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Universal mechanism of spin relaxation in solids

E. M. Chudnovsky,[1] D. A. Garanin,[1,2] and R. Schilling[2]
[1]*Physics Department, Lehman College, City University of New York, 250 Bedford Park Boulevard West, Bronx, New York 10468-1589, USA*
[2]*Institut für Physik, Johannes-Gutenberg-Universität, D-55099 Mainz, Germany*

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We consider relaxation of a rigid spin cluster in an elastic medium in the presence of the magnetic field. A universal simple expression for spin-phonon matrix elements due to local rotations of the lattice is derived. The equivalence of the lattice frame and the laboratory frame approaches is established. For spin Hamiltonians with strong uniaxial anisotropy, the field dependence of the transition rates due to rotations is analytically calculated and its universality is demonstrated. The role of time-reversal symmetry in spin-phonon transitions has been elucidated. The theory provides a lower bound on the decoherence of any spin-based solid-state qubit.

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I. INTRODUCTION

Understanding spin-lattice interactions has fundamental importance for applications of magnetic phenomena, such as, e.g., magnetic relaxation, magnetic resonance, and decoherence of spin-based qubits. The studies of spin-lattice interactions are almost as old as the quantum theory of solids.[1–5] Van Vleck[4] was among the first who attempted to compute the rates of phonon-induced transitions (in titanium and chromalum) from the first principles, that is, considering atomic wave functions in the crystal field and spin-orbit interaction. These calculations are very involved, and they are hardly possible for more complicated materials such as magnetic molecules or clusters, each cluster containing several magnetic atoms and tens or hundreds of nonmagnetic atoms.

On the other hand, for most materials the orbital moment of electrons is quenched by a strong crystal field and it does not contribute to the magnetic properties. The latter are due to the spin **S** that is relatively weakly coupled to the orbital moment via the spin-orbit interaction and thus it feels the crystal field indirectly. While microscopic calculation of the crystal-field Hamiltonian for **S** is difficult, one can use an alternative approach[5,6] and start with a phenomenological expression containing all permitted by symmetry combinations of spin **S**. We shall apply this approach to clusters of magnetic atoms for which we shall assume that the length, S, of the spin is fixed by the strong exchange interaction within the cluster. The relevant spin states are then superpositions of states characterized by the magnetic quantum number m. The energy distances between such states are determined by the spin-orbit interaction. Thus, in general, they must be small compared to the energy distances between spin states belonging to different S manifolds. This makes a fixed-S crystal-field Hamiltonian a good low-temperature approximation for many systems, including clusters of three-dimensional magnetic atoms and molecular nanomagnets. Some examples of the crystal-field Hamiltonian that results in the uniaxial, biaxial, and cubic magnetic anisotropy of the cluster are

$$\hat{H}_A = -D(\mathbf{S}\cdot\mathbf{e}^{(3)})^2, \tag{1}$$

$$\hat{H}_A = -D(\mathbf{S}\cdot\mathbf{e}^{(3)})^2 + E[(\mathbf{S}\cdot\mathbf{e}^{(1)})^2 - (\mathbf{S}\cdot\mathbf{e}^{(2)})^2], \tag{2}$$

$$\hat{H}_A = C\sum_{\alpha\neq\beta}(\mathbf{S}\cdot\mathbf{e}^{(\alpha)})^2(\mathbf{S}\cdot\mathbf{e}^{(\beta)})^2, \tag{3}$$

where $\mathbf{e}^{(\alpha)}$ with $\alpha=1,2,3$ are the unit vectors of the coordinate frame that is rigidly coupled with the symmetry axes of the cluster (in the following it will be called "lattice frame"). The advantage of this approach is that the form of $\hat{H}_A$ is uniquely determined by symmetry, while the phenomenological constants (D, E, C, etc.) can be easily obtained from experiment. The expressions for $\hat{H}_A$ above, as well as all other physically acceptable forms of $\hat{H}_A$, possess a full rotational invariance, i.e., the form of $\hat{H}_A$ does not depend on the orientation of laboratory coordinate axes. The full rotational invariance implies conservation of the total angular momentum (spin+lattice).

Lattice vibrations couple to the spin by modifying coefficients in Eqs. (1)–(3), changing directions of the lattice vectors $\mathbf{e}^{(\alpha)}$, as well as by lowering the symmetry of the crystal field. Due to translational invariance, the phonon displacement field **u** enters the Hamiltonian only through its spatial derivatives $\partial u_i/\partial x_j$ or their symmetric and antisymmetric combinations. Again, one can write down a phenomenological expression for the spin-phonon Hamiltonian $\hat{H}_{\text{s-ph}}$ that contains all terms permitted by the symmetry of a particular material.[7] However, the general form of $\hat{H}_{\text{s-ph}}$ usually contains too many different coefficients that are comparable with each other and cannot be measured independently.

The problem of spin-lattice relaxation can be simplified if one notices that longitudinal phonons have a larger sound velocity than the transverse phonons. Since the rate of one-phonon processes (emission and absorption of a phonon) is inversely proportional to the fifth power of the sound velocity, procecces involving longitudinal phonons can be neglected. The same is valid for multiphonon processes such as the Raman process, because their rates contain even higher powers of the sound velocity.

The terms of $\hat{H}_{\text{s-ph}}$ due to transverse phonons can be split into two groups. The first group describes distorsions of the lattice cell due to transverse phonons whereas the second group of terms describes local rotations of the lattice without distortion of the crystal environment of magnetic atoms. Whereas the first group of terms contains phenomenological coupling coefficients, the terms of $\hat{H}_{\text{s-ph}}$ due to local rotations are parameter free and are defined solely by the form of $\hat{H}_A$. The significance of the latter was noticed in the past,[8–15] and different kinds of magnetoelastic problems have been considered. However, early applications of the theory have not included spin-lattice relaxation. Much later the relaxation between the adjacent spin levels of the spin Hamiltonian of Eq. (1) due to the parameter-free spin-lattice interaction arising from the tilting of $\mathbf{e}^{(3)}$ by transverse phonons was considered in Ref. 16.

In general, processes due to the distortion of the lattice and those due to the local rotation of the lattice should result in comparable relaxation rates. Even in this case, the latter are of a fundamental importance because they provide a parameter-free lower bound on the decoherence of any spin-based qubit. In the case of a magnetic molecule or a cluster in a solid, if the cluster is more rigid than its environment, it resists any distortions due to long-wave deformations of the solid. That is, $\mathbf{S}$ interacts only with the long-wave deformations of the crystal lattice that rotate the local frame $(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{e}^{(3)})$ as a whole, so that the spin-phonon interaction can be obtained from $\hat{H}_A$ without any phenomenological parameters. The corresponding parameter-free description of spin-lattice relaxation becomes *exact* in this case.

It has been noticed[17–20] that for an arbitrary spin Hamiltonian the parameter-free spin-phonon transition rates can be conveniently computed by switching to the lattice frame where the form of $\hat{H}_A$ is preserved, while the spin-phonon interaction is of a kinematic origin and it has a universal form that is independent from $\hat{H}_A$. With this method, one could easily calculate the relaxation rates between the tunnel-split states of $\hat{H}_A$, while it was unclear how this problem could be solved by conventional methods in the laboratory frame. A striking feature of the lattice-frame approach is that both the calculation and the final result for the relaxation rate are universal and insensitive to the detailed form of $\hat{H}_A$. One obtains the relaxation rate that is expressed via the quantities that can be directly measured in experiment, such as the tunnel splitting Δ.

The aim of the present work is to investigate the relation between the lattice-frame and laboratory-frame approaches in more detail. We will show that also in the laboratory frame one can formulate a method of calculating parameter-free spin-phonon rates that is similar to the lattice-frame approach and leads to the same results. We will extend the theory by taking into account the magnetic field, including the case in which the tunnel splitting is solely due to the magnetic field.

The body of this paper is organized as follows. In Sec. II we derive exact expressions for the spin-phonon interaction induced by rotations in the laboratory (Sec. II A) and lattice (Sec. II B) frames. In Sec. III a simple universal formula for the spin-phonon matrix element is obtained for an arbitrary spin Hamiltonian in the presence of the magnetic field. Equivalence of the laboratory- and lattice-frame treatments of the spin-phonon interaction is demonstrated. The advantage of our method is that it requires only the knowledge of the matrix elements of the operator $\mathbf{S}$ between the eigenstates of the Hamiltonian, in contrast to the traditional method that requires the knowledge of a matrix element of a model-dependent product of the components of $\mathbf{S}$. In Sec. IV spin-matrix elements for transitions between spin states split by the crystal field or by the magnetic field are calculated analytically for Hamiltonians that are dominated by the uniaxial anisotropy. We show that these matrix elements are parameter free and their field dependence is universal. At the end of this section we discuss the role of time-reversal symmetry. In Sec. V we obtain universal parameter-free formulas for the rates of spin-phonon transitions between tunnel-split states in the presence of the arbitrarily directed magnetic field. Cases of the tunnel splitting due to the crystal field and due to transverse magnetic field are considered in Secs. V A and V B, respectively. Implications of our results for experiment are discussed in Sec. VI. Some illustrations for uniaxial and biaxial spin models with the magnetic field, as well as an in-depth study of the role of the time-reversal symmetry, are presented in the Appendixes. In particular, in Appendix B we show that the same expressions for the rates of relaxation between tunnel-split states can be obtained by traditional methods but the required effort greatly exceeds the effort of our method.

