Negative g Factors, Berry Phases, and Magnetic Properties of Complexes

L. F. Chibotaru and L. Ungur

Division of Quantum and Physical Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

(Received 25 July 2012; published 11 December 2012)

It is shown that the sign of the product of three Zeeman splitting factors corresponding to the main magnetic axes defines the sign of the Berry phase of a (pseudo) spin in an applied magneic field. *Ab initio* calculations show that $g_X g_Y g_Z < 0$ is often the case for lanthanide and transition metal complexes, while we prove that it is never achieved in S complexes with dominant second-order magnetic anisotropy. In the case of polynuclear compounds, it is argued that the signs of *individual* g_i, $i = X, Y, Z$, on each metal site can be extracted from experiment.

DOI: 10.1103/PhysRevLett.109.246403 PACS numbers: 71.70.Ej, 31.15.aj, 32.60.+i

The effects of magnetic anisotropy in metal complexes and adatoms have been the object of intensive investigations in the last decade [1,2] in view of their potential applications in storage and information processing technologies [3–9]. These effects arise due to the interplay of the spin-orbit coupling on the metal sites and the crystal (ligand) field from surrounding atoms [10]. One of the effects produced by these joint interactions is the change of sign of the Zeeman spliting factors (g factors) in some complexes. While at a first glance the signs of the g factors seem to be unimportant, Pryce has shown [11] that the sign of the product of the three main components of the g tensor, $g_X g_Y g_Z$, determines the direction of precession of the magnetic moment around the applied field. The latter can be probed directly in resonance experiments with circularly polarized radiation (Sec. 2, Ch. III, in Ref. [10]). This was first demonstrated for $\mathrm{NpF_6}$ by using circularly polarized light [12], where it was found that $g_X g_Y g_Z < 0$. The sign of this product was also deduced relative to the sign of the hyperfine coupling [11], in which way it was found negative for $\mathrm{PaCl_6^{2-}}$ [13]. Later, a negative product of g_i factors was found for $\mathrm{UF_6^-}$ in different environments by using circularly polarized EPR [14].

Despite experimental proof of its manifestation [11–14] and the demonstration of the possibility of its unequivocal determination from *ab initio* calculations [15], the sign of the g factors receives yet little attention. However, a recent investigation of magnetism of a $\mathrm{Co_5}$ complex [16] has required the assumption of negative g factors on some $\mathrm{Co^{2+}}$ ions. This example, which will undoubtedly be followed by many others, prompts for a deeper understanding of the origin of negative g factors and their implications for magnetic properties of complexes. These questions are addressed in the present Letter.

Consider a metal complex or a single-metal fragment with arbitrary spin-orbit coupling. In a general case of low-symmetric complexes, no angular momentum is conserved, so an arbitrary multiplet involving N states is described by a fictive spin (pseudospin) $\tilde{S}$ whose value is chosen from $2\tilde{S} + 1 = N$. The simplest relation between the components of magnetic moment in a given multiplet, $\{\mu_\alpha\}$, and the components of the pseudospin operators, $\{\tilde{S}_\alpha\}$ [17], is linear and can always be brought to a diagonal form:

$$\mu_i = -\mu_B g_i \tilde{S}_i, \tag{1}$$

in a coordinate system coinciding with the main magnetic axes, $i = X, Y, Z$ [10]. The multiplet $\tilde{S}$ interacts with an applied magnetic field $\mathbf{B} = \{B_X, B_Y, B_Z\}$ via the Zeeman Hamiltonian:

$$H_{\mathrm{Zee}} = -\sum_i \mu_i B_i, \tag{2}$$

which leads, in particular, to the precession of the magnetic moment around the applied field in the direction defined by the sign of the product $g_X g_Y g_Z$ [11].

