structure of the Ni(II) complex.[62] Molecular coordinate axes (*x, y, z*) are shown by black arrows. The *ab initio* calculated main magnetic axes (X_m, Y_m, Z_m) are shown by green arrows and main anisotropy axes (X_a, Y_a, Z_a) by purple arrows. Color scheme: turquoise Ni^{2+}; red O; blue N; grey C; white H.

Table V shows the three magnetic axes do not coincide with the three anisotropy axes, which is another consequence of the lack of axial symmetry. Despite the fact that the zero-field splitting is obtained in the range expected for weak spin-orbit coupling regime, we note that the approach based on the Λ tensor[2,43] is strictly speaking not applicable even in this case. Indeed, as Table V shows, there is significant angle between (X_a, Y_a) and (X_m, Y_m) axes in this complex.

D. Example: The ZFS and *g* tensors of U(IV) fragments in UO_2

The U^{4+} ion has 2 electrons in the 5f shell. The ground atomic multiplet $^3H_4$ of U^{4+} arises from antiparallel coupling of $S = 1$ and $L = 4$ angular momenta in the ground term. In cubic environment the $^3H_4$ multiplet splits in several multiplets: a ground triplet Γ_5 and an excited doublet Γ_3, a triplet Γ_4, and a singlet Γ_1 (Fig. 6). Due to first-order coupling between S and L, none of these momenta is conserved, even approximately, while the states of the total angular momentum $J = 4$ are strongly split in the crystal. Therefore, the only way to describe adequately the ground triplet Γ_5 is to assign its three wave functions to the eigenfunctions of a pseudospin $\tilde{S} = 1$.

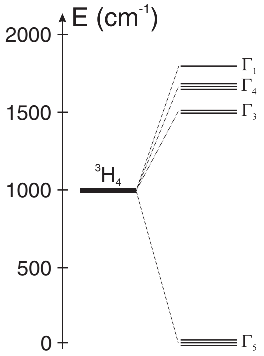

FIG. 6. *Ab initio* calculated multiplets of the U^{4+} fragment of UO_2, corresponding to the $^3H_4$ atomic multiplet for the undistorted lattice (column A in Table VI).

We have performed *ab initio* calculations of the CASSCF/RASSI-SO/SINGLE_ANISO type using MOLCAS-7.6 program package[39] on three model U^{4+} fragments in UO_2. The first calculation (A) corresponds to the structure of UO_2 at room temperature (fcc fluorite lattice). The second one (B) corresponds to the monoclinic distortion of the oxygen sublattice, where the two opposite planes of oxygens move towards each other (distortion of 2k type). The third calculation (C) corresponds to a more complex distortion of the oxygen sublattice (distortion of 3k type).[88,89] Computational details are presented in the Appendix B 5. Table VI shows the calculated energies of the levels corresponding to the atomic $^3H_4$ multiplet for the three structures, and the *g* and *D* tensors of the ground triplet Γ_5 of U^{4+} fragments. Figure 7 shows the orientation of the main magnetic axes and the main anisotropy axes with respect to the calculated UO_2 cluster. For the structure C a pure axial anisotropy is obtained, while in the case of structure B a rhombic ZFS arises. These differences are also seen for the calculated main values of the *g* tensors (Table VI) and are obviously due to different symmetries of U^{4+} environment in these two structures. Accordingly a full magnetic isotropy is realised for the cubic structure A.

V. HIGHER PSEUDOSPINS: IRREDUCIBLE TENSOR DESCRIPTION OF PSEUDOSPIN HAMILTONIANS

We have seen in Subsections III A and IV A that the Zeeman pseudospin Hamiltonian is linear in pseudospin operators for $\tilde{S} = 1/2$ and 1, Eqs. (18) and (26), respectively. For the pseudospin $\tilde{S} = 3/2$ this decomposition acquires also third order terms in pseudospin operators.[2] The reason for such a raising of the order of polynomial in $\tilde{S}_\alpha$ is the increased dimension of the matrix of Zeeman Hamiltonian (for $\tilde{S} = 3/2$ it is $N = 2\tilde{S} + 1 = 4$), which cannot be decomposed only in three matrices $\tilde{S}_\alpha$. The same can be said about the pseudospin Hamiltonian H_{ZFS}. The polynomial decomposition in $\tilde{S}_\alpha$ for the pseudospin operators can be done, in principle, for

TABLE VI. Energies of the lowest spin orbit states originating from the $^3H_4$ multiplet of the U^{4+} ion in UO_2 complex for undistorted structure (A) and two different distortion types: 2k-type (B) and 3k-type (C) (in cm^{-1}).

Ground multiplet	Spin-orbit energies		
	A	B	C
$^3H_4$	0.000	0.000	0.000
	0.006	17.940	0.000
	0.058	36.953	33.015
	1496.522	1503.205	1503.115
	1496.542	1519.187	1503.115
	1665.009	1659.873	1668.372
	1665.029	1692.243	1668.372
	1665.047	1697.471	1692.863
	1796.323	1805.147	1797.920
g_I	The g tensor of the ground Γ_5 triplet ($\tilde{S} = 1$)		
g_X	1.907	1.859	1.877
g_Y	1.907	1.906	1.877
g_Z	1.907	1.949	1.959
Sign of $g_X g_Y g_Z$	+	+	+
	The ZFS tensor for the ground Γ_5 triplet ($\tilde{S} = 1$)		
D_X	0.000	18.298	11.005
D_Y	0.000	0.357	11.005
D_Z	0.000	− 18.655	− 22.010
D	0.000	− 27.983	− 33.015
E	0.000	8.970	0.000

arbitrary pseudospins by applying the same procedure which lead to Eq. (26). This is, however, quite tedious already for $\tilde{S} = 3/2$ and, more importantly, not at all systematic. For instance, following this procedure we cannot foresee that the additional terms beside the linear in the decomposition of μ for $\tilde{S} = 3/2$ should be only of third and not of higher order, e.g., fifth. The situation becomes worse for higher pseudospins.

In the theory of angular momentum a powerful technique based on irreducible tensor operators (ITO) (Ref. 45) is widely applied to manage multiples and powers of angular momentum operators (S_α, L_α, or J_α). The ITO which are used here are operators transforming under the rotations of the coordinate system as spherical harmonics $Y_{lm}(\mathbf{r}/r)$ and, therefore, are similar combinations of the angular momentum operators ($Y_{lm}(\mathbf{S})$, $Y_{lm}(\mathbf{L})$, $Y_{lm}(\mathbf{J})$). Among many advantages, the ITO technique allows the application of Wigner-Eckart theorem[2,3,45] (in Eq. (A1) $T_{kq} \sim Y_{kq}(\mathbf{J})$). Formally, the applicability of Wigner-Eckart theorem does not require the correct transformation properties of these operators with respect to *real space* rotations but only that they form the combinations $Y_{\kappa q}(\hat{\mathbf{J}})$ from the operators $\hat{J}_\alpha$ and that the latter act on the basis functions $|JM\rangle$ as corresponding angular momentum operators (i.e., $\hat{J}_\alpha$ written in the basis of these functions coincide with corresponding angular momentum matrices J_α). This means that we can apply the Wigner-Eckart theorem also for the "irreducible" combinations $Y_{nm}(\tilde{\mathbf{S}})$ of pseudospin matrices $\tilde{S}_\alpha$, for which no rotations of pseudospin vector $\tilde{\mathbf{S}}$ induced by real space rotations are assumed to exist (as in complexes with low symmetry). The combinations $Y_{nm}(\tilde{\mathbf{S}})$ can, however, be viewed as true irreducible tensors when their transformations are considered with respect to the rotations in the pseudospin space, induced by the unitary transformations of the basis set.

