Effect of environmental spins on Landau-Zener transitions

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Landau-Zener (LZ) transitions of a two-level system (e.g., electronic spin in molecular magnets) coupled to one or many environmental spins (e.g., nuclear spins) are studied. For rather general interactions the LZ problem is reduced to that of a Landau-Zener grid. It is shown analytically that environmental spins initially in their ground state do not influence the staying probability P. This changes if they are prepared in a statistical ensemble. For a more specific model with environmental spins in a transverse field, LZ transitions are studied in the case of well-separated resonances in the LZ grid. The full evolution of the system is described as a succession of elementary transitions at avoided crossings and free evolution between them. If the environmental spins are strongly coupled to the central spin, their effect on P is weak. In other cases LZ transitions are strongly suppressed and P is decreasing very slowly with the sweep-rate parameter $\varepsilon \propto 1/v$, v being the energy sweep rate.

I. INTRODUCTION

Spin tunneling in molecular magnets[1–3] (see Ref. 4 for a review) is strongly affected by the interaction between the spins S of magnetic molecules (henceforth electronic spins or simply spins) and nuclear spins I (see, e.g., Refs. 5–7). Since the tunnel splitting Δ is typically rather small, interaction with nuclear spins create an energy bias W on electronic spins that can largely exceed Δ and thus bring them in or off tunneling resonance. Coupling to nuclear spins renders the problem many-body character, especially if the coupling to electronic spins is strong enough and thus tunneling transitions of the electronic spins strongly perturb the nuclear subsystem.

An important kind of experiments on molecular magnets is the so-called Landau-Zener (LZ) experiment[8,9] in which the external magnetic field is time-linearly swept through the resonance, and the magnetization change resulting from spin transitions is monitored. The asymptotic staying probability in the standard LZ effect is given by[10–13]

$$P = e^{-\varepsilon}, \quad \varepsilon \equiv \frac{\pi \Delta^2}{2\hbar v}, \tag{1}$$

where $v = \dot{W} = \text{const}$ is the energy sweep rate (contributions of the four authors are reviewed in Ref. 14). Relating P to the observed magnetization change allowed to extract the splitting Δ for the molecular magnet Fe_8.[8] The results were in accord with theoretical predictions that the dependence of Δ on a magnetic field along the hard axis shows periodic suppression of tunneling.[15] In addition, experimental results for the effective splitting $\Delta^{\text{eff}}(\varepsilon)$ have demonstrated the existence of an isotope effect originating from different nuclear spins of the investigated Fe_8 isotopes.[9] A remarkable property of the LZ effect with linear sweep is independence of the result for P of the damping of quantum levels[16] that can exceed Δ. Another remarkable feature is that in the fast-sweep limit $\varepsilon \ll 1$ the lowest-order result $P \cong 1 - \varepsilon$ is robust with respect to the effects of the interaction discussed below. This allowed successful interpretation of the experiments at fast sweep in terms of the standard LZ effect, except for the isotope effect.[9]

In the LZ setting, all spins go through the tunneling resonance at some moment of time, in spite of the internal bias due to nuclear spins, as well as dipole-dipole interaction (DDI) between electronic spins. However, the internal bias has a nontrivial time dependence that makes the total energy sweep time nonlinearly and drastically changes the LZ effect. In the quantum-mechanical language, crossing of two energy levels in the one-particle LZ effect transforms into a series of crossings of many energy levels in the many-body case (see, e.g., Fig. 1 of Ref. 17, Fig. 2 of Ref. 18 or figures in Refs. 19 and 20, where many-body LZ effect is described by random matrices). The result of multiple quantum transitions at all crossings is in most cases to increase the staying probability P for the initial quantum state, compared to the noninteracting case. Especially strong increase in P (that is, the reduction of the transition probability $1 - P$) takes place for the ferromagnetic coupling between the electronic spins.