While the equactions of motion for μ_i involve the product of three g factors, it is interesting to see whether it is also the case for the Berry's phase accumulated along a given closed path in the parameter ($\mathbf{B}$) space. The Hamiltonian (2) is diagonalized by passing to a quantization axis z' with the coordinates

$$\langle i|z'\rangle = \frac{g_i \zeta_i}{g_{\mathbf{B}}}, \qquad i = X, Y, Z, \\ g_{\mathbf{B}} = \sqrt{g_X^2 \zeta_X^2 + g_Y^2 \zeta_Y^2 + g_Z^2 \zeta_Z^2}, \tag{3}$$

where $\{\zeta_i\}$ are directional cosines of $\mathbf{B}$. The eigenfunctions $|\tilde{S}M\rangle$ of (2) are characterized by a definite projection of pseudospin on the z' axis, i.e., are eigenfunctions of the pseudospin operator $\tilde{S}_{z'} = \sum_i \langle i|z'\rangle \tilde{S}_i$. The corresponding eigenvalues are given by [10]

$$E_M = \mu_B g_{\mathbf{B}} M B, \tag{4}$$

where $B = |\mathbf{B}|$. The phase change $\gamma_M(C)$ of an eigenstate $|\tilde{S}M\rangle$, when the vector of applied field $\mathbf{B}$ is varied over a closed path C, is calculated as

$$\gamma_M(C) = -Mg_Xg_Yg_Z \times \iint_C \frac{d\Omega}{(g_Z^2\cos^2\theta + g_X^2\sin^2\theta\cos^2\phi + g_Y^2\sin^2\theta\sin^2\phi)^{3/2}}, \tag{5}$$

where θ, ϕ are spherical angles in the XYZ coordinate system with the origin at the degeneracy point ($\mathbf{B} = 0$) and $d\Omega$ is the element of a solid angle measured from this origin. In the case $|g_i| = g$, Eq. (5) reduces to

$$\gamma_M(C) = -\mathrm{sign}\{g_Xg_Yg_Z\}M\Omega(C), \tag{6}$$

where $\Omega(C)$ is the solid angle that contour C subtends at $\mathbf{B} = 0$. Equation (6) differs from the corresponding Berry's expression for an isotropic spin [18] only by the sign factor $\mathrm{sign}\{g_Xg_Yg_Z\}$. In the case of arbitrary g_i, the Berry's phase, Eq. (5), will not be simply proportional to the solid angle $\Omega(C)$; however, its sign will always be determined by the sign of the product $g_Xg_Yg_Z$.

Given the physical meaning of $\mathrm{sign}\{g_Xg_Yg_Z\}$, one might expect that it should be determined via measurable quantities. Indeed, taking the commutation of the matrices of magnetic moments μ_X and μ_Z given by Eq. (1) and having in mind that the pseudospin matrices commute similarly to the ordinary spin matrices [17], we obtain

$$\frac{g_Xg_Z}{g_Y} = -\frac{i}{\mu_B}\frac{\mu_X\mu_Z - \mu_Z\mu_X}{\mu_Y} = -\frac{i}{\mu_B}\frac{\sum_l(\langle\Psi_n|\hat{\mu}_X|\Psi_l\rangle\langle\Psi_l|\hat{\mu}_Z|\Psi_m\rangle - \langle\Psi_n|\hat{\mu}_Z|\Psi_l\rangle\langle\Psi_l|\hat{\mu}_X|\Psi_m\rangle)}{\langle\Psi_n|\hat{\mu}_Y|\Psi_m\rangle}. \tag{7}$$

The sign of this expression coincides with the sign of $g_Xg_Yg_Z$, while it is written only via the matrix elements of magnetic moments on the wave functions characterizing a given multiplet $\tilde{S}$. The second equality means that it is sufficient to consider one single matrix element on any two wave functions Ψ_n and Ψ_m which give $\langle\Psi_n|\hat{\mu}_Y|\Psi_m\rangle \neq 0$. We stress that the above equation is invariant with respect to unitary transformations of the basis set of functions characterizing a given multiplet, so the wave functions entering Eq. (7) are *arbitrary* combinations of this basis set. The only requirement in (7) is the knowledge of the main magnetic axes, with respect to which the magnetic moments are defined. Their theoretical determination represents a separate tractable problem [19].