A. ITO decomposition of Zeeman and ZFS pseudospin Hamiltonians

We further consider the decomposition of H_{Zee} (or μ) and H_{ZFS} into $\{Y_{nm}(\tilde{\mathbf{S}})\}$. We remind that the matrices of these Hamiltonians are written in the basis of combinations of *ab initio* eigenfunctions of a chosen manifold, $\{\Psi_i\}$, obeying the appropriate time inversion relations and assigned to $|\tilde{S}M\rangle$, eigenfunctions of the matrix $\tilde{S}_z$. According to Wigner-Eckart theorem, Eq. (A1), the matrix elements of $Y_{nm}(\tilde{\mathbf{S}})$ are proportional to the corresponding Clebsch-Gordan coefficients $C^{\tilde{S}M_1}_{nm\tilde{S}M_2}$, for which the sum of any two momenta among the three indices (n, $\tilde{S}$ and $\tilde{S}$) should not be smaller than the third one.[45,47] As a particular consequence of this rule we obtain $n \leq 2\tilde{S}$. This means that only irreducible tensors whose rank n does not exceed $2\tilde{S}$ will enter the decomposition of the Hamiltonian matrices. Since H_{Zee} and μ are time-odd

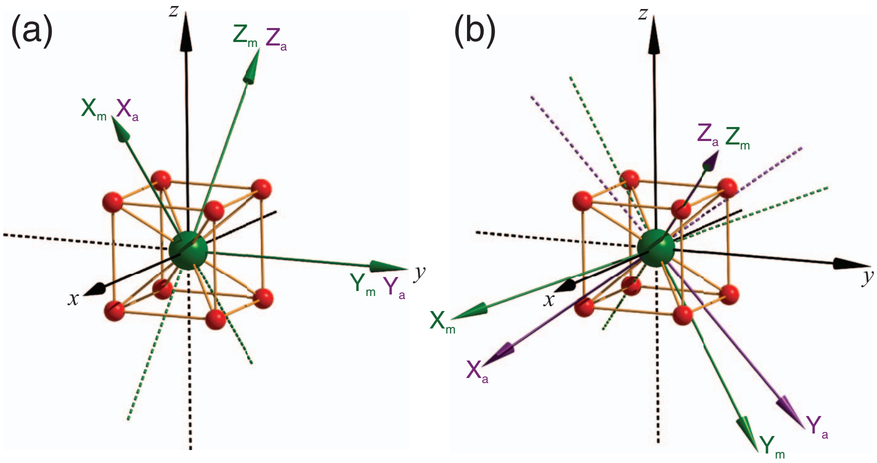

FIG. 7. Orientations of the main magnetic axes (X_m, Y_m, Z_m) and the main anisotropy axes (X_a, Y_a, Z_a) with respect to the unit cell of the distorted UO_2 of 2k-type (a) and 3k-type (b).

TABLE VII. Tensorial decomposition of Zeeman and ZFS pseudospin Hamiltonians.

$\tilde{S}$	$\mathrm{H}_{\mathrm{Zee}} = -\mu \cdot B$	$\mathrm{H}_{\mathrm{ZFS}}$
$\frac{1}{2}$	μ^1	…
1	μ^1	H^2
$\frac{3}{2}$	$\mu^1 + \mu^3$	H^2
2	$\mu^1 + \mu^3$	$\mathrm{H}^2 + \mathrm{H}^4$
$\frac{5}{2}$	$\mu^1 + \mu^3 + \mu^5$	$\mathrm{H}^2 + \mathrm{H}^4$
3	$\mu^1 + \mu^3 + \mu^5$	$\mathrm{H}^2 + \mathrm{H}^4 + \mathrm{H}^6$
$\frac{7}{2}$	$\mu^1 + \mu^3 + \mu^5 + \mu^7$	$\mathrm{H}^2 + \mathrm{H}^4 + \mathrm{H}^6$

operators, while $\mathrm{H}_{\mathrm{ZFS}}$ is a time-even operator, only odd-rank irreducible tensors will enter the decomposition of the formers and only even-rank irreducible tensor will contribute to the latter. The tensorial decomposition of Zeeman and ZFS Hamiltonians is given in Table VII.

The above results immediately explain why we can only have terms of order not higher than three in the pseudospin operator of magnetic moment corresponding to $\tilde{S} = 3/2$. Indeed, three is the highest rank which does not exceed $2\tilde{S} = 3$. More than that, we may conclude in advance that we have in a general case seven third order operators in such decomposition: this is the total number of irreducible tensor operators $Y_{3m}(\tilde{\mathbf{S}})$, $m = -3, \ldots 3$. Together with the linear terms in $\tilde{S}_\alpha$, from which components of first rank tensor $Y_{1m}(\tilde{\mathbf{S}})$, $m = -1, 0, 1$ can be constructed (see Eq. (A2)), we obtain ten irreducible tensor components in the general decomposition of μ_α.

In practice, the (pseudo)spin Hamiltonians are written in terms of Stevens operators $O_n^{\pm m} \sim Y_n^{\pm m}$, $m \geq 0$ (Ref. 73) which do not include the normalization coefficient of spherical harmonics. The spherical harmonics operators themselves are not Hermitean but obey the relations[45] $(Y_n^{+m})^\dagger = (-1)^m Y_n^{-m}$. Therefore, it is convenient to use instead of $O_n^{\pm m}$ their Hermitean combinations,[73]

$$\begin{aligned} O_n^m &= \frac{1}{2}\big((-1)^m O_n^{+m} + O_n^{-m}\big), \\ \Omega_n^m &= \frac{i}{2}\big(O_n^{-m} - (-1)^m O_n^{+m}\big), \end{aligned} \tag{37}$$

because in this case the decomposition coefficients are real (note that $\Omega_n^0 = 0$). In terms of Hermitean Stevens operators the matrix of magnetic moment is decomposed as follows:

$$\begin{aligned} \mu_\alpha &= \mu_\alpha^1 + \mu_\alpha^3 + \mu_\alpha^5 + \cdots, \\ \mu_\alpha^n &= \sum_{m=0}^{n} \big(b_{nm}^\alpha O_n^m + c_{nm}^\alpha \Omega_n^m\big), \end{aligned} \tag{38}$$

and the ZFS Hamiltonian has the form

$$\begin{aligned} \mathrm{H}_{\mathrm{ZFS}} &= \mathrm{H}_{\mathrm{ZFS}}^2 + \mathrm{H}_{\mathrm{ZFS}}^4 + \mathrm{H}_{\mathrm{ZFS}}^6 + \cdots, \\ \mathrm{H}_{\mathrm{ZFS}}^n &= \sum_{m=0}^{n} \big(e_{nm} O_n^m + f_{nm} \Omega_n^m\big). \end{aligned} \tag{39}$$

Next we should find the decomposition coefficients in Eqs. (38) and (39). Using the projection property of irreducible tensor operators,[45]

$$\mathrm{Sp}\{\mathrm{T}_{\kappa p}\mathrm{T}_{\nu q}\} \sim \delta_{\kappa,\nu}\delta_{p,-q}, \tag{40}$$

we obtain

$$\begin{aligned} b_{nm}^\alpha &= \frac{\mathrm{Sp}\{\mu_\alpha O_n^{+m}\} + (-1)^m \mathrm{Sp}\{\mu_\alpha O_n^{-m}\}}{\mathrm{Sp}\{O_n^{+m} O_n^{-m}\}}, \\ c_{nm}^\alpha &= -i\,\frac{\mathrm{Sp}\{\mu_\alpha O_n^{+m}\} - (-1)^m \mathrm{Sp}\{\mu_\alpha O_n^{-m}\}}{\mathrm{Sp}\{O_n^{+m} O_n^{-m}\}}, \\ e_{nm} &= \frac{\mathrm{Sp}\{\mathrm{H}_{\mathrm{ZFS}} O_n^{+m}\} + (-1)^m \mathrm{Sp}\{\mathrm{H}_{\mathrm{ZFS}} O_n^{-m}\}}{\mathrm{Sp}\{O_n^{+m} O_n^{-m}\}}, \\ f_{nm} &= -i\,\frac{\mathrm{Sp}\{\mathrm{H}_{\mathrm{ZFS}} O_n^{+m}\} - (-1)^m \mathrm{Sp}\{\mathrm{H}_{\mathrm{ZFS}} O_n^{-m}\}}{\mathrm{Sp}\{O_n^{+m} O_n^{-m}\}}. \end{aligned} \tag{41}$$