Analytical and numerical solution of the many-body LZ problem is in general a formidable task. In particular, a full quantum-mechanical solution is prohibitive because of a huge Hilbert space, 2^N for N spins 1/2. Quantum mean-field approximation (MFA)[17,21] makes the problem tractable numerically, since the size of the numerical problem is only N. A toy model of the many-body LZ effect, N spins all coupled with the same strength with each other,[17] also leads to a numerical problem of size N, which allows to accurately study the effect of many crossings and to test the validity of the MFA. Probability for *all* spins to remain in their initial states (that is not related to the magnetization change) in the LZ model with pairwise interaction between spins can be calculated analytically.[22]

Effect of realistic interactions such as DDI on the LZ effect could only be studied in the fast-sweep limit, where a perturbative analytical solution in order ε^2 can be found.[18] This allowed to theoretically explain the experimentally observed onset of the many-body regime at slower sweeps.[9] Up to now no way to theoretically study the effect of DDI on the

LZ effect in molecular magnets at arbitrary sweep rate could be proposed.

The interaction with nuclear spins strongly reduces the effect of DDI on the LZ effect that otherwise would be too strong. In Mn$_{12}$, there are 12 Mn nuclear spins $I=5/2$ in each molecule, coupled to the electronic spin S via the contact hyperfine interaction. Since for nuclear spins this interaction is much stronger than other interactions such as the Zeeman interaction with the external field and the nuclear quadrupole interaction, one can neglect the latter. Then nuclear spins do not have any dynamics and simply act on the electronic spins as frozen-in random bias fields. The ensuing inhomogeneous broadening of tunneling resonances strongly reduces the influence of spin-spin interactions on the LZ effect.[18]

In fact, there are a lot of other atoms in magnetic molecules, mainly hydrogen atoms that possess nuclear spins. These nuclear spins interact with the electronic spins via the nuclear dipole-dipole interaction (NDDI). As the nuclear magnetic moment is by a factor of 10^3 smaller than the electronic magnetic moment, NDDI is much weaker than DDI. However, because of a large number of nuclear spins (120 protons in a Fe$_8$ molecule[23]) their cumulative influence on the electronic spins is appreciable. In contrast to Mn nuclear spins in Mn$_{12}$, interaction of the remote nuclear spins with the electronic spins is not necessarily dominating, hence these nuclear spins should have their own dynamics and the field they produce on the electronic spins is not frozen in.

For a rather general electronic-nuclear spin Hamiltonian, a perturbative approach up to second order in the bare tunneling matrix element is used in Ref. 24, which does yield the dependence on the nuclear spins, which are described as fluctuating fields.[25] Restricting to a simpler model, a renormalized splitting obtained by an instanton technique is used to calculate the transition probability up to second order. The result[24] coincides with that for the fluctuating fields, i.e., no isotope effect exists in this approach. A similar approach by eliminating the nuclear spins within a coherent spin path integral formalism for the electronic spins has been performed in Ref. 26 to predict suppression of macroscopic quantum coherence. Since this was done without a sweeping field, no predictions for the LZ probability can be deduced. A purely numerical solution of the problem has been presented in Ref. 27.

The aim of the present paper is to clarify the role of nuclear spins possessing their own dynamics on the basis of standard quantum mechanics with no usage of stochastic arguments or functional techniques. We will be using the same simplest model as Ref. 24, an electronic spin coupled to several nuclear spins that also experience an effective field in the perpendicular direction and are initially in the thermally equilibrium state. Our approach consists of two steps. First we prove analytically that the LZ problem for a rather general electronic-nuclear spin Hamiltonian can be exactly mapped to that of a Landau-Zener grid consisting of two families of parallel ascending and descending lines vs the energy bias W. This allows one to obtain some general predictions without specifying the explicit form of the nuclear spin interactions. Then, in the second step, we construct an analytical solution based on the standard LZ scattering matrix at every elementary crossing of the system's energy levels including quantum-mechanical phases.

