Universal mechanism of spin relaxation in solids

E. M. Chudnovsky, D. A. Garanin, and R. Schilling

1Physics Department, Lehman College, City University of New York, 250 Bedford Park Boulevard West, Bronx, New York 10468-1589, U.S.A.
2Institut für Physik, Johannes-Gutenberg-Universität, D-55099 Mainz, Germany

(Dated: 9 March 2005)

We consider relaxation of a rigid spin cluster in an elastic medium in the presence of the magnetic field. 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 lower bound on the decoherence of any spin-based solid-state qubit.

PACS numbers: 76.60.Es,75.50.Xx,75.10.Dg

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. Van Vleck 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 and start with a phenomenological expression containing all permitted by symmetry combinations of spin $S$. Some examples of the crystal-field Hamiltonian that results in the uniaxial, biaxial, and cubic magnetic anisotropy of the cluster are given below:

$$\hat{H}_A = -D(S \cdot e(3))^2$$ (1)
$$\hat{H}_A = -D(S \cdot e(3))^2 + E[(S \cdot e(1))^2 - (S \cdot e(2))^2]$$ (2)
$$\hat{H}_A = C \sum_{\alpha \neq \beta} (S \cdot e(\alpha))^2(S \cdot e(\beta))^2$$ (3)

where $e(\alpha)$ 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). Eqs. (1–3) are also applicable to magnetic molecules or clusters, $S$ being the total spin of the cluster formed by a strong exchange interaction between the individual magnetic atoms.

Lattice vibrations couple to the spin by modifying coefficients in Eqs. (1–3), changing directions of the lattice vectors $e(\alpha)$, 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 $\partial u/\partial x_j$, or their symmetric and antisymmetric combinations. Again, one can write down a phenomenological expression for the spin-phonon Hamiltonian $\hat{H}_{s\text{-}ph}$ that contains all terms permitted by the symmetry of a particular material. However the general form of $\hat{H}_{s\text{-}ph}$ 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, processes 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 $\hat{H}_{s\text{-}ph}$ due to transverse phonons can be split into two groups. The first group describes distortions 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 $\hat{H}_{s\text{-}ph}$ 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 and dif-
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. I due to the parameter-free spin-lattice interaction arising from tilting of $e^{(3)}$ by transverse phonons was considered in Ref. 19.

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, $S$ interacts only with the long-wave deformations of the crystal lattice that rotate the local frame $(e^{(1)}, e^{(2)}, e^{(3)})$ as a whole, so that the spin-phonon interaction can be obtained from $H_A$ without any phenomenological parameters. The corresponding parameter-free description of spin-lattice relaxation becomes exact in this case.

It has been noticed 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 $H_A$ is preserved, while the spin-phonon interaction is of a kinematic origin and it has a universal form that is independent from the lattice-frame approach and leads to the same relaxation rates between the tunnel-split states of $H_A$ without any phenomenological parameters. The corresponding parameter-free description of spin-lattice relaxation becomes exact in this case.

The body of this paper is organized as follows. In Sec. II we derive exact expressions for the spin-phonon interaction in the laboratory frame. A striking feature of the lattice-frame approach is that both the calculation of the rates of relaxation between the tunnel-split states of $H_A$ are universal and insensitive to the detailed form of $H_A$. As is known, $\frac{1}{2}N \gamma \Delta S^2$ etc. A transverse phonon, $u(r)$, rotates the axes of the local crystal field, $(e^{(1)}, e^{(2)}, e^{(3)})$. This rotation can be described by

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

and it is performed by the $(3 \times 3)$ rotation matrix $R$, $e^{(\alpha)} \rightarrow R e^{(\alpha)}$, i.e.,

$$e^{(\alpha)} \rightarrow R_{\beta \gamma} e^{(\alpha)}.$$

For small $\delta \phi$, one has

$$R_{\alpha \beta} = \delta_{\alpha \beta} - \epsilon_{\gamma \beta \alpha} \delta \phi_{\gamma}.$$

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

$$S \rightarrow \tilde{R} S \tilde{R}^{-1} , \quad \tilde{R} = e^{-i S \cdot \delta \phi} .$$

The total Hamiltonian can be written in the form

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

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

$$\hat{H}_Z = -g \mu_B \mathbf{H} \cdot \mathbf{S}.$$
is the Zeeman Hamiltonian, and $\hat{H}_{ph}$ is the Hamiltonian of harmonic phonons.

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

$$u = \sqrt{\frac{\hbar}{2MN}} \sum_{k\lambda} \epsilon_{k\lambda} e^{i\mathbf{k} \cdot \mathbf{r}} \left( a_{k\lambda} + a_{k\lambda}^\dagger \right)$$

where $M$ is the mass of the unit cell, $N$ is the number of cells in the crystal, $\epsilon_{k\lambda}$ are unit polarization vectors, $\lambda = t_1, t_2, l$ denotes polarization, and $\omega_{k\lambda} = \nu_{k\lambda} v_{k\lambda}$ 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

$$\hat{H} = \hat{H}_0 + \hat{H}_{s-ph}, \quad \hat{H}_{s-ph} = i \left[ \hat{H}_A, \mathbf{S} \right] \cdot \delta \phi.$$