To evaluate the traces in these expressions we should multiply the entering matrices (of the dimension $2\tilde{S} + 1$) and sum up the diagonal elements of the resulting matrix. The matrices of $O_n^{\pm m}$ are tabulated in several textbooks (e.g., in Refs. 2 and 20) and other versions of these operators have also been proposed in the last years.[74,75] We can evaluate the coefficients (41) in a simple way if define the Stevens operators $O_n^{\pm m}$ to be proportional to $Y_n^{\pm m}$ with the *same* proportionality coefficient k_n for all m. For instance, we can extract this coefficient from the relation $Y_n^0 = k_n O_n^0$, where O_n^0 is the original Stevens operator (see Table XV in Ref. 2 or Appendix V in Ref. 20), and define the other Stevens operators as follows:

$$O_n^{\pm m} = \frac{1}{k_n} Y_n^{\pm m}. \tag{42}$$

For these operators we can apply the Wigner-Eckart theorem (A1) for the evaluation of their matrix elements,

$$\begin{aligned} \langle \tilde{S}M | O_n^{\pm m} | \tilde{S}M' \rangle &= \langle \tilde{S} \parallel O_n \parallel \tilde{S} \rangle \mathrm{C}_{n\pm m \tilde{S}M'}^{\tilde{S}M}, \\ \langle \tilde{S} \parallel O_n \parallel \tilde{S} \rangle &= \frac{\langle \tilde{S}\tilde{S} | O_n^0 | \tilde{S}\tilde{S} \rangle}{\mathrm{C}_{n0\tilde{S}\tilde{S}}^{\tilde{S}\tilde{S}}} \\ &= (-1)^{2\tilde{S}+n} \frac{O_n^0(\tilde{S})}{\sqrt{2\tilde{S}+1}} \\ &\quad \times \frac{\sqrt{(2\tilde{S}-n)!(2\tilde{S}+n+1)!}}{(2\tilde{S})!}, \end{aligned} \tag{43}$$

where $O_n^0(\tilde{S})$ is the Stevens operator O_n^0 in which the spin matrix $\tilde{\mathrm{S}}_z$ (the only spin operator) is replaced by the number $\tilde{S}$. With the reduced matrix element given in (43) the denominator in Eqs. (41) also simplifies,[45]

$$\mathrm{Sp}\{O_n^{+m} O_n^{-m}\} = \frac{2\tilde{S}+1}{2n+1} |\langle \tilde{S} \parallel O_n \parallel \tilde{S} \rangle|^2. \tag{44}$$

1. *Zeeman g tensors for arbitrary pseudospins*

For the first rank contribution to the magnetic moment we will keep the conventional representation via the g tensor,

$$\mu_\alpha^1 = -\mu_{\mathrm{B}} \sum_\gamma g_{\alpha\gamma} \tilde{\mathrm{S}}_\gamma, \tag{45}$$

which is derived as follows. Multiplying (45) by a similar expression for μ_β^1 and taking the trace from the both sides we obtain the following expression for the Abragam-Bleaney tensor (20):

$$\mu_{\mathrm{B}}^2 \mathbf{G} = \frac{6}{\tilde{S}(\tilde{S}+1)(2\tilde{S}+1)} \mathbf{A}^1, \tag{46}$$

which is a generalization of the previous expressions for small pseudospins, Eqs. (21) and (28), over arbitrary $\tilde{S}$. The tensor $\mathbf{A}^1$ is defined as

$$A_{\alpha\beta}^1 = \frac{1}{2} \mathrm{Sp}\{\mu_\alpha^1 \mu_\beta^1\}, \tag{47}$$

i.e., has a similar form as the tensor $\mathbf{A}$ in Eq. (15) but involves only first rank components of the magnetic moment. In deriving Eq. (46) we made use of known expressions for the trace of the products of spin operators.[20,45] Having found the Abragam-Bleaney tensor the main magnetic axes correspond to a coordinate system where $\mathbf{G}$ or, equivalently, $\mathbf{A}^1$ is diagonal and are found by their diagonalization (cf. Eq. (17)),

$$\mathbf{R}_r{}^{-1} \mathbf{A}^1 \mathbf{R}_r = \tilde{\mathbf{A}}_{\mathrm{diag}}^1 \equiv \{\tilde{A}_{XX}^1, \tilde{A}_{YY}^1, \tilde{A}_{ZZ}^1\}, \tag{48}$$

while the main components of the g tensor are given by the expressions (cf. Eqs. (22) and (29))

$$g_i = \sqrt{G_{ii}} = \pm \frac{6}{\mu_{\mathrm{B}} \tilde{S}(\tilde{S}+1)(2\tilde{S}+1)} \sqrt{\tilde{A}_{ii}^1}, \quad i = X, Y, Z, \tag{49}$$

which are again, as in the case of small pseudospins, defined up to the sign.

2. ZFS D tensors for arbitrary pseudospins

The second rank contribution to the ZFS pseudospin Hamiltonian, $\mathrm{H}_{\mathrm{ZFS}}^2$, can be expressed as usually via the ZFS $\mathbf{D}$ tensor. We define the second rank Stevens operators $O_2^{\pm m}$ via the relation (42) with $k_2 = \sqrt{5/16\pi}$, which gives for O_2^0 the original definition[2,20,73] and via Eqs. (37) – the following Hermitean operators:

$$O_2^0 = 3\tilde{\mathrm{S}}_z^2 - \tilde{S}(\tilde{S}+1), \quad O_2^1 = \sqrt{\frac{3}{2}}(\tilde{\mathrm{S}}_z\tilde{\mathrm{S}}_x + \tilde{\mathrm{S}}_x\tilde{\mathrm{S}}_z),$$
$$O_2^2 = \sqrt{\frac{3}{2}}(\tilde{\mathrm{S}}_x^2 - \tilde{\mathrm{S}}_y^2), \tag{50}$$
$$\Omega_2^1 = \sqrt{\frac{3}{2}}(\tilde{\mathrm{S}}_z\tilde{\mathrm{S}}_y + \tilde{\mathrm{S}}_y\tilde{\mathrm{S}}_z), \quad \Omega_2^2 = \sqrt{\frac{3}{2}}(\tilde{\mathrm{S}}_x\tilde{\mathrm{S}}_y + \tilde{\mathrm{S}}_y\tilde{\mathrm{S}}_x).$$

These expressions (except O_2^0) differ from the originally defined[2,20] only by coefficients in front of brackets. Substituting them into Eq. (39) for $\mathrm{H}_{\mathrm{ZFS}}^2$ and comparing the resulting ZFS Hamiltonian with its usual formulation (33) in terms of the $\mathbf{D}$ tensor, we can relate its elements to the decomposition coefficients in (39),

$$D_{xx} = \sqrt{\frac{3}{2}} e_{22} - e_{20}, \quad D_{yy} = -\sqrt{\frac{3}{2}} e_{22} - e_{20}, \quad D_{zz} = 2e_{20},$$
$$D_{xz} = D_{zx} = \sqrt{\frac{3}{2}} e_{21}, \quad D_{yz} = D_{zy} = \sqrt{\frac{3}{2}} f_{21}, \tag{51}$$
$$D_{xy} = D_{yx} = \sqrt{\frac{3}{2}} f_{22}.$$