Problems of this kind have been considered previously.[24,28–30] Demkov and Osherov have shown that in the case of one level crossing several energy levels, the staying probability after all crossings is a product of all elementary staying probabilities.[28] Noteworthy is that this conclusion is valid even in the case of crossings that are *not well separated* with each other. In the case of *several* parallel lines crossing another set of parallel lines, Brundobler and Elser made a conjecture that the same result, multiplication of probabilities, holds for every ascending line.[31] Refs. 32 and 33 present derivations of the Demkov-Osherov-Brundobler-Elser (DOBE) formula with different methods. On the other hand, the probability of transition to upper ascending lines is exactly zero since it would require evolution in a negative time direction (the so-called no-go theorem[32,34,35]).

For the probabilities of transitions to lower ascending lines and to descending lines, no general analytical result exists. Since there are different "trajectories" through different intermediate levels on the way between the initial and final levels, transition probabilities oscillate because of quantum-mechanical interference (see, e.g., Ref. 36). As in most cases these oscillations should be averaged out because of the distribution of system's parameters, an incoherent formalism[24,29] neglecting nondiagonal density matrix coefficients has been used.

What concerns the problem with nuclear spins that we are considering here, one of our results is that nuclear spins initially in their ground state do not influence the asymptotic staying probability P for the electronic spin. This surprising result has been found numerically for an electronic spin with hyperfine coupling to nuclear spins.[37] A similar result has been found independently for a spin-boson Hamiltonian[38] and for an electronic spin coupled to a more general bath.[39] On the other hand, here is a substantial increase of P if the nuclear spins are initially in their excited states. In the latter case and more generally for nuclear spins at finite temperatures, the staying probability exhibits an isotope effect. However, the effect disappears again if nuclear spins are strongly coupled to the electronic spin, as well as for arbitrary coupling constant in the fast-sweep limit.

The paper is organized as follows. Section II introduces a general model for a central spin 1/2 coupled to environmental spins and undergoing a LZ transition. The Hamiltonian of environmental spins can be arbitrary, including their interaction with each other. It is shown how the Hamiltonian of the system can be diagonalized with respect to the environmental spins, which leads to the Landau-Zener grid. In Sec. III a particular model is introduced, the model with one nuclear spin I in an arbitrarily directed effective field. This model can be easily diagonalized by choosing an appropriate frame for the nuclear spin having the z' axis along the total field. In Sec. IV the staying probability P on the LZ grid is calculated for well-separated resonances by multiplying LZ scattering matrices of elementary avoided crossings. In Sec. V the model is generalized for N equivalent nuclear spins I. This model can be reduced to the model with one nuclear spin as the states of the nuclear subsystem can be classified in the total nuclear spin I_{tot} that is dynamically conserved. In this section the effect of quantum-mechanical phase oscillations

is considered. Averaging over initial thermal distribution of nuclear spins and over different I_{tot} leads to only partial averaging out of the oscillations for the simulated system sizes. Here the more realistic incoherent approximation is introduced that leads to smooth dependences $P(\varepsilon)$. The concluding section contains a discussion of the two main cases: Mn^{55} nuclear spins in the Mn_{12} molecular magnet and nuclear spins of the protons.

II. GENERAL FORMULATION

Tunneling of an electronic spin S of a magnetic molecule under the barrier can be considered in the approximation of two resonant levels as dynamics of a pseudospin 1/2 coupled to N environmental spins, say, nuclear spins I. The Hamiltonian has the form

$$\hat{H}(t) = -\frac{1}{2}W(t)\sigma_z - \frac{1}{2}\Delta\sigma_x - \sigma_z\hat{V}(\{\mathbf{I}\}) + \hat{H}_{\text{nuc}}(\{\mathbf{I}\}), \quad (2)$$

where $\{\mathbf{I}\} \equiv \mathbf{I}_1, \ldots, \mathbf{I}_N$, and σ_z, σ_x are Pauli matrices. We assume a time-linear energy sweep $W(t) = vt$ with $v = $ const. The third term here describes the contact hyperfine coupling or dipole-dipole interaction between the electronic spin and nuclear spins. The fourth term is the nuclear Hamiltonian that can also contain interaction between nuclear spins.