The total Hamiltonian can be written as

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

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

$$\hat{H}_0 = \hat{H}_A + \hat{H}_{ph},$$

and

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

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 $\delta \phi$:

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

Here

$$\hat{H}_{ph}' = \hat{R}^{-1} \hat{H}_{ph} \hat{R} \cong \hat{H}_{ph} - i \left[ \hat{H}_{ph}, \delta \phi \right] \cdot \mathbf{S}, \quad \text{(17)}$$

and

$$\hat{H}_Z' = \hat{R}^{-1} \hat{H}_Z \hat{R} \cong \hat{H}_Z - i \left[ \hat{H}_Z, \mathbf{S} \right] \cdot \delta \phi$$

$$= \hat{H}_Z - g \mu_B [\mathbf{H} \times \delta \phi] \cdot \mathbf{S}, \quad \text{(18)}$$

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 $\delta \phi$ is thus

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

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

$$\hat{H}_{s-ph}' = -i \left[ \hat{H}_{ph}, \delta \phi \right] \cdot \mathbf{S} - g \mu_B [\mathbf{H} \times \delta \phi] \cdot \mathbf{S}. \quad \text{(20)}$$

With account of the relation

$$\delta \phi = \frac{i}{\hbar} [\hat{H}_{ph}, \delta \phi]$$

one obtains

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

where

$$\Omega = \delta \phi + \gamma [\mathbf{H} \times \delta \phi], \quad \text{(23)}$$

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

$$\hat{H}' = \hat{H}_0 - \hbar \Omega \cdot \mathbf{S}. \quad \text{(24)}$$

$-\hbar \Omega \cdot \mathbf{S}$ is of kinematic origin: in the rotating coordinate frame the rotation is equivalent to the magnetic field $\mathbf{H}_{eff} = \delta \phi / \gamma$ acting on the spin. The second term in Eq. 25 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. MATRIX ELEMENTS OF SPIN-LATTICE INTERACTION

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

$$| \Psi_{\pm} \rangle = | \psi_{\pm} \rangle \otimes | \phi_{\pm} \rangle. \quad \text{(24)}$$

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 $\hat{H}_{ph}$ with energies $E_{ph, \pm}$. For $\hat{H}_{s-ph}$ linear in phonon amplitudes, the states $| \phi_{\pm} \rangle$ differ by one emitted or absorbed phonon with a wave vector $k$. Thus we will use the designations

$$| \phi_+ \rangle \equiv | n_k \rangle, \quad | \phi_- \rangle \equiv | n_k + 1 \rangle. \quad \text{(25)}$$

Spin-phonon transitions conserve energy:

$$E_+ + E_{ph, +} = E_- + E_{ph, -}. \quad \text{(26)}$$

We calculate spin-phonon relaxation rates in both lattice frame and 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 $| \psi_+ \rangle \rightarrow | \psi_- \rangle$ in the lattice frame. From Eq. 24 one obtains

$$\langle \Psi_- | \hat{H}_{s-ph}' | \Psi_+ \rangle = -\hbar \Omega_{-+} \cdot \langle \psi_- | \mathbf{S} | \psi_+ \rangle, \quad \text{(27)}$$
where
\[ \Omega_{-+} \equiv \langle \phi_- | \hat{\Omega} | \phi_+ \rangle. \] (28)

To calculate the matrix element \( \Omega_{-+} \), it is convenient to step back and use the commutator form of \( \delta \hat{\phi} \) given by Eq. (21). One has
\[ \langle \phi_- | [\hat{H}_{\text{ph}}, \delta \hat{\phi}] | \phi_+ \rangle = (E_{\text{ph},-} - E_{\text{ph},+}) \delta \phi_{-+}, \] (29)
where
\[ \delta \phi_{-+} \equiv \langle \phi_- | \delta \phi | \phi_+ \rangle. \] (30)

It follows from the energy conservation, Eq. (26), that
\[ E_{\text{ph},-} = E_{\text{ph},+} = E_+ - E_- \equiv \hbar \omega_0. \] (31)

Thus one finally obtains
\[ \Omega_{-+} = i \omega_0 \delta \phi_{-+} + \gamma [\hat{H} \times \delta \phi_{-+}]. \] (32)

### B. Laboratory frame

To check the consistency of our method, let us now obtain the expression for the matrix element in the laboratory frame. Eq. (12) gives
\[ \langle \psi_- | \hat{H}_{s-\text{ph}} | \psi_+ \rangle = i \langle \psi_- | [\hat{H}_{A}, \hat{S}] | \psi_+ \rangle \cdot \delta \phi_{-+}. \] (33)

It is convenient to avoid explicitly working out the commutator in the spin matrix element. To this end, we add and subtract \( \hat{H}_Z \):
\[ \langle \psi_- | [\hat{H}_{A}, \hat{S}] | \psi_+ \rangle = \langle \psi_- | [\hat{H}_S, \hat{S}] | \psi_+ \rangle \]
\[ - i \langle \psi_- | [\hat{H}_Z, \hat{S}] | \psi_+ \rangle. \] (34)

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 \( E_{\pm} \):
\[ \langle \psi_- | [\hat{H}_S, \hat{S}] | \psi_+ \rangle = (E_- - E_+) \langle \psi_- | \hat{S} | \psi_+ \rangle. \] (35)

The Zeeman term in Eq. (31) can be done as in Eq. (18). With the help of Eq. (31), one then obtains
\[ \langle \psi_- | \hat{H}_{s-\text{ph}} | \psi_+ \rangle = -i \hbar \Omega_{-+} \cdot \langle \psi_- | \hat{S} | \psi_+ \rangle, \] (36)
where \( \Omega_{-+} \) is given by Eq. (22). We see that the spin-phonon matrix elements computed in the laboratory and lattice frames, Eqs. (27) and (36), are exactly the same.