Using the *ab initio* ZFS matrix (32), defined now for arbitrary $\tilde{S}$, we can express via its elements the decomposition coefficients e_{2m} and f_{2m} by applying Eqs. (41), (43), and (44). Then substituting the obtained expressions into (51) we finally obtain

$$D_{xx} - D_{yy} = 2\sqrt{\frac{3}{2}} K_{\tilde{S}} \sum_M \big((\mathrm{H}_{\mathrm{ZFS}})_{M-2M} \mathrm{C}_{22\tilde{S}M-2}^{\tilde{S}M}$$
$$+ (\mathrm{H}_{\mathrm{ZFS}})_{M+2M} \mathrm{C}_{2-2\tilde{S}M+2}^{\tilde{S}M}\big),$$
$$D_{zz} = 2K_{\tilde{S}} \sum_M (\mathrm{H}_{\mathrm{ZFS}})_{MM} \mathrm{C}_{20\tilde{S}M}^{\tilde{S}M},$$
$$D_{xz} = D_{zx} = \sqrt{\frac{3}{2}} K_{\tilde{S}} \sum_M \big(-(\mathrm{H}_{\mathrm{ZFS}})_{M-1M} \mathrm{C}_{21\tilde{S}M-1}^{\tilde{S}M}$$
$$+ (\mathrm{H}_{\mathrm{ZFS}})_{M+1M} \mathrm{C}_{2-1\tilde{S}M+1}^{\tilde{S}M}\big), \tag{52}$$
$$D_{yz} = D_{zy} = -i\sqrt{\frac{3}{2}} K_{\tilde{S}} \sum_M \big((\mathrm{H}_{\mathrm{ZFS}})_{M-1M} \mathrm{C}_{21\tilde{S}M-1}^{\tilde{S}M}$$
$$+ (\mathrm{H}_{\mathrm{ZFS}})_{M+1M} \mathrm{C}_{2-1\tilde{S}M+1}^{\tilde{S}M}\big),$$
$$D_{xy} = D_{yx} = -i\sqrt{\frac{3}{2}} K_{\tilde{S}} \sum_M \big((\mathrm{H}_{\mathrm{ZFS}})_{M-2M} \mathrm{C}_{22\tilde{S}M-2}^{\tilde{S}M}$$
$$- (\mathrm{H}_{\mathrm{ZFS}})_{M+2M} \mathrm{C}_{2-2\tilde{S}M+2}^{\tilde{S}M}\big),$$

where

$$K_{\tilde{S}} = (-1)^{2\tilde{S}} \frac{5}{(2\tilde{S}+1)\sqrt{\tilde{S}(\tilde{S}+1)(2\tilde{S}-1)(2\tilde{S}+3)}}, \tag{53}$$

and we have in mind that the tensor is traceless, $D_{xx} + D_{yy} + D_{zz} = 0$. Substituting $\tilde{S} = 1$ and the corresponding Clebsch-Gordan coefficients into the above equations one can check that they reproduce the expressions (34) for the $\mathbf{D}$ tensor of a triplet (in order to make this comparison we should use the relations $(\mathrm{H}_{\mathrm{ZFS}})_{0-1} = -(\mathrm{H}_{\mathrm{ZFS}})_{10}$ and $(\mathrm{H}_{\mathrm{ZFS}})_{-10} = -(\mathrm{H}_{\mathrm{ZFS}})_{01}$ valid for $\tilde{S} = 1$). In a similar way we obtain the expressions for $D_{\alpha\beta}$ corresponding to higher pseudospins.

3. Symmetry aspects

The symmetry of the complex imposes constraints on the form of pseudospin Hamiltonian. The use of ITO greatly simplifies the task of constructing symmetry-invariant pseudospin Hamiltonians because the transformation properties of $Y_n^{\pm m}$ (and O_n^m and Ω_n^m) are well-known and documented in many textbooks, also the allowed forms of pseudospin Hamiltonians (see, e.g., in Ref. 20). For instance, the projection of the magnetic moment corresponding to $\tilde{S} = 3/2$ on the tetragonal axis Z of a cubic complex will only include the operators O_1^0 $(=\tilde{\mathrm{S}}_Z)$ and O_3^0,[73]

$$O_3^0 = 5\tilde{\mathrm{S}}_Z^3 - (3\tilde{S}(\tilde{S}+1) - 1)\tilde{\mathrm{S}}_Z, \tag{54}$$

because all other first and third rank ITOs will not be invariant under symmetry operations which leave $\tilde{\mathrm{S}}_Z$ unchanged. Thus,

μ_Z (and the other two components) is parametrized by only two real parameters. We stress that by applying the procedure given by Eqs. (38)–(41) we obtain automatically the necessary symmetry form of the pseudospin Hamiltonians because the corresponding *ab initio* ZFS and magnetic moment operators already include the effect of the symmetry. The simplest form of resulting pseudospin Hamiltonians is achieved in a coordinate system with axes parallel to the main axes of the tensor $\mathbf{A}^1$ in (47) because the latter always coincide with the symmetry axes of the complex.

B. Approximate definition of pseudospin for $\tilde{S} \geq 3/2$

The application of the described ITO technique for the construction of pseudospin Hamiltonians does not require, as a prerequisite, a rigorous assignment of *ab initio* wave functions to pseudospin eigenfunctions. The only constraint imposed on the basis set $\{\Psi_i\}$ is that it should obey proper time reversal requirements specific to a given pseudospin. Constructing such a basis set from the *ab initio* wave functions of a chosen manifold does not pose any problems (such a set is obtained automatically via the diagonalization of any $\hat{\mu}_\alpha$). Hence, in order to construct unique pseudospin Hamiltonians, we should use in the corresponding expressions of Sec. V A the matrices $\tilde{\mathrm{S}}_\alpha$ written in the basis of unique combinations of Ψ_i which should be put in correspondence to the pseudospin wave functions in a given coordinate system (see Sec. II A).

In order to find such combinations of $\{\Psi_i\}$ one needs first to identify a matrix operator (written in the basis of $\{\Psi_i\}$) which would correspond to any of $\tilde{\mathrm{S}}_\alpha$ or their linear (Hermitean) combination. Diagonalizing such a matrix will give us by definition a matrix $\tilde{\mathrm{S}}_{z'}$, corresponding to pseudospin projection on some unknown direction $\mathbf{z}'$,[76] and (as eigenfunctions) the combinations of $\{\Psi_i\}$ which can be put in correspondence to $|\tilde{S}M\rangle$, with M being the projection of pseudospin on $\mathbf{z}'$. Defining the three pseudospin matrices in this basis, we can project out the first-rank contributions μ_α^1 from *ab initio* matrices of magnetic moment operators μ_α and then to construct the tensor $\mathbf{A}^1$, Eq. (47). Diagonalizing the latter, Eq. (48), will yield the directions of the main magnetic axes X, Y, Z, and, finally, the eigenfunctions of μ_Z^1 will define the pseudospin in a unique way (see Sec. II A). This approach works automatically in the case of $\tilde{S} = 1/2$ and 1 because then the magnetic moment operators $\{\mu_\alpha\}$ are already linear combinations of $\{\tilde{\mathrm{S}}_\beta\}$, which allows us to use directly the tensor $\mathbf{A}$ in Eq. (15) to find the main magnetic axis and define the pseudospin as described in Secs. III and IV.