II. SPIN-LATTICE INTERACTION

A. Laboratory frame

In the absence of phonons, one can choose the coordinate system in which in Eqs. (1)–(3) $e_\beta^{(\alpha)}=\delta_{\alpha\beta}$, i.e., $\hat{H}_A=-DS_z^2$, etc. A transverse phonon, $\mathbf{u}(\mathbf{r})$, rotates the axes of the local crystal field, $(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{e}^{(3)})$. This rotation can be described by

$$\delta\boldsymbol{\phi}(\mathbf{r}) = \frac{1}{2}\nabla \times \mathbf{u}(\mathbf{r}) \tag{4}$$

and it is performed by the (3×3) rotation matrix $\mathbb{R}$,

$$\mathbf{e}^{(\alpha)} \rightarrow \mathbb{R}\mathbf{e}^{(\alpha)}, \tag{5}$$

i.e., $e_\beta^{(\alpha)} \rightarrow \mathbb{R}_{\beta\beta'}e_{\beta'}^{(\alpha)}$. For small $\delta\boldsymbol{\phi}$, one has

$$\mathbb{R}_{\alpha\beta} = \delta_{\alpha\beta} - \epsilon_{\alpha\beta\gamma}\delta\phi_\gamma. \tag{6}$$

We now notice that due to the rotational invariance of $\hat{H}_A$, the rotation of the local frame $(\mathbf{e}^{(1)},\mathbf{e}^{(2)},\mathbf{e}^{(3)})$ is equivalent to the rotation of the vector $\mathbf{S}$ in the opposite direction, $\mathbf{S}\rightarrow\mathbb{R}^{-1}\mathbf{S}$. As is known,[21] this rotation can be equivalently performed by the $(2S+1)\times(2S+1)$ matrix in the spin space,

$$\mathbf{S} \rightarrow \hat{R}\mathbf{S}\hat{R}^{-1}, \quad \hat{R} = e^{-i\mathbf{S}\cdot\delta\boldsymbol{\phi}}. \tag{7}$$

The total Hamiltonian can be written in the form

$$\hat{H} = \hat{R}\hat{H}_A\hat{R}^{-1} + \hat{H}_Z + \hat{H}_{\text{ph}}, \tag{8}$$

where $\hat{H}_A$ is the crystal-field Hamiltonian in the absence of phonons,

$$\hat{H}_Z = -g\mu_B \mathbf{H}\cdot\mathbf{S} \tag{9}$$

is the Zeeman Hamiltonian, and $\hat{H}_{\text{ph}}$ is the Hamiltonian of harmonic phonons.

In the above formulas, $\mathbf{u}$ and $\boldsymbol{\phi}$ must be treated as operators. Canonical quantization of phonons and Eq. (4) give

$$\mathbf{u} = \sqrt{\frac{\hbar}{2MN}}\sum_{\mathbf{k}\lambda}\frac{\mathbf{e}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}\lambda}}}(a_{\mathbf{k}\lambda}+a^{\dagger}_{-\mathbf{k}\lambda}), \tag{10}$$

$$\delta\boldsymbol{\phi} = \frac{1}{2}\sqrt{\frac{\hbar}{2MN}}\sum_{\mathbf{k}\lambda}\frac{[i\mathbf{k}\times\mathbf{e}_{\mathbf{k}\lambda}]e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}\lambda}}}(a_{\mathbf{k}\lambda}+a^{\dagger}_{-\mathbf{k}\lambda}), \tag{11}$$

where M is the mass of the unit cell, N is the number of cells in the crystal, $\mathbf{e}_{\mathbf{k}\lambda}$ are unit polarization vectors, $\lambda = t_1, t_2, l$ denotes polarization, and $\omega_{k\lambda} = v_\lambda k$ is the phonon frequency. In application to rigid magnetic clusters, Eqs. (10) and (11) describe quantized long-wave phonons in the elastic environment of the cluster. In the linear order in phonon amplitudes one obtains

$$\hat{R}\hat{H}_A\hat{R}^{-1} \cong \hat{H}_A + \hat{H}_{\text{s-ph}}, \quad \hat{H}_{\text{s-ph}} = i[\hat{H}_A,\mathbf{S}]\cdot\delta\boldsymbol{\phi}. \tag{12}$$

The total Hamiltonian can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{s-ph}}, \tag{13}$$

where $\hat{H}_0$ is the Hamiltonian of noninteracting spin and phonons,

$$\hat{H}_0 = \hat{H}_S + \hat{H}_{\text{ph}}, \tag{14}$$

and

$$\hat{H}_S = \hat{H}_A + \hat{H}_Z, \tag{15}$$

is the spin Hamiltonian.

B. Lattice frame

The anisotropy Hamiltonian $\hat{H}_A$ is defined in the lattice frame and thus, in this frame, it is not changed by the lattice rotations. Unitary transformation to the lattice frame corresponds to the rotation of $\hat{H}$ of Eq. (8) by the angle $\delta\boldsymbol{\phi}$:

$$\hat{H}' = \hat{R}^{-1}\hat{H}\hat{R} = \hat{H}_A + \hat{H}'_Z + \hat{H}'_{\text{ph}}. \tag{16}$$

Here

$$\hat{H}'_{\text{ph}} = \hat{R}^{-1}\hat{H}_{\text{ph}}\hat{R} \cong \hat{H}_{\text{ph}} - i[\hat{H}_{\text{ph}},\delta\boldsymbol{\phi}]\cdot\mathbf{S}, \tag{17}$$

and

$$\hat{H}'_Z = \hat{R}^{-1}\hat{H}_Z\hat{R} \cong \hat{H}_Z - i[\hat{H}_Z,\mathbf{S}]\cdot\delta\boldsymbol{\phi} = \hat{H}_Z - g\mu_B[\mathbf{H}\times\delta\boldsymbol{\phi}]\cdot\mathbf{S}, \tag{18}$$

where we have used $[(\mathbf{A}\cdot\mathbf{S}),(\mathbf{B}\cdot\mathbf{S})] = i\mathbf{S}\cdot[\mathbf{A}\times\mathbf{B}]$.

The full Hamiltonian in the lattice frame up to the first order in $\delta\boldsymbol{\phi}$ is thus

$$\hat{H}' = \hat{H}_0 + \hat{H}'_{\text{s-ph}}, \tag{19}$$

where $\hat{H}_0$ is given by Eq. (14) and

$$\hat{H}'_{\text{s-ph}} = -i[\hat{H}_{\text{ph}},\delta\boldsymbol{\phi}]\cdot\mathbf{S} - g\mu_B[\mathbf{H}\times\delta\boldsymbol{\phi}]\cdot\mathbf{S}. \tag{20}$$

With account of the relation

$$\delta\dot{\boldsymbol{\phi}} = \frac{i}{\hbar}[\hat{H}_{\text{ph}},\delta\boldsymbol{\phi}], \tag{21}$$

one obtains

$$\hat{H}'_{\text{s-ph}} = -\hbar\hat{\boldsymbol{\Omega}}\cdot\mathbf{S}, \tag{22}$$

where

$$\hat{\boldsymbol{\Omega}} = \delta\dot{\boldsymbol{\phi}} + \gamma[\mathbf{H}\times\delta\boldsymbol{\phi}], \tag{23}$$

and $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio for $\mathbf{S}$.

Note that in the absence of the magnetic field the spin-lattice interaction in the lattice frame can be obtained by simply writing[17–20] $\hat{H}' = \hat{H}_0 - \hbar\delta\dot{\boldsymbol{\phi}}\cdot\mathbf{S}$. The term $-\hbar\delta\dot{\boldsymbol{\phi}}\cdot\mathbf{S}$ is of kinematic origin: in the rotating coordinate frame, the rotation is equivalent to the magnetic field $\mathbf{H}_{\text{eff}} = \delta\dot{\boldsymbol{\phi}}/\gamma$ acting on the spin. The second term in Eq. (23) describes the fact that the external magnetic field, which is constant in the laboratory frame, makes rotation in the lattice frame due to the transverse phonon.