### IV. SPIN MATRIX ELEMENTS FOR TUNNEL-SPLIT STATES

The method of the computation of transition rates outlined in the previous sections has significant advantage over conventional methods. Regardless of the explicit form of the spin Hamiltonian, only the matrix elements of the operator \( \hat{S} \) need to be computed. Especially interesting is the case of strong uniaxial anisotropy, in which \( \hat{H}_S \) nearly commutes with \( \hat{S}_z \), so that the energy levels can be approximately described with the help of the quantum number \( m \):
\[ E_m = E_m^{(A)} - g \mu_B H_z m, \] (37)
where \( E_m^{(A)} \) is the contribution of the crystal field that satisfies \( E_{m-} = E_{m+} \). 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
\[ g \mu_B H_z^{(\text{res})} = \frac{E_{m'} - E_{m}}{m - m'} \equiv \frac{\hbar \omega_{m,m'}^{(A)}}{m - m'}. \] (38)

For Mn12 the dominant term in the uniaxial anisotropy energy is \( E_{m}^{(A)} = -2Dm^2 \) and thus \( g \mu_B H_z^{(\text{res})} = -2D(m + m') = Dk \), where \( k \) is the resonance number (see Fig. 1). The level bias is given by
\[ W \equiv E_m - E_{m'} = g \mu_B \left( H_z - H_z^{(\text{res})} \right)(m' - m) \]
\[ = (m' - m) g \mu_B H_z + h \omega_{m,m'}^{(A)}. \] (39)

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

#### A. The two-state model: \( \langle \psi_- | \hat{S}_z | \psi_+ \rangle \)

Due to the terms in \( \hat{H}_S \) that do not commute with \( \hat{S}_z \), the true eigenstates of \( \hat{H}_S \) are expansions over the

![FIG. 1: Spin energy levels of a Mn12Ac molecule for \( H_z = 0 \) and \( H_z = D \) corresponding to the first resonance, \( k = 1 \).](image-url)
complete \(|m\) basis:
\[
|\psi_\pm\rangle = \sum_{m''=-S}^{S} c_{\pm,m} |m''\rangle.
\]
(40)

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 \(|\bar{m}\rangle\):
\[
|\bar{m}\rangle = \sum_{m''=-S}^{S} c_{mm''} |m''\rangle,
\]
(41)
where \(|c_{mm}| \equiv 1\) and all other coefficients are small. Hybridization of the states \(|\bar{m}\rangle\) and \(|\bar{m}'\rangle\) can be taken into account in the framework of the two-state model
\[
\langle \bar{m}_i | \hat{H}_S | \bar{m}_i \rangle = E_{m_i}, \quad m_i = m, m',
\]
\[
\langle \bar{m} | \hat{H}_S | \bar{m}' \rangle = \frac{1}{2} \Delta e^{i\varphi},
\]
(42)
where \(\Delta\) 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 \(\varphi\) is a phase. If \(\hat{H}_S\) expressed in terms of \(S_x\) and \(S_z\) is real, then the only two possibilities are \(\varphi = 0, \pi\), so that \(e^{i\varphi} = \pm 1\). Diagonalizing this \(2 \times 2\) matrix yields the eigenvalues
\[
E_\pm = \frac{1}{2} \left( E_m + E_{m'} \pm \sqrt{W^2 + \Delta^2} \right).
\]
(43)
The energy difference is
\[
E_+ - E_- = \hbar \omega_0 \equiv \sqrt{W^2 + \Delta^2}.
\]
(44)
The corresponding eigenvectors can be represented in the form
\[
|\psi_\pm\rangle = \frac{1}{\sqrt{2}} \left( C_+ e^{i\varphi/2} |\bar{m}\rangle \pm C_- e^{-i\varphi/2} |\bar{m}'\rangle \right),
\]
(45)
where
\[
C_\pm = \sqrt{1 \pm \frac{W}{\sqrt{W^2 + \Delta^2}}}.
\]
(46)
Far from the resonance, \(|W| \gg \Delta\), the eigenstates and energy eigenvalues reduce to those of \(|\bar{m}\rangle\) and \(|\bar{m}'\rangle\) states. For \(W > 0\) and \(W \gg \Delta\) one has \(|\psi_+\rangle \equiv e^{i\varphi/2} |\bar{m}\rangle\) and \(|\psi_-\rangle \equiv e^{-i\varphi/2} |\bar{m}'\rangle\). On the contrary, for \(W < 0\) and \(|W| \gg \Delta\) one has \(|\psi_+\rangle \equiv e^{-i\varphi/2} |\bar{m}'\rangle\) and \(|\psi_-\rangle \equiv e^{i\varphi/2} |\bar{m}\rangle\). Exactly at the resonance, \(W = 0\), the eigenstates \(|\psi_\pm\rangle\) are superpositions of \(|\bar{m}\rangle\) and \(|\bar{m}'\rangle\) with equal weights, and signs depending on the phase \(\varphi\).