In the case of $\tilde{S} \geq 3/2$ higher tensorial components enter the decomposition of magnetic moments (see Table VII), therefore, we should first separate from μ_α the matrix corresponding to μ_α^1 only. In a general case, this is not possible because the projection (41) can only yield the necessary first rank tensors if the matrix μ_α is already written in the basis of suitable combinations of *ab initio* wave functions which can be assigned to $|\tilde{S}M\rangle$ in any coordinate system. Indeed, if we rewrite any first rank operator, e.g., the matrix $\tilde{\mathrm{S}}_{z'}$ in a new basis set corresponding to arbitrary unitary transformations of $|\tilde{S}M\rangle$ allowed by time inversion constraints then the resulting matrix will contain in its decomposition (41) not only matrices corresponding to the first rank but also to third and higher rank tensors depending on the size of pseudospin $\tilde{S}$. The outlined problem is actually the major one for the definition of pseudospin in a general case and will be tackled separately.[44]

Although not applicable for the identification of pseudospin in a general case, the described ITO procedure can be used for approximate definition of pseudospin and construction on this basis of pseudospin Hamiltonians, in the cases when first rank tensor contributions to the magnetic moment can be considered dominant. This is certainly the case of weak and sometimes intermediate spin-orbit coupling effects, and therefore the method described in this subsection should be applicable to the majority of transition metal complexes, some lanthanide, e.g., Gd(III), and actinide containing complexes.

In the decomposition of magnetic moment operators (38), consider μ_α^1 to be quantities of zeroth order and μ_α^n, $n \geq 3$, of first order of smallness. Then using the relation (40) we can calculate the tensor $\mathbf{A}$ defined in Eq. (15) as follows:

$$A_{\alpha\beta} = \frac{1}{2}\mathrm{Sp}\{\mu_\alpha^1\mu_\beta^1\} + \frac{1}{2}\mathrm{Sp}\{\mu_\alpha^3\mu_\beta^3\} + \frac{1}{2}\mathrm{Sp}\{\mu_\alpha^5\mu_\beta^5\} + \cdots. \tag{55}$$

The first term in the right hand side of this equation is just $A_{\alpha\beta}^1$, Eq. (47), a quantity of zeroth order of smallness, while all other terms are quantities of second order of smallness. Then the higher rank contributions can be considered negligible and we can equate in a good approximation the tensor $\mathbf{A}^1$ with $\mathbf{A}$ which is calculated by substituting the *ab initio* matrices μ_α in Eq. (15). Then using Eq. (46) we can find the Abragam-Bleaney tensor, which yields the main magnetic axes X, Y, Z after diagonalization, Eq. (48).

In the next step, we construct the matrix corresponding to the magnetic moment along the main magnetic axis Z,

$$\mu_Z = \sum_\alpha (R_r)_{Z\alpha}\mu_\alpha, \tag{56}$$

written in arbitrary basis of *ab initio* wave functions, which after diagonalization gives approximate eigenfunctions of $\tilde{\mathrm{S}}_Z$. Note that since the effects of spin-orbit coupling are not considered to be strong, there is no problem with the signs of the g_i factors (and with the assignment of the eigenfunctions of μ_Z to $|\tilde{S}M\rangle$) – they are always positive.

Having established the suitable combinations of *ab initio* wave functions which can be put in correspondence to eigenfunctions of $\tilde{\mathrm{S}}_Z$, we rewrite in their basis the *ab initio* μ_α and $\tilde{\mathrm{H}}_{\mathrm{ZFS}}$ matrices and apply the projection (41) to construct the corresponding pseudospin Hamiltonians in the ITO representations via Eqs. (38) and (39). For the first rank contribution to the magnetic moment (and to the $\tilde{\mathrm{H}}_{\mathrm{Zee}}$) we can apply again Eqs. (47)–(49) to obtain its description via the $\mathbf{g}$ tensor, while for the second rank contribution to $\tilde{\mathrm{H}}_{\mathrm{ZFS}}$ we can apply Eqs. (52) and (53) to calculate the $\mathbf{D}$ tensor.

It follows from the construction of this procedure that the relative errors in the definition of pseudospin Hamiltonians (compared to the case of a rigorous definition of pseudospin) are of the first order of smallness. This means that the procedure is quite reliable for the case of complexes with weak and intermediate spin-orbit coupling effects.

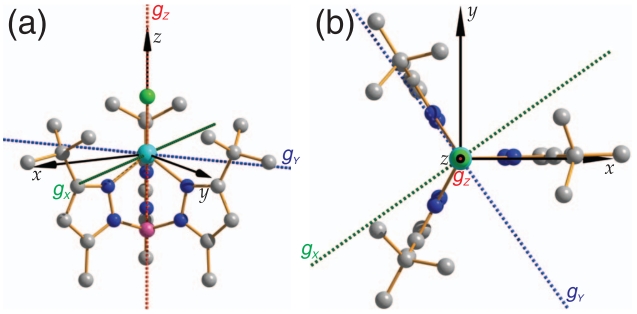

FIG. 8. Orientation of the main magnetic axes (X_m, Y_m, Z_m) (dashed line) of the ground quartet (pseudospin $\tilde{S} = 3/2$) of the $\mathrm{Tp^{t\text{-}Bu,Me}CoCl}$ complex with respect to the molecular frame shown from a side (a) and along the threefold axis (b). Color scheme: Co-cyan, N-blue, C-grey, B-pink. Hydrogens were omitted for clarity.

C. Example: *D*, *g* and higher rank Zeeman tensors for a high-spin Co(II) complex

An example of a pseudospin $\tilde{S} = 3/2$ is offered by the Co(II) ion in a pseudo-tetrahedral environment. The electronic configuration of Co(II) is d^7, while in a tetrahedral ligand field the ground electronic state is an orbitally nondegenerate quartet $^4A_2$. For a symmetry lower than cubic, the mixing of ground and excited molecular terms through the spin-orbit interaction leads to a zero-field splitting of the $^4A_2$ quartet in two Kramers doublets, with relatively small energy separation. In such a situation, an applied magnetic field will mix efficiently both Kramers doublets, so the Zeeman splitting seen, e.g., in EPR measurements should be rationalized by the pseudospin $\tilde{S} = 3/2$.

Krzystek *et al.*[90] have studied experimentally a series of mononuclear Co(II) complexes where the metal ion is tetrahedrally coordinated, while preserving the local symmetry around the metal ion close to C_{3v} (Fig. 8). Due to relatively small zero-field splitting in these complexes, it was possible to perform high-field EPR for them, which were rationalized using the "spin" Hamiltonian S=3/2.[90] We have studied the magnetic anisotropy in one complex from this series, the $\mathrm{Tp^{t\text{-}Bu,Me}CoCl}$ (Fig. 8), using the *ab initio* methodology developed in Sec. V (see Appendix B 6 for computational details). Table VIII shows the energies of the obtained low-lying molecular terms and Kramers doublets, while Table IX shows the *g* and *D* tensors corresponding to the lowest two Kramers doublets described by the pseudospin $\tilde{S} = 3/2$.

TABLE VIII. Energies of the lowest spin-free states and the energies of the lowest spin-orbit Kramers doublets of the $\mathrm{Tp^{t\text{-}Bu,Me}CoCl}$ complex.

Atomic term	Spin free states CASSCF	Spin free states MS-CASPT2	Kramers doublets CASSCF	Kramers doublets MS-CASPT2	Exp. (Ref. 90)
$^4A_2$	0.000	0.000	0.000	0.000	
	1975.721	1895.580	31.991	29.004	23.04
$^4T_2$	1976.235	1923.913	1843.672	1702.771	
	4740.192	4183.332	2037.927	1927.403	
	5486.174	5472.280	2150.638	2102.722	
$^4T_1$	5486.650	5706.704	2311.952	2311.918	
	9592.976	10 783.282	4885.872	4338.544	

TABLE IX. Main values and main axes of the *g* and *D* tensors of the $\mathrm{Tp^{t\text{-}Bu,Me}CoCl}$ complex.