III. SPIN-LATTICE RELAXATION RATE

We study spin-phonon transitions between the eigenstates of $\hat{H}_0$ that are direct products of the spin and phonon states,

$$|\Psi_\pm\rangle = |\psi_\pm\rangle \otimes |\phi_\pm\rangle. \tag{24}$$

Here $|\psi_\pm\rangle$ are the eigenstates of $\hat{H}_S$ with eigenvalues $E_\pm (E_+ > E_-)$ and $|\phi_\pm\rangle$ are the eigenstates of $\hat{H}_{\text{ph}}$ with energies $E_{\text{ph},\pm}$. For $\hat{H}_{\text{s-ph}}$ linear in phonon amplitudes, the states $|\phi_\pm\rangle$ differ by one emitted or absorbed phonon with a wave vector $\mathbf{k}$ and polarization λ. Thus we will use the designations

$$|\phi_+\rangle \equiv |n_{\mathbf{k}\lambda}\rangle, \quad |\phi_-\rangle \equiv |n_{\mathbf{k}\lambda}+1\rangle. \tag{25}$$

Spin-phonon transitions conserve energy,

$$E_+ + E_{\text{ph},+} = E_- + E_{\text{ph},-}. \tag{26}$$

We calculate spin-phonon relaxation rates in both the lattice frame and the laboratory frame and show that the result is the same, as physically expected.

A. Lattice frame

We first calculate the matrix element corresponding to the decay of the spin $|\psi_+\rangle \to |\psi_-\rangle$ in the lattice frame. From Eq. (22) one obtains

$$\langle\Psi_-|\hat{H}'_{\text{s-ph}}|\Psi_+\rangle = -\hbar\boldsymbol{\Omega}_{-+}\cdot\langle\psi_-|\mathbf{S}|\psi_+\rangle, \tag{27}$$

where

$$\mathbf{\Omega}_{-+} \equiv \langle \phi_- | \hat{\mathbf{\Omega}} | \phi_+ \rangle \equiv \langle n_{\mathbf{k}\lambda} + 1 | \hat{\mathbf{\Omega}} | n_{\mathbf{k}\lambda} \rangle \equiv \hat{\mathbf{\Omega}}_{\mathbf{k}\lambda}. \tag{28}$$

To calculate the matrix element $\mathbf{\Omega}_{-+}$, it is convenient to step back and use the commutator form of $\delta\dot{\boldsymbol{\phi}}$ given by Eq. (21). One has

$$\langle \phi_- | [\hat{H}_{\mathrm{ph}}, \delta\boldsymbol{\phi}] | \phi_+ \rangle = (E_{\mathrm{ph},-} - E_{\mathrm{ph},+}) \delta\boldsymbol{\phi}_{-+}, \tag{29}$$

where

$$\delta\boldsymbol{\phi}_{-+} \equiv \langle \phi_- | \delta\boldsymbol{\phi} | \phi_+ \rangle \equiv \langle n_{\mathbf{k}\lambda} + 1 | \delta\boldsymbol{\phi} | n_{\mathbf{k}\lambda} \rangle \equiv \delta\boldsymbol{\phi}_{\mathbf{k}\lambda}. \tag{30}$$

It follows from the energy conservation, Eq. (26), that

$$E_{\mathrm{ph},-} - E_{\mathrm{ph},+} = E_+ - E_- \equiv \hbar\omega_0. \tag{31}$$

Thus one finally obtains

$$\mathbf{\Omega}_{-+} = i\omega_0 \delta\boldsymbol{\phi}_{-+} + \gamma [\mathbf{H} \times \delta\boldsymbol{\phi}_{-+}] \tag{32}$$

or, with notations more suitable for phonons,

$$\mathbf{\Omega}_{\mathbf{k}\lambda} = i\omega_0 \delta\boldsymbol{\phi}_{\mathbf{k}\lambda} + \gamma [\mathbf{H} \times \delta\boldsymbol{\phi}_{\mathbf{k}\lambda}]. \tag{33}$$

B. Laboratory frame

To check the consistency of our method, let us now obtain the expression for the matrix element in the laboratory frame. Equation (12) gives

$$\langle \Psi_- | \hat{H}_{\text{s-ph}} | \Psi_+ \rangle = i \langle \psi_- | [\hat{H}_A, \mathbf{S}] | \psi_+ \rangle \cdot \delta\boldsymbol{\phi}_{-+}. \tag{34}$$

It is convenient to avoid explicitly working out the commutator in the spin-matrix element. To this end, we add and subtract $\hat{H}_Z$:

$$\langle \psi_- | [\hat{H}_A, \mathbf{S}] | \psi_+ \rangle = \langle \psi_- | [\hat{H}_S, \mathbf{S}] | \psi_+ \rangle - i \langle \psi_- | [\hat{H}_Z, \mathbf{S}] | \psi_+ \rangle. \tag{35}$$

Now we can take into account that the states $|\psi_\pm\rangle$ are exact eigenstates of the spin Hamiltonian $\hat{H}_S$ of Eq. (15) with energies $E_\pm$:

$$\langle \psi_- | [\hat{H}_S, \mathbf{S}] | \psi_+ \rangle = (E_- - E_+) \langle \psi_- | \mathbf{S} | \psi_+ \rangle. \tag{36}$$

The Zeeman term in Eq. (35) can be done as in Eq. (18). With the help of Eq. (31) one then obtains

$$\langle \Psi_- | \hat{H}_{\text{s-ph}} | \Psi_+ \rangle = -\hbar \mathbf{\Omega}_{-+} \cdot \langle \psi_- | \mathbf{S} | \psi_+ \rangle, \tag{37}$$

where $\mathbf{\Omega}_{-+}$ is given by Eq. (32). We see that the spin-phonon matrix elements computed in the laboratory and lattice frames, Eqs. (27) and (37), are exactly the same.

C. Relaxation rate

To calculate the spin-lattice relaxation rate, it is convenient to rewrite the spin-phonon matrix element in the form

$$\langle \boldsymbol{\Psi}_- | \hat{H}_{\text{s-ph}} | \boldsymbol{\Psi}_+ \rangle = \mathbf{\Xi} \cdot \delta\boldsymbol{\phi}_{\mathbf{k}\lambda} \tag{38}$$

(or the same with $\hat{H}'_{\text{s-ph}}$ if we are using the lattice frame), where $\mathbf{\Xi}$ is the spin matrix element

$$\mathbf{\Xi} = -i\hbar\omega_0 \langle \psi_- | \mathbf{S} | \psi_+ \rangle - [\langle \psi_- | \mathbf{S} | \psi_+ \rangle \times g\mu_B \mathbf{H}]. \tag{39}$$

With the help of Eq. (11), Eq. (38) can be expressed as

$$\langle \Psi_- | \hat{H}_{\text{s-ph}} | \Psi_+ \rangle = \frac{\hbar}{\sqrt{N}} \sum_{\mathbf{k}\lambda} V_{\mathbf{k}\lambda} \langle n_{\mathbf{k}} + 1 | (a_{\mathbf{k}\lambda} + a^\dagger_{-\mathbf{k}\lambda}) | n_{\mathbf{k}} \rangle, \tag{40}$$

where we used the designations of Eq. (25) and

$$V_{\mathbf{k}\lambda} \equiv \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{8M\hbar\omega_{\mathbf{k}\lambda}}} \mathbf{\Xi} \cdot [\mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}]. \tag{41}$$

The decay rate Γ_{-+} of the upper spin state into the lower state, accompanied by the emission of a phonon, and the rate Γ_{+-} of the inverse process are given by

$$\begin{Bmatrix} \Gamma_{-+} \\ \Gamma_{+-} \end{Bmatrix} = \Gamma_0 \begin{Bmatrix} n_{\omega_0} + 1 \\ n_{\omega_0} \end{Bmatrix}, \tag{42}$$

where $n_{\omega_0} = (e^{\beta\hbar\omega_0} - 1)^{-1}$ with $\beta = 1/(k_B T)$ is the phonon occupation number at equilibrium and

$$\Gamma_0 = \frac{1}{N} \sum_{\mathbf{k}\lambda} |V_{\mathbf{k}\lambda}|^2 2\pi\delta(\omega_{\mathbf{k}\lambda} - \omega_0). \tag{43}$$

The master equation for the populations of the spin states n_+ and n_- satisfying $n_+ + n_- = 1$

$$\dot{n}_+ = -\Gamma_{-+} n_+ + \Gamma_{+-} n_- = -\Gamma n_+ + W_{+-} \tag{44}$$

defines the relaxation rate

$$\Gamma = \Gamma_{+-} + \Gamma_{-+} = \Gamma_0 (2n_{\omega_0} + 1). \tag{45}$$

One can see from Eq. (41) that only transverse phonons, $\lambda = t$, are active in the relaxation process. One can use $[\mathbf{k} \times \mathbf{e}_{\mathbf{k}t}] = \pm k \mathbf{e}_{\mathbf{k}t'}$, where t and t' denote different transverse phonons. Summation over polarization vectors of transverse phonons and averaging over the directions of $\mathbf{k}$ can be performed with the help of the formulas given in Appendix A. Replacing $N^{-1}\Sigma_{\mathbf{k}} \ldots$ by $v_0 \int d^3k/(2\pi)^3 \ldots$ (v_0 being the unit cell volume) and using Eq. (57) one obtains the general result

$$\Gamma_0 = \frac{1}{12\pi\hbar} \frac{|\mathbf{\Xi}|^2}{M v_t^2} \frac{\omega_0^3}{\omega_D^3} = \frac{1}{12\pi\hbar} \frac{|\mathbf{\Xi}|^2 \omega_0^3}{\rho v_t^5}, \tag{46}$$

where ρ is the mass density, $\omega_D \equiv v_t / v_0^{1/3}$ is the Debye frequency for the tranverse phonons, ω_0 is given by Eq. (54), and $\mathbf{\Xi}$ is given by Eq. (39). Expressions for the spin-lattice relaxation rate in different cases considered below only differ by the spin factor $|\mathbf{\Xi}|^2 \equiv \Sigma_{\gamma=1,2,3} \Xi^*_\gamma \Xi_\gamma$.