Eq. (14) is sufficient to calculate the matrix element
\[
\langle \psi_- | S_\pm | \psi_+ \rangle = -\frac{\Delta}{\sqrt{W^2 + \Delta^2}} \frac{m' - m}{2}.
\]
(47)
This result does not depend on the detailed form of \(\hat{H}_A\), provided that the condition of strong uniaxial anisotropy is fulfilled, 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 \(\Delta\) 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 \(\Delta\) 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 subsection.

### 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:
\[
\hat{H}_Z = -g\mu_B H_x S_z - g\mu_B H_y S_x
\]
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 \(H_x\):
\[
\frac{\Delta}{2} = \left[ V_{m,m+1} + \frac{1}{2} \frac{1}{E_{m+1} - E_m} V_{m+1,m+2} \cdots V_{m'\rightarrow m} \right],
\]
(49)
where
\[
V_{m,m+1} = -\frac{1}{2} g\mu_B H_x \langle m | S_- | m + 1 \rangle.
\]
(50)
In the particular case \(\hat{H}_A = -D S_z^2\) the calculation in Eq. (19) yields
\[
\Delta = \frac{2D}{[(m' - m - 1)]^2} \times \sqrt{\frac{(S + m')!(S - m')!}{(S - m)!(S + m)!}} \left( \frac{g\mu_B H_x}{2D} \right)^{m' - m}.
\]
(51)
One can see from this calculation that in our case in Eq. (19) is
\[
e^{i\varphi} = (-1)^{m' - m}
\]
(52)
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 \(|\bar{m}\rangle\) and \(|\bar{m}'\rangle\) are not pure \(|m\rangle\) and \(|m'\rangle\) states, see Eq. (11), one obtains small values for \(\langle \bar{m} | S_- | \bar{m} \rangle\) and \(\langle \bar{m}' | S_+ | \bar{m} \rangle\) that are, however, essential in the spin-phonon relaxation in the case when \(\Delta\) 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. (19). 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

$$\langle \hat{m} | S_- | \hat{m}' \rangle = \langle \hat{m}' | S_+ | \hat{m} \rangle = (-1)^{m' - m + 1} \frac{(m' - m) \Delta}{g\mu_B H_x}. \quad (53)$$

Note that this result does not use the specific form of $\hat{H}_A$ and it is thus universal, similarly to Eq. (17). 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. (45) with $m \Rightarrow \hat{m}$, $m' \Rightarrow \hat{m}'$, and $\varphi = 0$ one obtains the unchanged result for $\langle \psi_- | S_z | \psi_+ \rangle$ that is given by Eq. (17). For transverse operators one obtains

$$\langle \psi_- | S_\pm | \psi_+ \rangle = \frac{(m' - m) \Delta}{2g\mu_B H_x} \left( \pm 1 + \frac{W}{\sqrt{W^2 + \Delta^2}} \right). \quad (54)$$

Below we will need

$$\langle \psi_- | S_z | \psi_+ \rangle = \frac{(m' - m) \Delta}{2g\mu_B H_x} \frac{W}{\sqrt{W^2 + \Delta^2}} \quad (55)$$

and

$$\langle \psi_- | S_y | \psi_+ \rangle = -i\frac{(m' - m) \Delta}{2g\mu_B H_x}. \quad (56)$$

Note that these results are only valid if $\Delta$ is due to the transverse field. When $[\hat{H}_A, S_z] \neq 0$ the dominating source of $\Delta$ 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 $H$ to be invariant under time reversal, the external field $H$ must be zero. Thus we will consider only this case here. For $H = 0$, 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 degeneracy 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 $\pm 1$, i.e. $|\psi_+\rangle$ and $|\psi_-\rangle$ have opposite parity with respect to time reversal. The spin-lattice Hamiltonian $\hat{H}_{S_{ph}}$ 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

$$\langle \psi_- | \hat{H}_{S_{ph}} | \psi_+ \rangle = -\langle \psi_- | \hat{H}_{S_{ph}} | \psi_+ \rangle^* \quad (57)$$

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. (57) 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 $\hat{H}_{S_{ph}}$ from the phonons rotating the lattice around $z$-axis is imaginary and is given by Eq. (55). On the other hand, eigenfunctions $|\psi_\pm\rangle$ of Eq. (45) are real for $E > 0$ [see comment below Eq. (24)]. Thus $\langle \psi_- | \hat{H}_{S_{ph}} | \psi_+ \rangle$ is imaginary and Eq. (57) is satisfied by $\langle \psi_- | \hat{H}_{S_{ph}} | \psi_+ \rangle \neq 0$.