	Using CASSCF/RASSI results				
	g_I	X_m	Y_m	Z_m	
g_X	2.4259	0.6033	− 0.7974	0.0004	2.35
g_Y	2.4258	− 0.7974	− 0.6033	− 0.0000	2.35
g_Z	2.2585	− 0.0002	0.0002	0.9999	2.24
Sign of $g_X g_Y g_Z$	+				
	D_I	X_a	Y_a	Z_a	
D_X	− 5.336	0.6119	− 0.7909	0.0004	
D_Y	− 5.321	− 0.7909	− 0.6119	− 0.0001	
D_Z	10.657	− 0.0003	0.0003	0.9999	
D	15.986				11.52
E	− 0.007				0.141
	Using MS-CASPT2/RASSI results				
	g_I	X_m	Y_m	Z_m	
g_X	2.4087	− 0.3247	0.9375	0.1244	2.35
g_Y	2.3887	− 0.9443	− 0.3287	0.0121	2.35
g_Z	2.2700	0.0523	− 0.1136	0.9921	2.24
Sign of $g_X g_Y g_Z$	+				
	D_I	X_a	Y_a	Z_a	
D_X	− 5.550	− 0.2530	0.9526	0.1684	
D_Y	− 4.080	− 0.9646	− 0.2617	0.0313	
D_Z	9.631	0.0739	− 0.1546	0.9852	
D	14.446				11.52
E	− 0.735				0.141

As we can see from Table VIII, the ground quartet state $^4A_2$ is well separated from the lowest excited states by a gap of ca. 2000 cm^{-1}. Both excited orbital triplets are split as $^4E + {}^4A$ in axial symmetry. The spin-orbit constant (ζ) of the Co(II) free ion is about 400–450 cm^{-1},[72] which means that the mixing of the excited states through the spin-orbit coupling will be relatively small for this complex. Indeed, the zero field splitting of the ground quartet state $^4A_2$ is obtained as 29–32 cm^{-1}, which is close to the experimental value of 23.04 cm^{-1}. The *g* tensor of the ground state pseudospin $\tilde{S} = 3/2$ compares well with the experimental values.

The calculated higher rank terms for the Zeeman pseudospin Hamiltonian are given in Table X. The results show that the third rank terms, allowed for $\tilde{S} = 3/2$ (see Table VII) are much smaller than the conventional first order contributions, which is what to be expected because the spin-orbit coupling effects are not strong in this complex.

An important aspect revealed by Tables VIII and IX is that the dynamical correlation treated here within MS CASPT2 method,[65] while reducing the energy gap between the lowest Kramers doublets (the ZFS), induces an artificial splitting of the excited ^4E orbital doublets, which destroys the equivalence of the g_X and g_Y components of the *g* tensor expected in trigonal symmetry. The same happens to the D_X and D_Y components of the *D* tensor meaning that the MS CASPT2 results should be treated with caution. This drawback can be in principle overcome by going beyond the MS CASPT2 approximation, e.g., by treating the dynamical correlation variationally like in the difference dedicated configuration interaction (DDCI) approach.[91] However, for the present relatively

TABLE X. Calculated parameters of 3rd rank Zeeman tensor, b_{3m}^{α} and c_{3m}^{α} (Eq. (41)) for the Tp$^{\text{t-Bu,Me}}$CoCl complex.

m	α	b_{3m}^{α}	c_{3m}^{α}
0	x	0.0000077793	0.0000000000
	y	0.0000004825	0.0000000000
	z	− 0.0023959922	0.0000000000
1	x	− 0.0010906510	0.0000000000
	y	− 0.0000037666	− 0.0010954168
	z	0.0000000000	0.0000000000
2	x	− 0.0063995409	0.0019040963
	y	0.0019026788	0.0064103986
	z	0.0000000000	− 0.0000000000
3	x	− 0.0000007166	− 0.0000001368
	y	0.0000006361	0.0000053052
	z	− 0.0000000000	0.0000000000

large compound such calculations would be much more demanding than MS CASPT2.

One can see from Table IX that the main magnetic axes (X_m, Y_m, Z_m) are obtained very close to the main anisotropy axes (X_a, Y_a, Z_a) which is the result of high symmetry of the complex. In particular, the axes corresponding to g_Z and D_Z are almost parallel to the symmetry axis C_3 of the complex (Fig. 8). The calculated D and E values are in reasonable agreement with the experimental values. The discrepancy can be partly attributed to the effects of the crystal environment, which were not considered in our calculations.

VI. CONCLUSIONS

The phenomenological magnetic Hamiltonians have been used for many decades to rationalize the experimental magnetic data of complexes. These Hamiltonians, despite the widespread name "spin Hamiltonians," are formulated in terms of pseudospins.[2,20] The parameters of pseudospin Hamiltonians are extracted from experiment by comparing their predictions with the measured energies and the transition probabilities. At the same time the nature of pseudospin cannot be revealed from this comparison. Modern *ab initio* methods can change qualitatively this situation. First, they can provide us with the explicit form of the multielectronic wave functions which form the functional space for the pseudospin operators. Second, the detailed knowledge about these wave functions can be used for the definition of pseudospin, when a one-to-one correspondence between these multielectronic states and the pseudospin eigenfunctions is achieved in a given coordinate system. On this basis a rigorous construction of pseudospin Hamiltonians can be done. In the present work, we have described the general methodology for nonperturbative derivation of pseudospin Hamiltonians and provided the working expressions for their parameters in terms of *ab initio* calculated quantities. The main points are the following:

(1) Two basic requirements are imposed on the pseudospin for its unique definition. First, the symmetry-allowed spatial transformations of the multielectronic wave functions, which are put in correspondence to the pseudospin eigenfunctions $|\tilde{S}M\rangle$, should be similar to the transformations of the corresponding eigenfunctions of a true angular momentum, e.g., the true spin eigenfunctions $|SM\rangle$. Second, the part of Zeeman Hamiltonian which is linear in pseudospin operators (described by the g tensor) should acquire a diagonal form, Eq. (8), when written in a coordinate system related to the main magnetic axes of the complex.

(2) In a general case of arbitrary spin-orbit coupling and lack of point symmetry there is still a number of constraints imposed on the pseudospin eigenfunctions by the time reversal symmetry, which reduce drastically the possible linear combinations of *ab initio* wave functions which can be put in correspondence to $|\tilde{S}M\rangle$, i.e., the dimensionality (the number of independent continuous parameters) of the allowed unitary transformations. These unitary transformations can be of rotational type or of general type. The former look similarly to the unitary transformation of true momentum eigenfunctions induced by the rotations of the coordinate system. This is via these transformations that we can identify the rotation of the pseudospin coordinate system.

(3) The minimal possible indeterminacy of pseudospin corresponds to situations when the allowed unitary transformations are only of rotational type. This is the case of pseudospins $\tilde{S} = 1/2$ and $\tilde{S} = 1$. Their eigenfunctions can be assigned in a general case (without using additional symmetry relations) only up to the sign of the pseudospin projection M on one of the magnetic axes, which is equivalent to the freedom to rotate the pseudospin coordinate system by π around each of the three main magnetic axes. For $\tilde{S} \geq 3/2$ the unitary transformations allowed by the time reversal symmetry contain more than three continuous parameters. A practical approach to define the pseudospin in an approximative way using the **A** tensor, Eq. (15), has been devised. This approach should be reliable for complexes with weak and intermediate spin-orbit coupling effect. A general approach valid for $\tilde{S} \geq 3/2$ and any strength of spin-orbit coupling effect, based on the principle of adiabatic connection, will be described elsewhere.[44]