IV. SPIN-MATRIX ELEMENTS FOR TUNNEL-SPLIT STATES

The method of the computation of transition rates outlined in the preceding sections has a significant advantage over conventional methods. Regardless of the explicit form of the spin Hamiltonian, only the matrix elements of the operator $\mathbf{S}$ need to be computed. Especially interesting is the case of

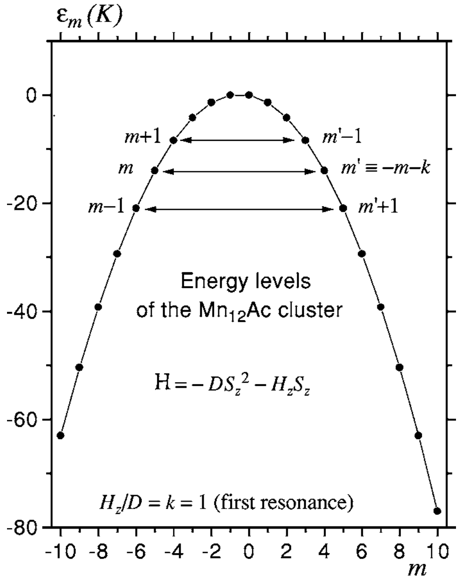

FIG. 1. Spin-energy levels of a Mn$_{12}$Ac molecule for $H_x=0$ and $H_z=D$ corresponding to the first resonance, $k=1$.

strong uniaxial anisotropy, in which $\hat{H}_S$ nearly commutes with S_z, so that the energy levels can be approximately described with the help of the quantum number m:

$$E_m = E_m^{(A)} - g\mu_B H_z m, \tag{47}$$

where $E_m^{(A)}$ is the contribution of the crystal field that satisfies $E_{-m}^{(A)}=E_m^{(A)}$. The structure of the energy levels for this model is shown in Fig. 1. The two levels m and m' are in resonance for the values of the magnetic field

$$g\mu_B H_{z,mm'}^{(\mathrm{res})} = \frac{E_m^{(A)} - E_{m'}^{(A)}}{m-m'} \equiv \frac{\hbar\omega_{mm'}^{(A)}}{m-m'}. \tag{48}$$

For Mn$_{12}$ the dominant term in the uniaxial anisotropy energy is $E_m^{(A)}=-Dm^2$ and thus $g\mu_B H_{z,mm'}^{(\mathrm{res})}=-D(m+m')=Dk$, where k is the resonance number (see Fig. 1). The level bias is given by

$$\begin{aligned} W \equiv E_m - E_{m'} &= g\mu_B (H_z - H_{z,mm'}^{(\mathrm{res})})(m'-m) \\ &= (m'-m) g\mu_B H_z + \hbar\omega_{mm'}^{(A)}. \end{aligned} \tag{49}$$

Choosing $dW/dH_z>0$ for certainty, makes $m'>m$ in all subsequent calculations.

A. The two-state model: $\langle\psi_-|S_z|\psi_+\rangle$

Due to the terms in $\hat{H}_S$ that do not commute with S_z, the true eigenstates of $\hat{H}_S$ are expansions over the complete $|m\rangle$ basis:

$$|\psi_\pm\rangle = \sum_{m''=-S}^{S} c_{\pm,m''}|m''\rangle. \tag{50}$$

If one neglects tunneling (i.e., hybridization of the states $|m\rangle$ and $|m'\rangle$ on different sides of the potential barrier, see Fig. 1), each pure state $|m\rangle$ should be replaced by $|\psi_m\rangle$,

$$|\psi_m\rangle = \sum_{m''=-S}^{S} c_{mm''}|m''\rangle, \tag{51}$$

where $|c_{mm}|\cong 1$ and all other coefficients are small. Hybridization of the states $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ can be taken into account in the framework of the two-state model

$$\langle\psi_{m_i}|\hat{H}_S|\psi_{m_i}\rangle = E_{m_i}, \quad m_i = m, m'$$

$$\langle\psi_m|\hat{H}_S|\psi_{m'}\rangle = \frac{1}{2}\Delta e^{i\varphi}, \tag{52}$$

where Δ is the tunnel splitting of the levels m and m' that can be calculated from the exact spin Hamiltonian $\hat{H}_S$ or determined experimentally and φ is a phase. If $\hat{H}_S$ expressed in terms of S_z and $S_\pm$ is real, then the only two possibilities are $\varphi=0,\pi$, so that $e^{i\varphi}=\pm 1$. Diagonalizing this (2×2) matrix yields the eigenvalues

$$E_\pm = \frac{1}{2}(E_m + E_{m'} \pm \sqrt{W^2+\Delta^2}). \tag{53}$$

The energy difference is

$$E_+ - E_- \equiv \hbar\omega_0 \equiv \sqrt{W^2+\Delta^2}. \tag{54}$$

The corresponding eigenvectors can be represented in the form

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}(C_\pm e^{i\varphi/2}|\psi_m\rangle \pm C_\mp e^{-i\varphi/2}|\psi_{m'}\rangle), \tag{55}$$

where

$$C_\pm = \sqrt{1 \pm \frac{W}{\sqrt{W^2+\Delta^2}}}. \tag{56}$$

Far from the resonance, $|W|\gg\Delta$, the eigenstates and energy eigenvalues reduce to those of $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ states. For $W>0$ and $W\gg\Delta$ one has $|\psi_+\rangle\cong e^{i\varphi/2}|\psi_m\rangle$ and $|\psi_-\rangle\cong -e^{-i\varphi/2}|\psi_{m'}\rangle$. On the contrary, for $W<0$ and $|W|\gg\Delta$ one has $|\psi_+\rangle\cong e^{-i\varphi/2}|\psi_{m'}\rangle$ and $|\psi_-\rangle\cong e^{i\varphi/2}|\psi_m\rangle$. Exactly at the resonance, $W=0$, the eigenstates $|\psi_\pm\rangle$ are superpositions of $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ with equal weights, and signs depending on the phase φ.

Equation (55) is sufficient to calculate the matrix element

$$\langle\psi_-|S_z|\psi_+\rangle = -\frac{\Delta}{\sqrt{W^2+\Delta^2}}\frac{m'-m}{2}. \tag{57}$$

This result does not depend on the detailed form of $\hat{H}_A$, provided that the condition of strong uniaxial anisotropy is fulfulled, and it is universal in this sense. It is large near the resonance, $W^2 \lesssim \Delta^2$, but it becomes small far from the resonance. This the only matrix element that plays a role in the relaxation for $H=0$, as will be shown in Sec. IV C. Also for $H\neq 0$ in the case where the tunnel splitting Δ is due to the transverse anisotropy, this matrix element is dominant. In another particular case when $[\hat{H}_A, S_z]=0$ and thus the only source of the splitting Δ is the transverse field one has to take into account matrix elements $\langle\psi_-|S_\pm|\psi_+\rangle$. This will be done in the next section.

B. Beyond the two-state model: $\langle\psi_-|S_\pm|\psi_+\rangle$

Consider the spin Hamiltonian $\hat{H}_S$ of Eq. (15), where $\hat{H}_A$ satisfies $[\hat{H}_A, S_z]=0$ and is strong in comparison to $\hat{H}_Z$. Due to this rotational invariance the orientation of the transverse field is unimportant, so we direct it along the x axis for simplicity,

$$\hat{H}_Z = -g\mu_B H_z S_z - g\mu_B H_x S_x \tag{58}$$

and assume $H_x > 0$. For strong uniaxial anisotropy $\hat{H}_A$ one can obtain the splitting of resonance levels $|m\rangle$ and $|m'\rangle$ $(m' > m)$ perturbatively in H_x,

$$\frac{\Delta}{2} = \left| V_{m,m+1}\frac{1}{E_{m+1}-E_m}V_{m+1,m+2}\cdots V_{m'-1,m'}\right|, \tag{59}$$

where

$$V_{m,m+1} = -\frac{1}{2}g\mu_B H_x\langle m|S_-|m+1\rangle. \tag{60}$$

In the particular case $\hat{H}_A = -DS_z^2$ the calculation in Eq. (59) yields[22]

$$\Delta = \frac{2D}{[(m'-m-1)!]^2} \times \sqrt{\frac{(S+m')!\,(S-m)!}{(S-m')!\,(S+m)!}}\left(\frac{g\mu_B H_x}{2D}\right)^{m'-m}. \tag{61}$$

One can see from this calculation that in our case in Eq. (52) is

$$e^{i\varphi} = (-1)^{m'-m} \tag{62}$$

for $H_x > 0$.