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 $S$ [see Eqs. (27) and (50)] between the states $|\psi_+\rangle$ and $|\psi_-\rangle$. In contrast to the spin part of $\hat{H}_{S_{ph}}$, the operator $S$ breaks time-reversal symmetry, see Eq. (43). Thus one obtains the relation

$$\langle \psi_- | S | \psi_+ \rangle = \langle \psi_- | S | \psi_+ \rangle^* \quad (58)$$

instead of Eq. (57). 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 $S_y = i/2(S_- - S_+)$. 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 obtains $\langle \psi_- | S_x | \psi_+ \rangle = 0$, too, that can be shown with the help of $S_x = (1/2)(S_- + S_+)$ and Eq. (45). Thus the matrix element $\langle \psi_- | S_z | \psi_+ \rangle$ given by Eq. (17), 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 $\Delta$ 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 $\Delta$ 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. (36) 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. (40)], whereas other matrix elements can be shown to be small. Thus one can write

\[
\langle \psi_- | \hat{H}_{s-ph} | \psi_+ \rangle = - \langle \psi_- | S_z | \psi_+ \rangle \hbar \Omega_{+,z} .
\] (59)

With the help of Eq. (11) and Eq. (28), Eq. (59) can be rewritten as

\[
\langle \psi_- | \hat{H}_{s-ph} | \psi_+ \rangle = \frac{\hbar}{\sqrt{N}} \sum_{k \lambda} V_{k \lambda} \left\{ n_k + 1 \left| (a_{k \lambda} + a^\dagger_{k \lambda}) \right| n_k \right\},
\] (60)

where we used the designations of Eq. (28) and

\[
V_{k \lambda} \equiv - \langle \psi_- | S_z | \psi_+ \rangle \frac{e^{i k \cdot r}}{\sqrt{8 M \omega_{k \lambda}^2}} \left\{ \hbar \omega_0 |k \times e_{k \lambda}\rangle \right\}_z + i \mu_B [H \times |k \times e_{k \lambda}\rangle]_z \right\}. \tag{61}
\]

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

\[
\begin{bmatrix}
W_{+-} \\
W_{-+} \\
\end{bmatrix} = W_0 \begin{bmatrix}
n_{\omega_0} + 1 \\
n_{\omega_0} \\
\end{bmatrix},
\] (62)

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

\[
W_0 = \frac{1}{\sqrt{N}} \sum_{k \lambda} |V_{k \lambda}|^2 2 \pi \delta (\omega_{k \lambda} - \omega_0) .
\] (63)

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

\[
\dot{n}_+ = -W_{-+} n_+ + W_{+-} n_- = -\Gamma n_+ + W_{+-}
\] (64)

defines the relaxation rate

\[
\Gamma = W_{+-} + W_{-+} = W_0 (2 n_{\omega_0} + 1) .
\] (65)

One can see that the two terms Eq. (61) do not interfere and that only transverse phonons, \(\lambda = t\), are active in the relaxation process. In the first term of Eq. (61) one can use \(|k \times e_{k \lambda}| = \pm \epsilon_{k} e_{k^t \lambda^t}\), where \(t\) and \(t^t\) denote different transverse phonons. Summation over polarization vectors of transverse phonons and averaging over the directions of \(k\) can be performed with the help of the formulas given in the Appendix D. Replacing \(N^{-1} \sum_{k \lambda} \ldots\) by \(v_0 \int d^3 k/(2\pi)^3 \ldots\) \((v_0\) being the unit cell volume) and using Eq. (12), one obtains

\[
W_0 = \frac{[(m' - m)/2]^2}{12\pi \hbar} \frac{\Delta^2}{\mu v_f^2} \frac{\omega_0^2 + \gamma^2 H_z^2}{\omega_0^2 + \gamma^2 H_z^2} = \frac{[(m' - m)/2]^2}{12\pi \hbar} \frac{\Delta^2}{\rho v_f^5} \frac{\omega_0^2 + \gamma^2 H_z^2}{\omega_0^2 + \gamma^2 H_z^2},
\] (66)

where \(\rho\) is the mass density, \(\omega_D \equiv v_f/v_0^{1/3}\) is the Debye frequency for the transverse phonons, \(\omega_0\) is given by Eq. (11), and \(H_z^2 = H_x^2 + H_y^2\). In Eq. (66) the term \(\omega_0^2\) in the brackets 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. (66) 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. Equations (32), (41), and (66) show that for \((m' - m)^2 \geqslant 1\) 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 C]. The calculation of \(\Omega_{+-}\) is more complicated than in the previous subsection because one has to take into account the transverse components in the field term in Eq. (93).

\[
\Omega_{+-} = (i \omega_0 e_x + \gamma H_z e_y) \delta \phi_{(-+,x)} + (i \omega_0 e_y - \gamma H_z e_x + \gamma H_x e_z) \delta \phi_{(-+,y)} + (i \omega_0 e_z - \gamma H_x e_y) \delta \phi_{(-+,z)} .
\] (67)

The transition matrix element, Eqs. (27) or (30), can be presented in the form

\[
\langle \psi_- | \hat{H}_{s-ph} | \psi_+ \rangle = K_x \delta \phi_{(-+,x)} + K_y \delta \phi_{(-+,y)} + K_z \delta \phi_{(-+,z)} .
\] (68)

Using Eqs. (17) and (40), one obtains

\[
K_x = -i \langle \psi_- | S_x | \psi_+ \rangle \hbar \omega_0 - \langle \psi_- | S_y | \psi_+ \rangle \mu_B H_z = 0 .
\] (69)