Let us introduce basis states

$$|\xi;\{m_I\}\rangle = |\xi\rangle \otimes |\{m_I\}\rangle, \quad \xi = \pm 1, \quad m_I^{(i)} = -I, \ldots, I, \quad (3)$$

$\{m_I\} \equiv m_I^{(1)}, \ldots, m_I^{(N)}$, which form an eigenbasis of σ_z and $I_z^{(i)}$:

$$\sigma_z|\xi;\{m_I\}\rangle = \xi|\xi;\{m_I\}\rangle,$$

$$I_z^{(i)}|\xi;\{m_I\}\rangle = m_I^{(i)}|\xi;\{m_I\}\rangle. \quad (4)$$

The Hamiltonian matrix

$$\mathbb{H}(t) \equiv \{\langle\xi';\{m_I'\}|\hat{H}(t)|\xi;\{m_I\}\rangle\} \quad (5)$$

can be represented in the following block form corresponding to the two electronic states:

$$\mathbb{H}(t) = \begin{pmatrix} \mathbb{H}_{--}(t) & \mathbb{H}_{-+} \\ \mathbb{H}_{+-} & \mathbb{H}_{++}(t) \end{pmatrix}, \quad (6)$$

where $\mathbb{H}_{+-} = \mathbb{H}_{-+} = -(\Delta/2)\mathbb{I}$, $\mathbb{I}$ being a unit matrix in nuclear indices, and

$$\mathbb{H}_{\pm\pm}(t) = \mp\frac{1}{2}W(t)\mathbb{I} \mp \mathbb{V} + \mathbb{H}_{\text{nuc}}.$$

Here the $(2I+1)^N \times (2I+1)^N$ matrices with respect to nuclear indices are defined by

$$\mathbb{V} \equiv \{\langle\{m_I'\}|\hat{V}|\{m_I\}\rangle\}, \quad (7)$$

etc.

Since $\mathbb{H}_{\pm\pm}$ is Hermitian, it can be diagonalized by a unitary transformation matrix $\mathbb{U}_\pm$

$$\mathbb{U}_\pm\mathbb{H}_{\pm\pm}(t)\mathbb{U}_\pm^{-1} = \mathbb{D}_\pm(t), \quad (8)$$

$\mathbb{D}_\pm(t)$ being diagonal. Applying the block unitary transformation

Energy levels/Δ

$m_I' = 0$ $m_I' = -1$ $A = 10$ $\Lambda_x = 2$

$m_I' = 1$

$m_I = -1$

$m_I = 0$ $m_I = 1$

(a)

Energy levels/Δ
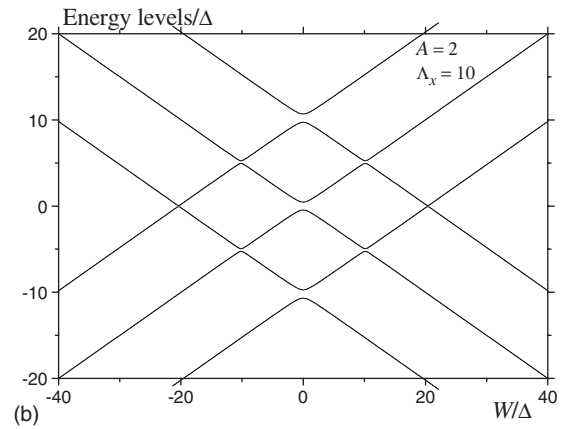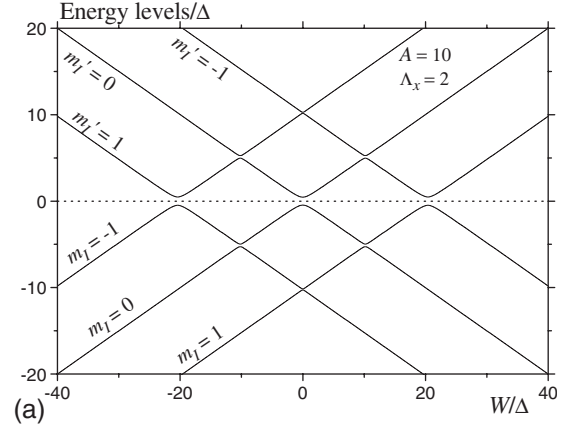
$A = 2$ $\Lambda_x = 10$