The negative sign of the product $g_Xg_Yg_Z$ means that either one single or all three g_i factors in Eq. (1) are negative. To understand how this can happen, consider a simple example of a cubic Γ_6 Kramers doublet arising from crystal-field splitting of a multiplet $J = 7/2$ (this is, for instance, the ground state of Yb^{3+} in an octahedral environment). The two wave functions of the Kramers doublet can be chosen to transform under cubic rotations like eigenfunctions of a spin $S = 1/2$ corresponding to projections $M_S = 1/2$ and $-1/2$, respectively. For a quantization axis chosen along one of the tetragonal axes (Z), these are expressed via the eigenfunctions of $J = 7/2$ as follows:

$$\begin{aligned}\left|\Gamma_6, \frac{1}{2}\right\rangle &= \frac{1}{\sqrt{12}}\left[\sqrt{7}\left|\frac{7}{2}, \frac{1}{2}\right\rangle + \sqrt{5}\left|\frac{7}{2}, \frac{-7}{2}\right\rangle\right],\\ \left|\Gamma_6, -\frac{1}{2}\right\rangle &= \theta\left|\Gamma_6, \frac{1}{2}\right\rangle,\end{aligned} \tag{8}$$

where $\hat{\theta}$ is the time reversal operator [10]. The magnetic moment in the 1/2 state is $\langle\Gamma_6, 1/2|\mu_Z|\Gamma_6, 1/2\rangle = (7/6)g_J\mu_B$. Taking into account that $g_J > 0$ [20], we obtain from Eq. (1) $g_Z = -7/3g_J < 0$. Due to the cubic symmetry, the same values are obtained also for g_X and g_Y; hence, $g_Xg_Yg_Z < 0$. The reason for the positive magnetic moment in the 1/2 state (for a true $S = 1/2$, this is always negative) is the large contribution of the $|7/2, -7/2\rangle$ state [see Eq. (8)], with a large projection of the total momentum ($-7/2$) pointing in the opposite direction to the pseudospin projection in the state $|\Gamma_6, 1/2\rangle$. A similar analysis of the sign of g_i in low-symmetry complexes requires the identification of pseudospin wave functions as a preliminary step [15,19].

Equation (7) allows for a straightforward calculation of the sign of $g_Xg_Yg_Z$ for arbitrary complexes by quantum chemistry methods. Below, we demonstrate that this sign can be negative in complexes of different type. The calculations have been done by the first-principles relativistic spin-orbit complete active space self-consistent field method [21] with an all-electron basis sets of quadruple- and triple-zeta polarization quality on the metals and triple- and double-zeta polarization quality on ligand atoms [22]. The *ab initio* based methodology for the description of magnetic properties has been described elsewhere [19,23]. In spite of previous experience that negative $g_Xg_Yg_Z$ is achieved in complexes with high symmetry (mostly octahedral) [10,12–15], we also find the same negative sign in metal complexes without any symmetry. For example, Fig. 1 shows the structure of a mononuclear Er^{3+} complex [24] for which the calculations give $g_Xg_Yg_Z < 0$ in the ground Kramers doublet. A similar situation was found in several other lanthanide fragments which were found in a low-symmetry environment [25,26].