To compute matrix elements of $S_\pm$ between the tunnel-split states $|\psi_\pm\rangle$ one has to go beyond the two-state model of the preceding section. Taking into account that the states $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ are not pure $|m\rangle$ and $|m'\rangle$ states [see Eq. (51)], one obtains small values for $\langle\psi_m|S_-|\psi_{m'}\rangle$ and $\langle\psi_{m'}|S_+|\psi_m\rangle$ that are, however, essential in the spin-phonon relaxation in the case when Δ is caused solely by the transverse field. These small terms can be calculated perturbatively by building chains of elementary matrix elements that join the pure states, $|m\rangle$ and $|m'\rangle$. These chains contain terms of $\hat{H}_S$ that do not commute with S_z and the corresponding energy denominators, similar to the perturbative chain of Eq. (59). The difference is that the elementary matrix element with the "external" operator S_- does not contain $-(1/2)g\mu_B H_x$, unlike all other elementary matrix elements, and the external operator S_- can be inserted into the chain at $m'-m$ different positions. For so defined indirect (real) matrix elements one obtains

$$\langle\psi_m|S_-|\psi_{m'}\rangle = \langle\psi_{m'}|S_+|\psi_m\rangle = (-1)^{m'-m+1}\frac{(m'-m)\Delta}{g\mu_B H_x}. \tag{63}$$

Note that this result does not use the specific form of $\hat{H}_A$ and it is thus universal, similar to Eq. (57). For $S=1/2$ one has $\Delta = g\mu_B H_x$ and $\langle -S|S_-|S\rangle = 1$, which is a correct result. Calculating the matrix elements between the tunnel-split states $|\psi_\pm\rangle$ given by Eq. (55) with $\varphi=0$ one obtains the unchanged result for $\langle\psi_-|S_z|\psi_+\rangle$ that is given by Eq. (57). For transverse operators one obtains

$$\langle\psi_-|S_\pm|\psi_+\rangle = \frac{(m'-m)\Delta}{2g\mu_B H_x}\left(\pm 1 + \frac{W}{\sqrt{W^2+\Delta^2}}\right). \tag{64}$$

Below we will need

$$\langle\psi_-|S_x|\psi_+\rangle = \frac{(m'-m)\Delta}{2g\mu_B H_x}\frac{W}{\sqrt{W^2+\Delta^2}} \tag{65}$$

and

$$\langle\psi_-|S_y|\psi_+\rangle = -i\frac{(m'-m)\Delta}{2g\mu_B H_x}. \tag{66}$$

Note that these results are only valid if Δ is due to the transverse field. When $[\hat{H}_A, S_z] \neq 0$ the dominating source of Δ is $\hat{H}_A$. In this case the matrix elements $\langle\psi_-|S_\pm|\psi_+\rangle$ are much smaller than $\langle\psi_-|S_z|\psi_+\rangle$ and they can be safely neglected.

C. Role of time-reversal symmetry

Let us now discuss the role of time-reversal symmetry for spin-phonon transitions. For the total Hamiltonian $\hat{H}$ to be invariant under time reversal, the external field $\mathbf{H}$ must be zero. Thus we will consider only this case here. For $\mathbf{H}=0$, tunneling can only arise from the transverse anisotropy which lifts the degeneracy of the eigenstates $|m\rangle$ and $|-m\rangle$ of the longitudinal part of the crystal-field Hamiltonian $\hat{H}_A$. According to the Kramers' theorem, this degeneragy is lifted only for integer spins S. Let $|\psi_\pm\rangle$ denote the corresponding tunnel-split eigenstates of $\hat{H}_A$. It will be shown in Appendix C that $|\psi_\pm\rangle$ are eigenstates of the time-reversal operator $\hat{K}$ with eigenvalues ±1, i.e., $|\psi_+\rangle$ and $|\psi_-\rangle$ have *opposite* parity with respect to time reversal. The spin-lattice Hamiltonian $\hat{H}_{\text{s-ph}}$ in the laboratory frame that is given by Eq. (12)) is invariant under time reversal. It will be proven in Appendix C that this property, together with the antiunitary character of $\hat{K}$, leads to the relation

$$\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle = -\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle^* \tag{67}$$

for the spin matrix element in the case of integer S. One can see that spin-phonon transitions are not ruled out by the time-reversal symmetry if the matrix element is imaginary. Complex conjugation in Eq. (67) makes the situation different from the cases of spatial symmetries.

A specific example showing the absence of a time-reversal selection rule is the crystal-field Hamiltonian $\hat{H}_A$

from Eq. (2). The contribution to $\hat{H}_{\text{s-ph}}$ from the phonons rotating the lattice around the z axis is imaginary and is given by Eq. (B5). On the other hand, eigenfunctions $|\psi_\pm\rangle$ of Eq. (55) are real for $E>0$ [see the comment below Eq. (B4)]. Thus $\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle$ is imaginary and Eq. (67) is satisfied by $\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle\neq 0$.

In the lattice frame, as well as in the laboratory frame, if our new method is used, one has to calculate matrix elements of the spin operator $\mathbf{S}$ [see Eqs. (27) and (37)] between the states $|\psi_+\rangle$ and $|\psi_-\rangle$. In contrast to the spin part of $\hat{H}_{\text{s-ph}}$, the operator $\mathbf{S}$ breaks time-reversal symmetry, see Eq. (C3). Thus one obtains the relation

$$\langle\psi_-|\mathbf{S}|\psi_+\rangle = \langle\psi_-|\mathbf{S}|\psi_+\rangle^* \tag{68}$$

instead of Eq. (67). For the biaxial model with $E>0$ the states $|\psi_+\rangle$ and $|\psi_-\rangle$ are real, and one obtains the selection rule $\langle\psi_-|S_y|\psi_+\rangle=0$ because $S_y=(i/2)(S_- - S_+)$ is imaginary. On the other hand, S_x and S_z are real, and time-reversal symmetry does not lead to selection rules for them. However, one also obtains $\langle\psi_-|S_x|\psi_+\rangle=0$, which can be shown with the help of $S_x=(1/2)(S_- + S_+)$ and Eq. (55). Thus the matrix element $\langle\psi_-|S_z|\psi_+\rangle$ given by Eq. (57), corresponding to phonons rotating the lattice about the z axis, is the only matrix element that is responsible for the relaxation between the tunnel-split states of the spin Hamiltonian for $H=0$.

V. SPIN-PHONON RELAXATION FOR TUNNEL-SPLIT STATES

The rates of spin-phonon transitions can be calculated with the help of the Fermi golden rule. One should distinguish between two situations: when the tunnel splitting Δ is caused by the terms in $\hat{H}_A$ that do not commute with S_z, such as the transverse anisotropy in Eq. (2), and when Δ is caused by the transverse field in $\hat{H}_Z$. The physical difference between these two cases is that $\hat{H}_A$ is defined in the lattice frame and thus it is rotated by the transverse phonons, whereas $\hat{H}_Z$ is defined in the laboratory frame and it is not rotated. We will see that in the first case, in the absence of the field, relaxation is due to the phonons rotating the lattice around the z axis. To the contrary, in the second case ($\hat{H}_A$ commutes with S_z) these phonons are decoupled from the spin and they produce no effect.

A. Tunneling induced by the anisotropy

In this case, as was shown at the end of Sec. IV C, the transition matrix element in Eq. (37) is due to the operator S_z only for $H=0$. For nonzero fields, S_z provides the dominant contribution to the matrix element because $\langle\psi_-|S_z|\psi_+\rangle\sim 1$ in the vicinity of the resonance [see Eq. (57)], whereas other matrix elements can be shown to be small. Neglecting these small matrix elements in Eq. (39) and substituting the result into Eq. (46) one obtains

$$\Gamma_0 = \frac{[(m'-m)/2]^2}{12\pi\hbar}\frac{\Delta^2}{Mv_t^2}\frac{\omega_0(\omega_0^2+\gamma^2 H_\perp^2)}{\omega_D^3} = \frac{[(m'-m)/2]^2}{12\pi\hbar}\frac{\Delta^2\omega_0(\omega_0^2+\gamma^2 H_\perp^2)}{\rho v_t^5}, \tag{69}$$

where $H_\perp^2=H_x^2+H_y^2$. In Eq. (69) the term ω_0^2 in the parentheses is due to the transverse phonons that rotate the lattice around the z axis, whereas the transverse-field term is due to the phonons that rotate the lattice around x and y axes.