This result was expected because phonons rotating the lattice around the \(z\) axis cannot cause any effect for \([H_A, S_z] = 0\). To the contrary, \(K_x\) and \(K_y\) are nonzero:

\[
K_x = -i \langle \psi_- | S_x | \psi_+ \rangle \hbar \omega_0 - \mu_B H_z \langle \psi_- | S_y | \psi_+ \rangle = -\frac{i (m' - m) \Delta}{2 \mu_B H_z} (W - \mu_B H_z) .
\] (70)

and

\[
K_y = -i \langle \psi_- | S_y | \psi_+ \rangle \hbar \omega_0 + \mu_B H_z \langle \psi_- | S_x | \psi_+ \rangle = -\mu_B H_z \langle \psi_- | S_y | \psi_+ \rangle - \frac{\mu_B H_z S(m' - m) \Delta}{2 \hbar \omega_0} \left( -A + \frac{W (W - \mu_B H_z)}{(\mu_B H_z)^2} \right) ,
\] (71)

where \(A\) is given by

\[
A = 1 - \frac{\Delta^2}{(\mu_B H_z)^2} .
\] (72)
and $W$ is related to $H_z$ by Eq. \ref{eq:W_Hz}

Quantization of the phonon field, Eq. \ref{eq:quantization}, yields Eq. \ref{eq:quantization_2}, where

$$V_{k\lambda} = \frac{e^{i k \cdot r}}{\sqrt{8 M \hbar \omega_{k\lambda}}} \left\{ K_x [k \times e_{k\lambda}]_x + K_y [k \times e_{k\lambda}]_y \right\}. \quad (73)$$

The relaxation rates between the states $m$ and $m'$ are given by Eq. \ref{eq:relaxation_rates}, where

$$W_0 = \frac{1}{12 \pi \hbar} \frac{|K_x|^2 + |K_y|^2}{M \gamma_H^2} \frac{\omega_D^2}{\omega_0^2} \quad (74)$$

and $K_x$ and $K_y$ are given by Eqs. \ref{eq:Kx} and \ref{eq:Ky}, respectively. The general result is cumbersome but it simplifies for the ground-state resonance, $m = -S$ and $m' = S$:

$$W_0 = \frac{S^2}{12 \pi \hbar} \frac{\Delta^2}{M \gamma_H^2} \frac{\omega_D^2}{\omega_0^2} Q, \quad (75)$$

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

$$Q = \left[ 1 - \left( \frac{\omega_0}{\gamma H_\perp} \right)^2 + \frac{1}{2S} \left( \frac{W}{g_H^2} \right)^2 \right]^2 + \left[ 1 - \frac{1}{2S} \left( \frac{W}{g_H^2} \right)^2 \left( \frac{\omega_0}{\gamma H_\perp} \right)^2 \right]^2. \quad (76)$$

In the case of $S = 1/2$ one has $\Delta = g_H H_\perp$, so that $Q$ and $W_0$ 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 $\Delta \ll g_H H_\perp$ for any $S > 1/2$.

\section*{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. Simple universal expression, Eqs. \ref{eq:universal} and \ref{eq:universal_2}, for the transition matrix element has been derived for an arbitrary spin Hamiltonian and an arbitrarily directed magnetic field. 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 $\mathbf{S}$ 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. \ref{sec:time_reversal} 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. \ref{eq:tunnel_split}. The second case if that of the tunnel splitting created by the transverse magnetic field in the presence of an uniaxial magnetic anisotropy, Eq. \ref{eq:transverse_split}.

The first case corresponds to, e.g., the intensively studied $S = 10$ Fe$_8$ molecular cluster, while the second corresponds to, e.g., the recently studied $S = 4$ Ni$_4$ molecular cluster.\footnote{The work of E.M.C. has been supported by the NSF Grant No. EIA-0310517. R.S. gratefully acknowledges stimulating discussions with Martin Reuter.}

\section*{APPENDIX A: SPIN-PHONON RELAXATION FOR ADJACENT LEVELS}

Here we shall study the spin Hamiltonian

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

The exact energy levels of this Hamiltonian are given by Eq. \ref{eq:energy_levels} with $E_{m}^{(A)} = -D m^2$. 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

$$W = \hbar \omega_0 = E_m - E_{m+1} = D(2m + 1) + g_H H_z. \quad (A2)$$

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. \ref{16024}. The method in this method one writes $\hat{H}_A$ in the form