Equation (8) shows that the necessary condition for $g_Xg_Yg_Z < 0$ is the appreciable mixture of wave functions with opposite projections of angular momentum. Given this condition, the nature of the angular momentum characterizing the multiplet is not important. For instance, the zero-field splitting (ZFS) of a true spin $S = 7/2$ in an octahedral field would yield the same Eq. (8) for the

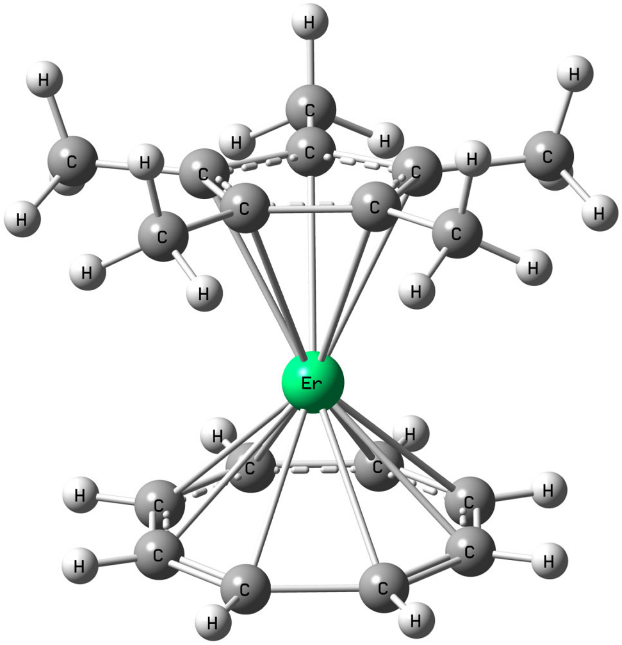

FIG. 1 (color online). The structure of the Er^{3+} complex [24] showing $g_X g_Y g_Z < 0$ in the ground state.

wave functions of the Γ_6 multiplet (in terms of $|S, M_S\rangle$) and the same expressions for g_i [27]. Note that this is the cubic ZFS effect, which arises in the fourth order of perturbation after spin-orbit coupling. Although this effect is present in spin complexes, it is rather weak [10], and we wonder whether $g_X g_Y g_Z < 0$ could not be achieved for true spin Kramers doublets arising from much stronger second-order anisotropy effects on S. In the coordinate system related to the main anisotropy axes, this ZFS Hamiltonian has the form [10]

$$H_{\mathrm{ZFS}} = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2). \tag{9}$$

Diagonalizing (9) for different odd values of S and using Eq. (7), we calculate $g_X g_Z / g_Y$ for all possible values of E/D. The results are shown in Fig. 2 for $S = 3/2$, $5/2$, and $7/2$. One can observe that in all cases the sign of $g_X g_Y g_Z$ is obtained positive. The same situation is kept for higher spins. We may conclude, therefore, that negative values of the product $g_X g_Y g_Z$ in S complexes can only be realized when fourth- and higher-order spin-orbit coupling effects become dominant. This regime is characterized by unquenched orbital momenta. Hence, their presence in complexes represents a necessary condition to achieve $g_X g_Z / g_Y < 0$. As a matter of fact, the magnetic moments in lanthanides always contain a significant contribution of the orbital moment.

Unquenched orbital moments are also encountered in transition metal complexes. A typical metal ion is Co^{2+}, for which we can also expect negative values of $g_X g_Z / g_Y$. The octahedral crystal field leads to the lowest spin-orbit

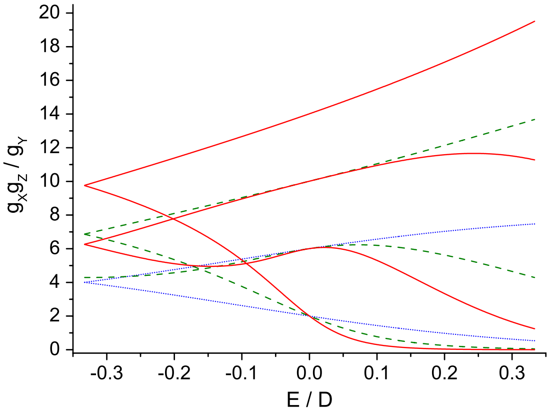

FIG. 2 (color online). The values of $g_X g_Z / g_Y$ for individual Kramers doublets arising from the zero-field splitting of $S = 3/2$ (dotted blue line), $S = 5/2$ (dashed green line), and $S = 7/2$ (solid red line) in the weak spin-orbit coupling limit.