The described methodology has been implemented in the routine SINGLE_ANISO which recently become a module of MOLCAS-7.6 package.[39] Although with this methodology the pseudospin description can be applied to any group of chosen spin-orbit levels of the complex, in order to be insightful it should refer to a "natural" group of levels which can be seen as originating from a given S-term, J-term, or a degenerate irreducible representation of the complex (Γ-term). Choosing such a manifold of states is a matter of intuition and depends on the problem we solve. At the same time care should be taken that the resulting pseudospin Hamiltonians are physically correct. For instance, choosing an even number of states in a non-Kramers complex (with even number of electrons) will require half-integer pseudospins and will result in nonphysical pseudospin Hamiltonians, a situation which should be avoided.[77] Another situation when a simple pseudospin description can face problems is encountered for (quasi)degenerate terms with strongly unquenched orbital momentum. Recent examples are ${}^{2S+1}$E-terms in high-spin trigonal Fe(II) complexes[78,79] and a high-spin tetragonal Co(II) complex[80] and probably other less symmetric high-spin Fe (II) complexes,[81,82] all exhibiting a single-molecule magnet behavior. Phenomenological crystal field analysis[83] and *ab initio* calculations[34,84] of the electronic structure of the trigonal high-spin Fe(II) complexes have shown that the ligand-field splitting of the orbital E components is of the order or smaller than the spin-orbit coupling, while the separation of the entire manifold of ${}^{2S+1}$E states from the excited ones is more than 5000 cm^{-1}.[34] In such a situation, an appropriate description should involve all states originating from this term, which should be done via orbital-pseudospin Zeeman and ZFS Hamiltonians. The *ab initio* derivation of orbital-pseudospin Hamiltonians will be given in a next publication. Such an approach represents a generalization of pseudospin Hamiltonian description and formally resembles the well-known Kugel-Khomskii Hamiltonians[85] describing the isotropic exchange interactions between orbitally degenerate metal sites. The *ab initio* simulations of such interactions have been already undertaken in the past for a Ti(III) dimer complex.[86]

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APPENDIX A: THE WIGNER-ECKART THEOREM

The advantage of using the irreducible tensor operators, $\hat{\mathrm{T}}_{\kappa q}$, where κ is the rank and q is the row index, allow to apply the Wigner-Eckart theorem[2,3] for the calculations of their matrix elements between eigenfunctions of arbitrary angular momentum $|JM\rangle$,

$$\langle J_1 M_1 | \hat{\mathrm{T}}_{\kappa q} | J_2 M_2 \rangle = \langle J_1 \parallel \hat{\mathrm{T}}_{\kappa} \parallel J_2 \rangle \mathrm{C}^{J_1 M_1}_{\kappa q J_2 M_2}, \tag{A1}$$

where $\mathrm{C}^{J_1 M_1}_{\kappa q J_2 M_2}$ is the Clebsch-Gordan coefficient[45] and $\langle J_1 \| \hat{\mathrm{T}}_{\kappa} \| J_2 \rangle$ is a common constant for all $\{M_1, q, M_2\}$ called reduced matrix element. Because of the relation $\mathrm{C}^{J_1 M_1}_{\kappa q J_2 M_2} = (-1)^{J_1+J_2+\kappa} \mathrm{C}^{J_1 M_1}_{J_2 M_2 \kappa q}$,[45] we can also use $\mathrm{C}^{J_1 M_1}_{J_2 M_2 \kappa q}$ in the right hand side of Eq. (A1) (the new reduced matrix element will correspond to the one in (A1) multiplied by $(-1)^{J_1+J_2+\kappa}$).

The Cartesian components of spin can be written as combinations of components of irreducible tensor of first rank $\hat{\mathrm{S}}_{1m}$, $m = -1, 0, 1$ (they are just cyclic coordinates of a vector[45]),

$$\begin{aligned} \hat{\mathrm{S}}_x &= \frac{1}{\sqrt{2}}(-\hat{\mathrm{S}}_{11} + \hat{\mathrm{S}}_{1-1}), \\ \hat{\mathrm{S}}_y &= \frac{i}{\sqrt{2}}(\hat{\mathrm{S}}_{11} + \hat{\mathrm{S}}_{1-1}), \\ \hat{\mathrm{S}}_z &= \hat{\mathrm{S}}_{10}. \end{aligned} \tag{A2}$$

These relations are equally valid for any other angular momentum operator and also for pseudospin operators $\tilde{\mathrm{S}}_\alpha$, given their coincidence with the matrices of the corresponding true spin operators $\tilde{\mathrm{S}}_\alpha$.

APPENDIX B: DETAILS OF *AB INITIO* CALCULATIONS

1. General computational approach

All *ab initio* calculations were done within the MOLCAS-7.6 program package.[39] Within the applied method, the relativistic effects are taken into account in two steps, both based on the Douglas-Kroll Hamiltonian.[40,41] In the first step, scalar relativistic effects are already taken into account in the basis set generation. All employed basis sets contain relativistic correction and were taken from the standard ANO-RCC[68,69] and ANO-DK3[70] basis set libraries available within the MOLCAS program package. In cases when the number of basis functions of the calculated system was more than 550 basis set functions, in order to save disc space and speed-up the calculation, the Cholesky decomposition of bielectronic integrals was employed, with a threshold of 0.5×10^{-7}.[39] Further, spin-free eigenstates were obtained in the complete active space self-consistent field (CASSCF) method,[63] as implemented in MOLCAS-7.6.[39] In the case of lanthanides the active space of the CASSCF included all electrons spanning seven last shell of orbitals. In the cases of Ni^{2+} and Co^{2+} the active space included, besides the initial set of five 3d orbitals, another set of five 3d' orbitals in order to account for the double shell effect, which was proved to be important for the atoms from the second part of the first row of transitional metals.[71,87] The dynamical correlation was included in the next step, by the CASPT2 method,[64–66] keeping the standard IPEA shift (0.25), and imposing an additional imaginary shift (0.1) to exclude any possible intruder state problems. The spin-orbit coupling is considered in the next step within the RASSI method,[42] which uses spin-free eigenstates as input, and in their basis computes the matrix elements of the magnetic moment. The spin-orbit coupling interaction within RASSI program is considered in the atomic mean field approximation.[41,67] In the last step, the SINGLE_ANISO program computes all magnetic properties and parameters of the pseudo-spin Hamiltonians on the basis of the above calculated spin-orbit eigenstates and matrix elements of the magnetic moment. This method has been previously applied for the elucidation of the local electronic and magnetic properties of other lanthanide complexes.[37,38]

The molecular structures of the calculated molecules were taken directly from the x-ray experiments and were not further optimized. The reduced fragments were obtained by deleting a part of the molecule, with subsequent saturation of all remaining bonds by hydrogens.

2. Computational details for Dy(III)

The entire structure of the DyZn$_3$ molecule was considered for the *ab initio* calculation. Figure 1 shows the structure of the calculated molecule. For the [Dy(H$_2$DABPH)$_2$]$^{3+}$ complex, two structural approximations were employed A – the reduced fragment, where the distant phenyl groups of the

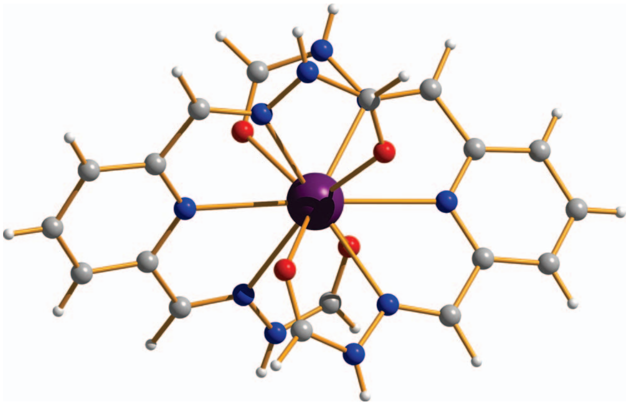

FIG. 9. Structure of the calculated Dy(III) fragment of the $[Dy(H_2DABPH)_2]^{3+}$ complex within the computational approximation A. Color scheme: Dy-violet, O-red, N-blue, C-grey, H-white.

ligand were replaced by hydrogens, and B – the entire molecule. Figure 9 shows the calculated structure of the fragment A.