The beauty of Eq. (69) is that it gives a universal expression for the transition rate, which does not depend on the exact form of the crystal-field Hamiltonian, provided that the uniaxial anisotropy dominates, and is expressed entirely in terms of independently measurable parameters. Eqs. (49), (54), and (69) show that for $(m'-m)^2\gg 1$ the contribution of the longitudinal bias field to the relaxation is much stronger than the contribution of the transverse field.

B. Tunneling induced by the transverse field

The spin-matrix elements for this case have been computed in Sec. IV B. For Ξ defined by Eq. (39) one obtains

$$\Xi_z = -i\langle\psi_-|S_z|\psi_+\rangle\hbar\omega_0 + \langle\psi_-|S_y|\psi_+\rangle g\mu_B H_x = 0 \tag{70}$$

that could be expected because phonons rotating the lattice around the z axis cannot cause any effect for $[\hat{H}_A, S_z]=0$. To the contrary, Ξ_x and Ξ_y are nonzero,

$$\Xi_x = -i\langle\psi_-|S_x|\psi_+\rangle\hbar\omega_0 - g\mu_B H_z\langle\psi_-|S_y|\psi_+\rangle = -\frac{i(m'-m)\Delta}{2g\mu_B H_x}(W - g\mu_B H_z) \tag{71}$$

and

$$\begin{aligned}\Xi_y &= -i\langle\psi_-|S_y|\psi_+\rangle\hbar\omega_0 + g\mu_B H_z\langle\psi_-|S_x|\psi_+\rangle \\ &\quad - g\mu_B H_x\langle\psi_-|S_z|\psi_+\rangle \\ &= -g\mu_B H_x S\frac{(m'-m)\Delta}{2\hbar\omega_0}\left(-A + \frac{W(W-g\mu_B H_z)}{(g\mu_B H_x)^2}\right).\end{aligned} \tag{72}$$

Here A is given by

$$A \equiv 1 - \frac{\Delta^2}{(g\mu_B H_x)^2} \tag{73}$$

and W is related to H_z by Eq. (49).

The spin-lattice relaxation rate is then given by Eq. (46) with $|\Xi|^2=|\Xi_x|^2+|\Xi_y|^2$. The general result is cumbersome but it simplifies for the ground-state resonance, $m=-S$ and $m'=S$,

$$\Gamma_0 = \frac{S^2}{12\pi\hbar}\frac{\Delta^2}{Mv_t^2}\frac{\omega_0(\gamma H_\perp)^2}{\omega_D^3}Q, \tag{74}$$

where we have replaced $H_x \Rightarrow H_\perp$, the field perpendicular to the anisotropy axes, and

$$Q \equiv \left[1-\left(\frac{\omega_0}{\gamma H_\perp}\right)^2+\frac{1}{2S}\left(\frac{W}{g\mu_B H_\perp}\right)^2\right]^2 + \left(1-\frac{1}{2S}\right)^2\left(\frac{W}{g\mu_B H_\perp}\right)^2\left(\frac{\omega_0}{\gamma H_\perp}\right)^2. \qquad (75)$$

In the case of $S=1/2$ one has $\Delta = g\mu_B H_\perp$, so that Q and Γ_0 are zero. This is expected as the crystal-field anisotropy $\hat{H}_A$ disappears for $S=1/2$ and phonons do not couple to the spin. In general, for the ground-state splitting one has $\Delta \propto H_\perp^{2S}$ and $\Delta \ll g\mu_B H_\perp$ for any $S>1/2$.

VI. DISCUSSION

We have studied a universal mechanism of the relaxation of a spin state in a solid in the presence of the magnetic field. It corresponds to the generation of the elastic twist mandated by conservation of energy and total angular momentum. This mode of relaxation must be the dominant one for a rigid spin cluster embedded in an elastic medium. A simple universal expression, Eqs. (27) and (37) with Eq. (28), for the transition matrix element has been derived for an arbitrary crystal-field spin Hamiltonian and an arbitrarily directed magnetic field. Our results apply to all rigid spin clusters whose low-temperature quantum spin states are due to the magnetic anisotropy.[26] A fixed-spin crystal-field Hamiltonian has proved to be a very good approximation for many molecular nanomagnets.[27] The method of computing the transition matrix elements, presented in this paper, consists of two steps. In the first (needed by any theory) step, one must obtain the eigenstates of the spin Hamiltonian, the transition between which is going to be studied. Once these eigenstates are known, the computation of the spin-phonon transition rate by our method reduces to the calculation of the matrix elements of **S** between the eigenstates of interest. We have studied in detail the transitions between tunnel-split spin states, which are difficult to compute by conventional methods. The role of the time-reversal symmetry has been analyzed. As demonstrated in Sec. IV C, not all transitions between spin states of different parity with respect to time reversal are ruled out by time-reversal symmetry. This is at variance with the case of spatial symmetries.

Universal formulas have been obtained for two particular cases of the strong uniaxial anisotropy. The first case is that of the tunnel splitting created by the crystal field, Eq. (69). The second case is that of the tunnel splitting created by the transverse magnetic field in the presence of a uniaxial magnetic anisotropy, Eq. (74). The first case corresponds to, e.g., the intensively studied $S=10$ Fe$_8$ molecular cluster, while the second case corresponds to, e.g., the recently studied $S=4$ Ni$_4$ molecular cluster.[23,24] For both cases, we have obtained relaxation rates and their field dependence, in terms of independently measurable constants and with no adjustable parameters. Among other applications, these rates are responsible for the linewidths measured in electron-spin-resonance experiments. Our results open the way for an accurate comparison between theory and experiment on the field dependence of the relaxation rate. Among many possible applications, our theory also has an important consequence for the industry of spin-based solid-state qubits. It provides a parameter-free, mandated by symmetry, lower bound on the decoherence of any such qubit.

While multiphonon processes can be studied by the same method, this paper is limited to the rates of direct one-phonon processes that dominate spin-lattice transitions at low temperature. Two-phonon Raman processes that contribute at higher temperatures will be studied elsewhere.

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APPENDIX A: SPIN-PHONON RELAXATION FOR ADJACENT LEVELS

Here we shall study the spin Hamiltonian

$$\hat{H}_S = \hat{H}_A + \hat{H}_Z = -DS_z^2 - g\mu_B H_z S_z. \qquad (A1)$$

The exact energy levels of this Hamiltonian are given by Eq. (47) with $E_m^{(A)} = -Dm^2$. We consider the spin-phonon relaxation between the adjacent levels of $\hat{H}_S$, m and $m' = m+1$. The energy difference between these levels is

$$W = \hbar\omega_0 = E_m - E_{m+1} = D(2m+1) + g\mu_B H_z \qquad (A2)$$

(we assume $W>0$). We first study the $(m, m+1)$ transitions by a conventional method that employs tilting of the anisotropy axis by transverse phonons, see, e.g., Refs. 16 and 25. In this method one writes $\hat{H}_A$ in the form

$$\hat{H}_A(\mathbf{n}) = -D(\mathbf{n}\cdot\mathbf{S})^2, \qquad (A3)$$

where $\mathbf{n}$ is the direction of the anisotropy axis,

$$\mathbf{n} = \mathbf{e}_z + \delta\mathbf{n}, \quad \delta\mathbf{n} = \delta\boldsymbol{\phi}\times\mathbf{n}. \qquad (A4)$$

Expanding $\hat{H}_A(\mathbf{n})$ up to the linear terms in $\delta\boldsymbol{\phi}$ one obtains $\hat{H}_A(\mathbf{n}) \cong -DS_z^2 + \hat{H}_{\text{s-ph}}$ with

$$\begin{aligned}\hat{H}_{\text{s-ph}} &= -D[(\delta\mathbf{n}\cdot\mathbf{S})(\mathbf{e}_z\cdot\mathbf{S}) + (\mathbf{e}_z\cdot\mathbf{S})(\delta\mathbf{n}\cdot\mathbf{S})] \\ &= -D[S_xS_z + S_zS_x]\delta\phi_y + D[S_yS_z + S_zS_y]\delta\phi_x.\end{aligned} \qquad (A5)$$

The same result follows from the calculation of the commutator in Eq. (12). We shall calculate the transition matrix element between the states $|\Psi_+\rangle = |m\rangle\otimes|n_{\mathbf{k}\lambda}\rangle$ and $|\Psi_-\rangle = |m+1\rangle\otimes|n_{\mathbf{k}\lambda}+1\rangle$. One obtains

$$\langle\Psi_-|\hat{H}_{\text{s-ph}}|\boldsymbol{\Psi}_+\rangle = \frac{iD}{2} l_{m,m+1}(2m+1)\delta\phi_{\mathbf{k}\lambda,-}, \qquad (A6)$$

where $l_{m,m+1} = \sqrt{S(S+1) - m(m+1)}$,

$$\delta\phi_{\mathbf{k}\lambda,-} \equiv \delta\phi_{\mathbf{k}\lambda,x} - i\delta\phi_{\mathbf{k}\lambda,y}, \qquad (A7)$$

and $\delta\boldsymbol{\phi}_{\mathbf{k}\lambda}$ is defined by Eq. (30). Note that the contribution to Eq. (A6) of the transverse phonons of definite chirality, Eq. (A7), having $l_z=1$ projection of the angular momentum onto the z axis, is in accordance with the conservation of the total angular momentum for the $(m+1,m)$ transition.