multiplets characterized by total pseudomomentum $\tilde{\mathbf{J}}$ arising from the coupling of $S = 3/2$ with the pseudo-orbital momentum $\tilde{L} = 1$ corresponding to the threefold orbital degeneracy of the ground molecular term. Figure 3(a)

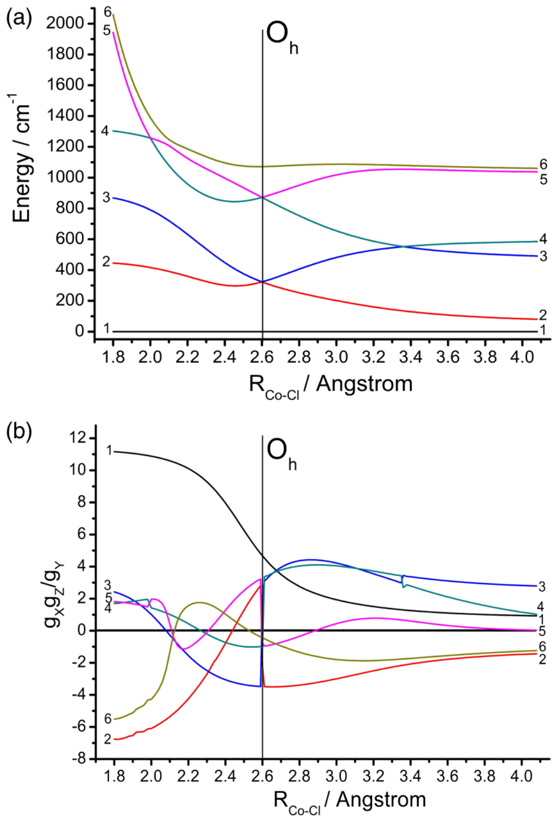

FIG. 3 (color online). (a) Energies and (b) $g_X g_Z / g_Y$ values of the lowest six Kramers doublets in CoCl$_6^{4-}$ as a function of tetragonal elongation or compression of two Co-Cl bonds along one axis. The octahedral geometry corresponds to $R_{\text{Cu-Cl}} = 2.60$ Å.

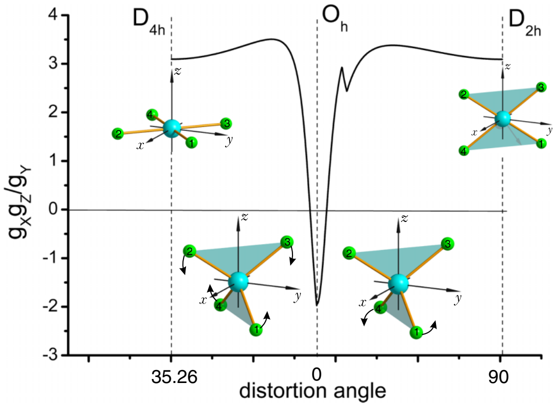

FIG. 4 (color online). Variations of $g_X g_Z/g_Y$ for the ground Kramers doublet of $CuCl_4^{2-}$ as a function of two deformation modes of the ligand environment.

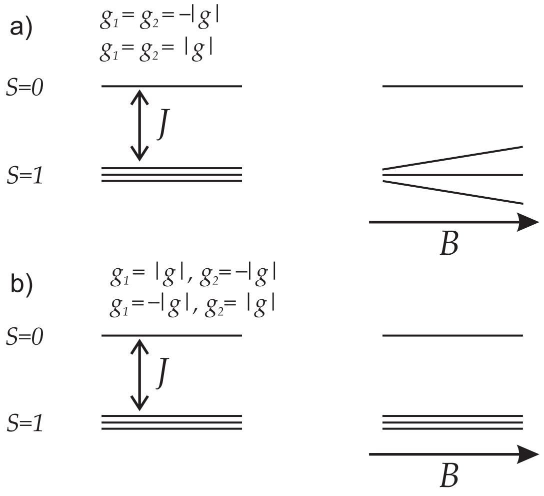

FIG. 5. Zeeman splitting of the exchange multiplets of a model binuclear system with (a) the same and (b) opposite signs of the g factors on the two metal sites.