Employed contractions of the basis sets:

Dy.ANO-RCC...8s7p5d4f2g1h.
Zn.ANO-RCC...5s4p2d1f.
O.ANO-RCC...4s3p2d. (close)
O.ANO-RCC...3s2p. (distant)
N.ANO-RCC...4s3p2d. (close)
N.ANO-RCC...3s2p. (distant)
C.ANO-RCC...4s3p2d. (close)
C.ANO-RCC...4s3p. (distant)
H.ANO-RCC...3s1p. (close)
H.ANO-RCC...2s. (distant)

Active space: 9 electrons spanning 7 orbitals of the 4f shell of the Dy^{3+} ion.

Number of roots considered within the CASSCF: 21 sextets, 224 quartets, and 490 doublets (all available roots).

Dynamical correlation within the CASPT2: not considered.

Number of roots mixed by the spin-orbit coupling in RASSI: 21 sextets, 128 quartets, and 130 doublets (due to the hardware limitation).

3. Computational details for Yb(III)

Figure 10 shows the structure of the calculated fragment within the computational model A. Within the computational model B the entire molecular structure was considered.

Employed contractions of the basis sets:

Yb.ANO-RCC...7s6p4d3f1g.
O.ANO-RCC...3s2p1d. (only for the close atoms, directly connected to Yb)
O.ANO-DK3.Tsuchiya.12s8p.2s1p. (all other atoms)
C.ANO-DK3.Tsuchiya.12s8p.2s1p.
N.ANO-DK3.Tsuchiya.12s8p.2s1p.
H.ANO-DK3.Tsuchiya.6s.1s.

Active space: 13 electrons spanning 7 orbitals of the 4f shell of the Yb^{3+} ion.

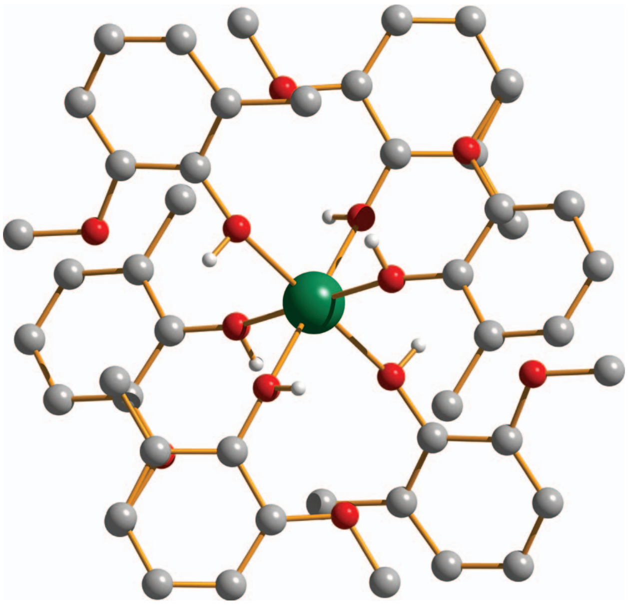

FIG. 10. Structure of the calculated Yb(III) fragment within the computational approximation A. Color scheme: Yb-sea green, O-red, C-grey, H-white. Distant hydrogens of the ligand were omitted for clarity.

Number of roots considered within the CASSCF: 7 doublets emerging from the ^2F ionic multiplet.

Dynamical correlation within the CASPT2: not considered.

Number of roots mixed by the spin-orbit coupling in RASSI: all roots available (i.e., 7 doublets emerging from the ^2F ionic multiplet).

The obtained orientations of the main anisotropy axes g_X, g_Y, and g_Z within the computational model A is very close to those obtained within the computational model B, presented in Fig. 3. The deviation angles are 4.6° for g_X and g_Y, and 5.4° for g_Z.

4. Computational details for Ni(II)

The entire molecular structure was considered.

Employed contractions of the basis sets:

Co.ANO-RCC...6s5p3d2f1g.
N.ANO-RCC...4s3p2d1f.
O.ANO-RCC...4s3p2d1f.
C.ANO-RCC...3s2p.
H.ANO-RCC...2s.

Active space: 8 electrons spanning 10 ($3d$+$3d$) orbitals of the Ni^{2+} ion.

Number of roots considered within the CASSCF: 10 triplet and 15 singlet states.

Dynamical correlation within the CASPT2: considered.

Number of roots mixed by the spin-orbit coupling in RASSI: all roots available (i.e., 10 triplet and 15 singlet states).

5. Computational details for U(IV)

The structure of UO_2 at high temperature is the fcc fluorite, with the lattice parameter $a_0 = 5.470$ Å. Each U^{4+} ion is surrounded by eight oxygen atoms. The calculated cluster is a $[UO_8]^{12-}$ anion, surrounded by four shells of point charges describing the Madelung potential. The distortions were employed only to the first coordinated oxygens and to the first shell of point charges (1252 pc).

Employed contractions of the basis sets:

U.ANO-RCC...9s8p6d4f2g1h.
O.ANO-RCC...4s3p2d.

Active space: 3 electrons spanning 7 orbitals of the 5f shell of the U^{4+} ion.

Number of roots considered within the CASSCF: 21 triplets and 28 singlets states.

Dynamical correlation within the CASPT2: not considered.

Number of roots mixed by the spin-orbit coupling in RASSI: all roots available (i.e., 21 triplets and 28 singlets states).

TABLE XI. Proportionality coefficients between the present ITO and the Stevens operators (Eq. (C1)).

n	m	k_n^m
2	0	1
	1	$\sqrt{2\cdot 3}$
	2	$\sqrt{\frac{3}{2}}$
3	0	1
	1	$\frac{\sqrt{3}}{2}$
	2	$\sqrt{\frac{3\cdot 5}{2}}$
	3	$\frac{\sqrt{5}}{2}$
4	0	1
	1	$2\sqrt{5}$
	2	$\sqrt{10}$
	3	$2\sqrt{5\cdot 7}$
	4	$\sqrt{\frac{5\cdot 7}{2}}$
5	0	1
	1	$\sqrt{\frac{3\cdot 5}{2}}$
	2	$\sqrt{2\cdot 3\cdot 5\cdot 7}$
	3	$\sqrt{\frac{5\cdot 7}{2}}$
	4	$3\sqrt{\frac{5\cdot 7}{2}}$
	5	$\frac{3\sqrt{7}}{2}$
6	0	1
	1	$\sqrt{2\cdot 3\cdot 7}$
	2	$\frac{\sqrt{3\cdot 5\cdot 7}}{2}$
	3	$\sqrt{3\cdot 5\cdot 7}$
	4	$3\sqrt{\frac{7}{2}}$
	5	$3\sqrt{7\cdot 11}$
	6	$\frac{\sqrt{3\cdot 7\cdot 11}}{2}$

6. Computational details for Co(II)

The entire molecular structure was considered.

Employed contractions of the basis sets:

Co.ANO-RCC...6s5p3d2f1g.
Cl.ANO-RCC...5s4p2d1f.
N.ANO-RCC...4s3p2d1f.
B.ANO-RCC...3s2p1d.
C.ANO-RCC...3s2p1d.
H.ANO-RCC...2s1p.

Active space: 7 electrons spanning 10 ($3d$+$3d'$) orbitals of the Co^{2+} ion.

Number of roots considered within the CASSCF: 10 quartet and 40 doublet states.

Dynamical correlation within the CASPT2: considered.

Number of roots mixed by the spin-orbit coupling in RASSI: all roots available (i.e., 10 quartet and 40 doublet states).

APPENDIX C: RELATIONS BETWEEN THE PRESENT ITO AND STEVENS OPERATORS

The ITO operators O_n^m and Ω_n^m used here are simply related to the conventional Stevens operators $O_n^m(St)$ and $\Omega_n^m(St)$,

$$\begin{aligned} O_n^m &= k_n^m O_n^m(St), \\ \Omega_n^m &= k_n^m \Omega_n^m(St). \end{aligned} \tag{C1}$$

The proportionality coefficients k_n^m are listed in Table XI.

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