Quantization of lattice rotations with the help of Eq. (11) yields Eq. (40) with

$$V_{\mathbf{k}\lambda} = \frac{iD}{2} l_{m,m+1}(2m+1)\frac{e^{i\mathbf{k}\cdot\mathbf{r}}[\mathbf{k}\times\mathbf{e}_{\mathbf{k}\lambda}]\cdot(\mathbf{e}_x - i\mathbf{e}_y)}{\sqrt{8M\hbar\omega_{\mathbf{k}\lambda}}}. \quad \text{(A8)}$$

The relaxation rates between the states m and $m+1$ are given by Eqs. (42) and (43) with $V_{\mathbf{k}\lambda}$ defined by Eq. (A8). With the help of the formulas listed in the Appendix A one obtains

$$\Gamma_0 = \frac{(2m+1)^2 l^2_{m,m+1}}{24\pi\hbar}\frac{D^2}{Mv_t^2}\frac{\omega^3_{m,m+1}}{\omega_D^3}. \quad \text{(A9)}$$

The limit of $D\rightarrow 0$ corresponds to a free spin. In that limit, although the states $|m\rangle$ and $|m+1\rangle$ are still separated in energy due to the magnetic field, the rotation of the lattice cannot cause any relaxation and Eq. (A9) produces zero result.

It is instructive to see how the above result can be obtained by our method using Eqs. (32) and (37) with $\mathbf{\Omega}_{-+}\equiv\hat{\mathbf{\Omega}}_{\mathbf{k}\lambda}$ defined by Eq. (28). As the transition $|m\rangle\rightarrow|m+1\rangle$ is due to the spin operator S_+, one obtains

$$\langle\Psi_-|\hat{H}_{\text{s-ph}}|\Psi_+\rangle = -\frac{\hbar}{2} l_{m,m+1}\hat{\Omega}_{\mathbf{k}\lambda,-}, \quad \text{(A10)}$$

where $\hat{\Omega}_-\equiv\hat{\Omega}_x - i\hat{\Omega}_y$. For $\mathbf{H}=H_z\mathbf{e}_z$ this gives

$$\langle\Psi_-|\hat{H}_{\text{s-ph}}|\Psi_+\rangle = \frac{i}{2} l_{m,m+1}(\hbar\omega_0 - g\mu_B H_z)\delta\phi_{\mathbf{k}\lambda,-}. \quad \text{(A11)}$$

Here the magnetic field cancels according to Eq. (A2) and one obtains Eq. (A6).

APPENDIX B: ROLE OF ROTATIONS AROUND THE z AXIS

In Sec. V A we have calculated the spin-phonon relaxation rate between the tunnel-split resonance states of the spin in the case when the tunnel splitting Δ is due to the terms in the crystal-field Hamiltonian $\hat{H}_A$ that do not commute with S_z. The result, Eq. (69), is universal and it does not depend on the detailed form of $\hat{H}_A$. We have seen that the relaxation is generated by the phonons rotating the lattice around the Z axis. The physics of this process is transparent: In the rotating frame the spin feels the magnetic field along the Z axis. This field couples to S_z, which produces the relaxation. In this appendix we will obtain this result for a biaxial spin model by the conventional method used in Appendix D: We shall demonstrate that in the conventional method the relaxation arises from the rotation of the hard axis by the phonons. As we shall see, the computation of this effect, even for the simplest spin Hamiltonian, is significantly more cumbersome that the computation of the transition rate by our method.

Consider the spin Hamiltonian $\hat{H}_S$ of Eq. (15) with $\hat{H}_Z$ given by Eq. (9) and

$$\hat{H}_A = -DS_z^2 + E(S_x^2 - S_y^2) = -DS_z^2 + \frac{1}{2}E(S_+^2 + S_-^2). \quad \text{(B1)}$$

We assume $E>0$ for simplicity. If E is negative, one can change its sign by rotating the coordinate system by $\pi/2$ around the z axis. For $E\ll D$ the energy levels of this system can be approximately characterized by the quantum number m. Any two levels $m'>m$ can be brought into resonance by the longitudinal component of the magtetic field H_z, see Sec. IV. The tunnel splitting Δ can be calculated with the help of the high-order perturbation theory,

$$\frac{\Delta}{2} = V_{m,m+2}\frac{1}{E_{m+2}-E_m}V_{m+2,m+4}\cdots V_{m'-2,m'}, \quad \text{(B2)}$$

where

$$V_{m,m+2} = \frac{1}{2}E\langle m|S_-^2|m+2\rangle = \frac{1}{2}El_{m,m+1}l_{m+1,m+2}. \quad \text{(B3)}$$

The calculation in Eq. (B2) yields[22]

$$\Delta = \frac{2D}{[(m'-m-2)!\,!]^2} \times\sqrt{\frac{(S+m')!\,(S-m)!}{(S-m')!\,(S+m)!}}\left(\frac{E}{2D}\right)^{(m'-m)/2}. \quad \text{(B4)}$$

One can see from this calculation that in our case in Eq. (52) is $e^{i\varphi}=1$. Let us now consider the phonons that rotate the lattice around the z axis. It is easy to obtain that the result of such rotation is

$$\hat{H}_{\text{s-ph}} = -iE(S_+^2 - S_-^2)\delta\phi_z \equiv \hat{V}\delta\phi_z. \quad \text{(B5)}$$

Now, similarly to the calculation in Sec. IV B, one can compute the matrix element of $\hat{H}_{\text{s-ph}}$ between slightly delocalized states $|\psi_m\rangle$ and $|\psi_{m'}\rangle$ [see Eq. (51)] by building a minimal perturbative chain between the pure states $|m\rangle$ and $|m'\rangle$ and identifying the result with Δ given by Eq. (B2). As $\hat{H}_{\text{s-ph}}$ can be inserted at $(m'-m)/2$ positions in the chain, one obtains

$$\langle\psi_m|S_-^2|\psi_{m'}\rangle = \langle\psi_{m'}|S_+^2|\psi_m\rangle = \frac{m'-m}{2}\frac{\Delta}{E} \quad \text{(B6)}$$

and thus

$$\langle\psi_m|\hat{V}|\psi_{m'}\rangle = i\frac{m'-m}{2}\Delta,$$

$$\langle\psi_{m'}|\hat{V}|\psi_m\rangle = -i\frac{m'-m}{2}\Delta. \quad \text{(B7)}$$

For the spin eigenfunctions given by Eq. (55) with $e^{i\varphi}=1$, one obtains

$$\langle\psi_-|\hat{V}|\psi_+\rangle = i\frac{m'-m}{2}\Delta. \quad \text{(B8)}$$

The spin-phonon matrix element is then given by

$$\langle \Psi_- | \hat{H}_{\text{s-ph}} | \Psi_+ \rangle = i \frac{m' - m}{2} \Delta \delta \phi_{\mathbf{k}\lambda,z}. \tag{B9}$$

The latter coincides with the result obtained by our new method, Eqs. (38) and (39) with $\mathbf{H}=0$ and $\langle \psi_- | S_z | \psi_+ \rangle$ given by Eq. (57). The advantage of the new method is apparent as it only involves the trivial computation of the matrix element of S_z.

To gain a deeper insight into the difference between the two methods, one can start with the general form of the eigenstates $|\Psi_\pm\rangle$ given by Eq. (50) and compare general expressions for the spin-phonon matrix element due to the rotation around the z axis, used by the two methods. The traditional method uses the worked out form of the commutator in Eq. (12) while our method uses Eq. (36). The equivalence of the two results relies on the identity

$$\sum_{m=-S}^{S} C_{+,m}^* V_{m,m+2} C_{-,m+2} = \frac{\Delta}{4} \sum_{m=-S}^{S} C_{+,m}^* m C_{-,m}, \tag{B10}$$

where $\Delta = E_+ - E_-$ and the matrix element $V_{m,m+2}$ is due to the terms in $\hat{H}_A$ that do not commute with S_z. (We consider for illustration the model with $V_{m,m+1}=0$ and zero bias, $H_z=0$.) The left-hand side (lhs) of Eq. (B10) corresponds to the worked out commutator and it vanishes if one approximates $|\boldsymbol{\Psi}_\pm\rangle$ by the two-state model of Sec. IV A, i.e., if one neglects all $C_{\pm,m''}$ with $m'' \neq m, m'$. Leaving $C_{\pm,m}$ with all m leads to the correct result of order Δ in the left-hand side of Eq. (B10), but only after one accurately accounts for the cancellation of many small terms containing powers of $E/D \ll 1$. On the contrary, in the right-hand side of Eq. (B10) the small quantity Δ has been already factored out, and it is sufficient to make the two-state approximation in the sum over m.