shows that $CoCl_6^{4-}$ in octahedral coordination has indeed a Lande-type spectrum of the lowest multiplets corresponding to $\tilde{J} = 1/2$, $3/2$, and $5/2$ (split by $\sim 200\ \mathrm{cm}^{-1}$). The calculated sign of $g_X g_Y g_Z$ is positive for each of the three $\tilde{J}$ multiplets. However, a tetragonal elongation or compression of this complex splits the $\tilde{J} = 3/2$ and $5/2$ multiplets into Kramers doublets, some of which show a negative value of $g_X g_Z/g_Y$ [Fig. 3(b)]. The same situation takes place in the opposite limit of a strongly covalent complex $Co(CN)_6^{4-}$ (see the Supplemental Material [28]).

Surprisingly enough, negative $g_X g_Z/g_Y$ are found in the complexes of Cu^{2+}, for which no strong spin-orbit coupling effects are usually expected. Figure 4 shows the results for the archetypal compound $CuCl_4^{2-}$ as a function of the deformations transforming its planar geometry into a tetrahedral-like one. We can see that close to the tetrahedral geometry the sign of $g_X g_Y g_Z$ becomes negative. This is again related to the presence of unquenched orbital momentum close to the tetrahedral point, at which the orbital term becomes threefold degenerate. In a tetrahedral geometry, the g tensor is isotropic, i.e., has similar main values, all equal to -1.80, according to our calculations. Curiously, the EPR of $CuCl_4^{2-}$ with different deviations from T_d symmetry was investigated many times but small deviations of extracted g_i from the free spin value have never made them "suspicious." These are the negative values of g_i that testify about strong spin-orbit coupling effects in this complex.

The derived Berry phase (5) and the previous investigations [10–14] indicate that the sign of the product of the main values of the g tensor has a physical meaning. At the same time, it is clear from the example in Eq. (8) that in the isotropic case the signs of all three main components are easily defined, and it was proved that this is also possible in a general case [15]. Here, we observe that the signs of individual g_i, $i = X, Y, Z$, of metal ions can be also extracted from the magnetism of exchange-coupled clusters. Indeed, the dc magnetization and susceptibility of any complexes are completely defined by the Zeeman splitting of its multiplets. In the case of individual (noninteracting) metal sites, this splitting is independent from the signs of the three g_i components [see Eq. (3) for $g_{\mathbf{B}}$]. The same is true for the magnetic ions with Ising exchange interaction having main anisotropy axes parallel to each other and to the applied magnetic field. In all other cases, the Zeeman splitting of the multiplets will be dependent on the relative signs of g_i of entering metal ions. Consider a model of two metal ions with isotropic exchange $(-J\mathbf{S}_1 \cdot \mathbf{S}_2)$ and Zeeman interactions. In the case of g factors of the same sign on both metal sites, we have a normal Zeeman splitting [Fig. 5(a)], while in the case of g factors of opposite sign the Zeeman splitting is absent for weak B [Fig. 5(b)]. Generalizing, we can state that, for known parameters of exchange interaction between two metal ions, the relative signs of their g_i can be extracted by measuring static magnetic properties for different directions of the applied field.