$$\hat{H}_A(n) = -D (n \cdot S)^2, \quad (A3)$$
where \( \mathbf{n} \) is the direction of the anisotropy axis,
\[
\mathbf{n} = \mathbf{e}_z + \delta \mathbf{n}, \quad \delta \mathbf{n} = \delta \phi \times \mathbf{n}.
\] (A4)
Expanding \( \hat{H}_A(\mathbf{n}) \) up to the linear terms in \( \delta \phi \) one obtains \( \hat{H}_A(\mathbf{n}) \simeq -DS_z^2 + \hat{H}_{s-ph} \) with
\[
\hat{H}_{s-ph} = -D [(\delta \mathbf{n} \cdot \mathbf{S}) (\mathbf{e}_z \cdot \mathbf{S}) + (\mathbf{e}_z \cdot \mathbf{S}) (\delta \mathbf{n} \cdot \mathbf{S})] = -D [S_x S_z + S_z S_x] \delta \phi_y + D [S_y S_z + S_z S_y] \delta \phi_x. \tag{A5}
\]
The result follows from the calculation of the commutator in Eq. (12). We shall calculate the transition matrix element between the states \( |\Psi_+\rangle = |m\rangle \otimes |n_k\rangle \) and \( |\Psi_-\rangle = |m+1\rangle \otimes |n_k+1\rangle \). One obtains
\[
\langle \Psi_- | \hat{H}_{s-ph} | \Psi_+ \rangle = \frac{iD}{2} l_{m,m+1} (2m+1) \langle n_k+1 | \delta \phi_- | n_k \rangle,
\] (A6)
where \( l_{m,m+1} = \sqrt{S(S+1) - m(m+1)} \) and
\[
\delta \phi_- \equiv \delta \phi_y - i \delta \phi_x \equiv \delta \phi_x - i \delta \phi_y. \tag{A7}
\]
Note that the contribution \( |A_4| \) 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. (60) with [cf. Eq. (61)]
\[
V_{kl} = \frac{iD}{2} l_{m,m+1} (2m+1) \frac{e^{i \lambda \cdot (k \times \mathbf{e}_k)} (\mathbf{e}_x - i \mathbf{e}_y)}{\sqrt{SM \omega_{k\lambda}}} \tag{A8}
\]
The relaxation rates between the states \( m \) and \( m+1 \) are given by Eqs. (62) and (63) with \( V_{kl} \) defined by Eq. (A8). With the help of the formulas listed in the Appendix B one obtains
\[
W_0 = \frac{(2m+1)^2 \omega_{m,m+1}^2}{24 \pi \hbar} \frac{D^2}{M v_f^2} \omega_D^3. \tag{A9}
\]
The limit of \( D \to 0 \) 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 new method using Eqs. (36) and (32) with \( \Omega_{-+} = \langle n_k+1 | \hat{H}_{s-ph} | n_k \rangle \). As the transition \( |m\rangle \to |m+1\rangle \) is due to the spin operator \( S_z \), one obtains
\[
\langle \Psi_- | \hat{H}_{s-ph} | \Psi_+ \rangle = -\frac{h}{2} \omega_{m,m+1} \langle n_k+1 | \Omega_- | n_k \rangle, \tag{A10}
\]
where \( \Omega_- \equiv \hat{\Omega}_x - i \hat{\Omega}_y \). For \( \hat{H} = H_z \mathbf{e}_z \) this gives
\[
\langle \Psi_- | \hat{H}_{s-ph} | \Psi_+ \rangle = \frac{i}{2} \omega_{m,m+1} \langle n_k+1 | \delta \phi_- | n_k \rangle. \tag{A11}
\]
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. 1.A2 we have calculated the spin-phonon relaxation rate between the tunnel-split resonance states of the spin in the case when the tunnel splitting \( \Delta \) is due to the terms in the crystal-field Hamiltonian \( \hat{H}_A \) that do not commute with \( S_z \). The result, Eq. (A6), 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 the phonons, which produces the relaxation. In this Appendix we will obtain this result for a biaxial spin model by the conventional method used in the previous Appendix. 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 new method.

Consider the spin Hamiltonian \( \hat{H}_S \) of Eq. (15) with \( \hat{H}_Z \) given by Eq. (34) and
\[
\hat{H}_A = -DS_z^2 + E \left( S_x^2 - S_y^2 \right) = -DS_z^2 + \frac{1}{2} E \left( S_x^2 + S_y^2 \right). \tag{B1}
\]
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 approximated by the quantum number \( m \). Any two levels \( m' > m \) can be brought into resonance by the longitudinal component of the magnetic field \( H_z \), see Sec. 1.A2. The tunnel splitting \( \Delta \) can be calculated with the help of the high-order perturbation theory:
\[
\frac{\Delta}{2} = \sqrt{\frac{W_{v_m+2}E_{m+2} - E_{m+2}E_{m+4} \cdots V_{m'-2,m'}}{E_{m+2} - E_{m+4} \cdots V_{m'-2,m'}}}, \quad \tag{B2}
\]
where
\[
W_{m,m+2} = \frac{1}{2} E \langle m \mid S_x^2 \mid m+2 \rangle = \frac{1}{2} E \langle m+1 \mid l_{m+1,m+2} \rangle. \tag{B3}
\]
Calculation in Eq. (B2) yields\textsuperscript{22}
\[
\Delta = \frac{2D}{[(m'-m-2)!]^2} \times \sqrt{\frac{(S+m')!(S-m')!}{(S'-m')!(S+m')!}} \left( E \right)^{(m'-m)/2}. \tag{B4}
\]
One can see from this calculation that in our case in Eq. (B2) is \( e^{i \phi} = 1 \). 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
\[
\hat{H}_{s-ph} = -i E \left( S_x^2 - S_y^2 \right) \delta \phi_z \equiv \hat{\nu} \delta \phi_z. \tag{B5}
\]
Now, similarly to the calculation in Sec. 1.A2 one can compute the matrix element of \( \hat{H}_{s-ph} \) between slightly
delocalized states $|\tilde{m}\rangle$ and $|\tilde{m}'\rangle$ [see Eq. (11)] by building a minimal perturbative chain between the pure states $|m\rangle$ and $|m'\rangle$ and identifying the result with $\Delta$ given by Eq. (12). As $H_{c-ph}$ can be inserted at $(m' - m)/2$ positions in the chain, one obtains

$$
\langle \tilde{m} | S_2^z | \tilde{m}' \rangle = \langle \tilde{m}' | S_2^z | \tilde{m} \rangle = \frac{m' - m}{2} \Delta
$$

and thus

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

$$
\langle \tilde{m}' | \hat{V} | \tilde{m} \rangle = -i \frac{m' - m}{2} \Delta.
$$