APPENDIX C: ROLE OF THE TIME-REVERSAL SYMMETRY

In quantum mechanics time reversal is represented by the operator $\hat{K}$ that satisfies $\hat{K}^{-1} = \hat{K}^\dagger$, and, in addition, performs complex conjugation.[21] The latter comes from the requirement that the lhs, $i\hbar \partial_t |\psi(t)\rangle$ of the time-dependent Schrödinger equation, is covariant under $t \to -t$ (which changes $i \to -i$) only if one takes its complex conjugate. The latter makes $\hat{K}$ antilinear:

$$\hat{K}[c_1|\psi_1\rangle + c_2|\psi_2\rangle] = c_1^* \hat{K}|\psi_1\rangle + c_2^* \hat{K}|\psi_2\rangle. \tag{C1}$$

Because of the antilinearity, one has to specify whether $\hat{K}$ acts to the right (by default) or to the left,

$$\langle \psi | \hat{K} | \varphi \rangle \equiv \langle \psi | (\hat{K} | \varphi \rangle) = (\langle \psi | \hat{K}) | \varphi \rangle)^*. \tag{C2}$$

Operator $\hat{K}$ is called *antiunitary* because of its antilinearity and its property $\hat{K}^{-1} = \hat{K}^\dagger$.

Transformation of the spin operator $\mathbf{S}$ under time reversal follows from the requirement that $\mathbf{S}$ should behave as the orbital momentum $\mathbf{L}$ and it thus should change its sign under time reversal,

$$\mathbf{S}' = \hat{K}\mathbf{S}\hat{K}^\dagger = \hat{K}\mathbf{S}\hat{K}^{-1} = -\mathbf{S}. \tag{C3}$$

An arbitrary spin state $|\psi\rangle$ can be represented as a superposition of the eigenstates $|m\rangle$ of S_z. Choosing the phase factor of $|m\rangle$ to be one, i.e., taking $|m\rangle$ as real makes the matrix elements $\langle m | S_z | m' \rangle$ and $\langle m | S_\pm | m' \rangle$ real. In that case the explicit form of the time-reversal operator is $\hat{K} = Q\hat{U} = \hat{U}Q$, where $\hat{U} = \exp(-i\pi S_y)$ is a unitary operator and Q makes complex conjugation. Indeed, $\hat{U}$ changes the signs of S_x and S_z, whereas Q changes the sign of S_y, so that Eq. (C3) is fulfilled.

In order to determine the action of $\hat{K}$ on the tunnel-split spin eigenstates $|\psi_\pm\rangle$ of the crystal-field Hamiltonian $\hat{H}_A$ we have at first to determine the action of $\hat{K}$ on $|m\rangle$. Application of $\hat{K}S_z = -S_z\hat{K}$ and $\hat{K}S_+ = -S_-\hat{K}$ [that follow from Eqs. (C1) and (C3)] onto $|m\rangle$ yields, up to an irrelevant global factor,

$$\hat{K}|m\rangle = (-1)^{S-m}|-m\rangle. \tag{C4}$$

As a consequence one obtains $\hat{K}^2|m\rangle = (-1)^{2S}|m\rangle$, i.e., $\hat{K}^2 = 1$ for integer spins S.

In zero field, $\hat{H}_S$ reduces to $\hat{H}_A$ that must be time reversible, $\hat{K}\hat{H}_A\hat{K}^{-1} = \hat{H}_A$, i.e., it satisfies $[\hat{K}, \hat{H}_A] = 0$. For integer S the tunnel-split eigenstates $|\psi_\pm\rangle$ of $\hat{H}_A$ are nondegenerate, thus they must be eigenstates of $\hat{K}$,

$$\hat{K}|\psi_\pm\rangle = \varepsilon_\pm |\psi_\pm\rangle \tag{C5}$$

with eigenvalues $\varepsilon_\pm$. Since $\hat{K}^2 = 1$ for integer spin S, it must be $\varepsilon_\pm \in \{-1, 1\}$. Let us prove now that ε_+ and ε_- have different signs. To this end, we decompose $\hat{H}_A$ into the longitudinal and transverse parts, $\hat{H}_A^{\text{long}}$ and $\hat{H}_A^{\text{trans}}$. The former satisfies $[S_z, \hat{H}_A^{\text{long}}] = 0$ and thus it has $|\pm m\rangle$ as at least twofold degenerate eigenstates. The transverse part $\hat{H}_A^{\text{trans}}$ has matrix elements between different $|m\rangle$ and thus it removes the degeneracy between $|\pm m\rangle$ for integer S. Let us introduce

$$\hat{H}_A(\lambda) = \hat{H}_A^{\text{long}} + \lambda \hat{H}_A^{\text{trans}} \tag{C6}$$

with λ real. In the limit $\lambda \to 0$ one can find $|\psi_\pm\rangle$ analytically. Using Eqs. (C1) and (C4), as well as the relation $(-1)^{2m} = 1$ for integer S, one can check that

$$|\psi_\pm(0)\rangle = \frac{1}{\sqrt{2}}[e^{i\chi}|m\rangle \pm e^{-i\chi}|-m\rangle] \tag{C7}$$

satisfy Eq. (C5) with

$$\varepsilon_\pm(0) = \pm(-1)^{S-m}. \tag{C8}$$

Since $\hat{H}_A(\lambda)$ is continuous in λ, the eigenstates $|\psi_\pm(\lambda)\rangle$ and, in turn $\varepsilon_\pm(\lambda)$, must be continuous, too. This continuity and the discreteness of $\varepsilon_\pm$ implies that $\varepsilon_\pm$ are independent of λ. Thus one obtains $\varepsilon_+(\lambda) = -\varepsilon_-(\lambda)$ for all λ, including $\lambda = 1$. Thus $|\psi_\pm\rangle \equiv |\psi_\pm(1)\rangle$ inherits its parity from the unperturbed eigenstates. Consequently, we get an interesting result that the tunnel split eigenstates of an *arbitrary* crystal-field

Hamiltonian must have *opposite* parity with respect to time-reversal symmetry, i.e.,

$$\varepsilon_+\varepsilon_- = -1. \tag{C9}$$

The spin-phonon Hamiltonian $\hat{H}_{\text{s-ph}}$ is invariant under time reversal, i.e., $\hat{H}'_{\text{s-ph}}=\hat{K}\hat{H}_{\text{s-ph}}\hat{K}^\dagger=\hat{H}_{\text{s-ph}}$. One can obtain a symmetry relation for the spin-matrix element if one makes time reversal of both $\hat{H}_{\text{s-ph}}$ and the spin states. Inserting $\hat{K}^\dagger K=\hat{K}^{-1}\hat{K}=1$ into the matrix element, one proceeds as follows:

$$\begin{aligned}\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle &= \langle\psi_-|\hat{K}^\dagger K\hat{H}_{\text{s-ph}}\hat{K}^\dagger K|\psi_+\rangle\\ &= \langle\psi_-|\hat{K}^\dagger\hat{H}_{\text{s-ph}}\hat{K}|\psi_+\rangle\\ &= [(\langle\psi_-|\hat{K}^\dagger)\hat{H}_{\text{s-ph}}\hat{K}|\psi_+\rangle]^*\\ &= \varepsilon_+\varepsilon_-\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle^*\\ &= -\langle\psi_-|\hat{H}_{\text{s-ph}}|\psi_+\rangle^*,\end{aligned} \tag{C10}$$

where we have used Eqs. (C2), (C5), and (C9). This proves Eq. (67). The spin operator changes sign under time reversal, Eq. (C3), thus a similar procedure leads to Eq. (68).

APPENDIX D: USEFUL RELATIONS

To calculate the spin-phonon relaxation rates, the following useful relations can be used. Summation over the two transverse polarizations:

$$[\mathbf{k}\times\mathbf{e}_{\mathbf{k}t_1}] = \pm k\mathbf{e}_{\mathbf{k}t_2} \tag{D1}$$

and

$$\sum_{t=t_1,t_2}(\mathbf{e}_{\mathbf{k}t}\cdot\mathbf{a})(\mathbf{e}_{\mathbf{k}t}\cdot\mathbf{b}) = (\mathbf{a}\cdot\mathbf{b}) - \frac{(\mathbf{k}\cdot\mathbf{a})(\mathbf{k}\cdot\mathbf{b})}{k^2}. \tag{D2}$$

Averaging over the directions of the vector **k**,

$$\langle(\mathbf{k}\cdot\mathbf{a})(\mathbf{k}\cdot\mathbf{b})\rangle = \frac{k^2}{3}(\mathbf{a}\cdot\mathbf{b}). \tag{D3}$$

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