In conclusion, we have shown that the sign of $g_X g_Y g_Z$ plays the role of a topological invariant because it is just the sign of the Berry phase for a given $\tilde{S}$. Accordingly, this sign can be calculated by using only measurable quantities [Eq. (7)]. *Ab initio* calculations reveal the ubiquity of the situation $g_X g_Y g_Z < 0$ in both lanthanide and transition metal complexes. However, it is never achieved in S complexes with predominant second-order magnetic anisotropy, a most often encountered situation. Finally, it is argued that the signs of individual g_i components can be measured in polynuclear complexes.

Financial support by the Flemish Science Foundation (FWO), INPAC and Methusalem programs of KU Leuven are gratefully acknowledged.

[1] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, Oxford, England, 2006).
[2] R. Wiesendanger, Curr. Opin. Solid State Mater. Sci. **15**, 1 (2011).
[3] D. D. Awschalom, D. P. Di Vincenzo, Phys. Today **48**, No. 4, 43 (1995).
[4] E. M. Chudnovsky, Science **274**, 938 (1996).
[5] G. Christou, D. Gatteschi, D. N. Hendrickson, and R. Sessoli, MRS Bull. **25**, 66 (2000).
[6] M. N. Leuenberger and D. Loss, Nature (London) **410**, 789 (2001).
[7] M. Affronte *et al.*, J. Phys. D **40**, 2999 (2007).
[8] L. Bogani and W. Wernsdorfer, Nat. Mater. **7**, 179 (2008).
[9] A. A. Khajetoorians, J. Wiebe, B. Chilian, and R. Wiesendanger, Science **332**, 1062 (2011).
[10] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, England, 1970).
[11] M. H. L. Pryce, Phys. Rev. Lett. **3**, 375 (1959).
[12] C. A. Hutchison and B. Weinstock, J. Chem. Phys. **32**, 56 (1960).
[13] J. D. Axe, H. J. Stapleton, and C. D. Jefries, Phys. Rev. **121**, 1630 (1961).
[14] P. Rigny and P. Plurien, J. Phys. Chem. Solids **28**, 2589 (1967).
[15] L. F. Chibotaru, A. Ceulemans, and H. Bolvin, Phys. Rev. Lett. **101**, 033003 (2008).
[16] F. Klöwer, Y. Lan, J. Nehrkorn, O. Waldmann, C. E. Anson, and A. K. Powell, Chem. Eur. J. **15**, 7413 (2009).
[17] These formally coincide with the spin matrices S_α.
[18] M. V. Berry, Proc. R. Soc. A **392**, 45 (1984).
[19] L. F. Chibotaru and L. Ungur, J. Chem. Phys. **137**, 064112 (2012).
[20] The Landé factor of an atomic or ionic J multiplet is always positive [10]. For $J = 7/2$ of Yb^{3+}, it equals $g_J = 8/7$.
[21] F. Aquilante *et al.*, J. Comput. Chem. **31**, 224 (2010).
[22] B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P.-O. Widmark, J. Phys. Chem. A **108**, 2851 (2004).
[23] L. F. Chibotaru, L. Ungur, C. Aronica, H. Elmoll, G. Pilet, and D. Luneau, J. Am. Chem. Soc. **130**, 12445 (2008).
[24] S.-D. Jiang, S.-S. Liu, L.-N. Zhou, B.-W. Wang, Z.-M. Wang, and S. Gao, Inorg. Chem. **51**, 3079 (2012).
[25] J.-L. Liu, K. Yuan, J.-D. Leng, L. Ungur, W. Wernsdorfer, F.-S. Guo, L. F. Chibotaru, and M.-L. Tong, Inorg. Chem. **51**, 8538 (2012).
[26] V. S. Mironov, L. F. Chibotaru, and A. Ceulemans, Phys. Rev. B **67**, 014424 (2003).
[27] The only difference is the replacement of g_J by g_S.
[28] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.246403 for deformation modes, relative energies of the lowest Kramers doublets and the values of $g_X g_Z / g_Y$ of calculated $[\mathrm{CuCl_4}]^{2-}$ and $[\mathrm{Co(CN)_6}]^{4-}$ ions as function of the deformation.