For the spin eigenfunctions given by Eq. (15) with $e^{i\phi} = 1$ one obtains

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

The spin-phonon matrix element is then given by

$$
\langle \Psi_- | \hat{H}_{S-ph} | \Psi_+ \rangle = i \frac{m' - m}{2} \Delta \delta_{\phi_{-z}}.
$$

The latter coincides with the result obtained by our new method, Eq. (26) with $\langle \psi_- | S_1^z | \psi_+ \rangle$ given by Eq. (27) and $i\hbar \Omega_{-z} = i\hbar \omega_0 \phi_{-z}$. 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. (10) 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 the new method uses Eq. (25). The equivalence of the two results relies on the identity

$$
\sum_{m=-S}^{S} C_{s,m} C_{-m} = \frac{\Delta}{4} \sum_{m=-S}^{S} C_{s,m} m C_{-m},
$$

where $\Delta = E_+ - E_-$ and the matrix element $V_{m,m+2}$ is due to the terms in $H_A$ 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 of Eq. (B10) corresponds to the worked out commutator and it vanishes if one approximates $|\Psi_{\pm}\rangle$ by the two-state model of Sec. IVA, i.e., if one neglects all $C_{s,m'}$ with $m' \neq m, m'$. Leaving $C_{s,m}$ with all $m$ leads to the correct result of order $\Delta$ 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 $\Delta$ 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. The latter coincides with the result obtained by our 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. (10) 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 the new method uses Eq. (25). The equivalence of the two results relies on the identity

$$
\sum_{m=-S}^{S} C_{s,m} C_{-m} = \frac{\Delta}{4} \sum_{m=-S}^{S} C_{s,m} m C_{-m},
$$

where $\Delta = E_+ - E_-$ and the matrix element $V_{m,m+2}$ is due to the terms in $H_A$ 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 of Eq. (B10) corresponds to the worked out commutator and it vanishes if one approximates $|\Psi_{\pm}\rangle$ by the two-state model of Sec. IVA, i.e., if one neglects all $C_{s,m'}$ with $m' \neq m, m'$. Leaving $C_{s,m}$ with all $m$ leads to the correct result of order $\Delta$ 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 $\Delta$ has been already factored out, and it is sufficient to make the two-state approximation in the sum over $m$.

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 $H_S$ reduces to $H_A$ that must be time-reversible, $\hat{K} H_A \hat{K}^{-1} = H_A$, i.e., it satisfies $\left[ \hat{K}, H_A \right] = 0$. For integer $S$ the tunnel-split eigenstates $|\psi_{\pm}\rangle$ of $H_A$ are nondegenerate, thus they must be eigenstates of $\hat{K}$:

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

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 $\varepsilon_+$ and $\varepsilon_-$ have different signs. To this end, we decompose $H_A$ into the longitudinal and transverse parts, $H_A^{long}$ and

$H_A^{trans}$
$\hat{H}_A^{\text{trans}}$. 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

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

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

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

satisfy Eq. (C5) with

$$\epsilon_{\pm}(0) = \pm(-1)^{S−m}. \quad (C8)$$

Since $\hat{H}_A(\lambda)$ is continuous in $\lambda$, the eigenstates $|\psi_{\pm}(\lambda)\rangle$ and, in turn $\epsilon_{\pm}(\lambda)$, must be continuous, too. This continuity and the discreteness of $\epsilon_{\pm}$ implies that $\epsilon_{\pm}$ are independent of $\lambda$. Thus one obtains $\epsilon_+(\lambda) = -\epsilon_-(\lambda)$ for all $\lambda$, 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.,

$$\epsilon_+\epsilon_- = −1. \quad (C9)$$

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

$$\langle \psi_- | \hat{H}_{s-ph} | \psi_+ \rangle = \langle \psi_- | \hat{K}^\dagger \hat{K}\hat{H}_{s-ph}\hat{K}^\dagger | \psi_+ \rangle = \langle \psi_- | \hat{K}^\dagger | \hat{H}_{s-ph} | \psi_+ \rangle^* = \epsilon_+\epsilon_- \langle \psi_- | \hat{H}_{s-ph} | \psi_+ \rangle^* \quad (C10)$$

where we have used Eqs. (C2), (C5), and (C9). This proves Eq. (C1). Spin operator changes sign under time reversal, Eq. (C6), thus a similar procedure leads to Eq. (C9).

**APPENDIX D: USEFUL RELATIONS**

To calculate the spin-phonon relaxation rates, the following useful relations can be used.

Summation over the two transverse polarizations:

$$[k \times e_{kt1}] = \pm ke_{kt2} \quad (D1)$$

and

$$\sum_{t=t_1, t_2} (e_{kt} \cdot a) (e_{kt} \cdot b) = (a \cdot b) - \frac{(k \cdot a)(k \cdot b)}{k^2}. \quad (D2)$$

Averaging over the directions of the vector $k$:

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