(b)

FIG. 1. Landau-Zener grid for one nuclear spin $I = 1$ and $\Lambda_z = 0$: (a) $A \gg \Lambda_x$; (b) $A \ll \Lambda_x$.

$$\mathbb{U} = \begin{pmatrix} \mathbb{U}_- & \mathbb{O} \\ \mathbb{O} & \mathbb{U}_+ \end{pmatrix} \quad (9)$$

to Eq. (6), $\mathbb{O}$ being zero matrix, one obtains the transformed Hamiltonian matrix

$$\mathbb{H}'(t) = \begin{pmatrix} \mathbb{D}_-(t) & \mathbb{V}' \\ \mathbb{V}'^\dagger & \mathbb{D}_+(t) \end{pmatrix}, \quad (10)$$

where

$$\mathbb{V}' = -(\Delta/2)\mathbb{U}_-\mathbb{U}_+^{-1}, \quad \mathbb{V}'^\dagger = -(\Delta/2)\mathbb{U}_+\mathbb{U}_-^{-1}. \quad (11)$$

In the new basis $|\xi;k\rangle$, there are two sets of nuclear states for the electronic spin up and down, $\xi = \pm 1$. Diagonal elements of the diagonal matrices $\mathbb{D}_\pm(t)$ have the form

$$D_{\xi,k}(t) = -\frac{\xi}{2}W(t) + d_{\xi,k}, \quad (12)$$

$k = 1, \ldots, (2I+1)^N$, sorted so that $d_{\xi,k}$ increases with k. Elements of $\mathbb{V}'$ are

$$V'_{kk'} = -(\Delta/2)(\mathbb{U}_-\mathbb{U}_+^{-1})_{kk'}. \quad (13)$$

Avoided crossing of $(2I+1)^N$ ascending ($\xi = -1$) lines with $(2I+1)^N$ descending ($\xi = 1$) lines forms the Landau-Zener grid shown in Fig. 1 in a particular case of one nuclear spin $I = 1$. In general, all crossings are avoided crossings with

splittings $\Delta_{kk'} = |2V'_{kk'}|$, as defined by Eq. (13). Crossing of $|1;k\rangle$ with $|-1;k'\rangle$ occurs at $D_{+,k}(t) = D_{-,k'}(t)$ or

$$W(t) = W_{kk'} \equiv d_{+,k} - d_{-,k'}. \tag{14}$$

If the system is prepared at $t = -\infty$ in the state $|-1, k\rangle$, then the probability P_{kk} to remain in this state is given by the DOBE formula as the product of staying probabilities at all crossings:[28,31–33]

$$P_{kk} = \exp\left[-\varepsilon \sum_{k'} (\Delta_{kk'}/\Delta)^2\right] = \exp\left[-\varepsilon \sum_{k'} |(U_-U_+^{-1})_{kk'}|^2\right]. \tag{15}$$

With the use of

$$\sum_{k'} |(U_-U_+^{-1})_{kk'}|^2 = \sum_{k'} (U_-U_+^{-1})_{kk'}(U_-U_+^{-1})^\dagger_{k'k}$$

$$= (U_-U_+^{-1}U_+U_-^{-1})_{kk}$$

$$= \{\mathbb{I}\}_{kk} = 1, \tag{16}$$

one obtains

$$P_{kk} = e^{-\varepsilon}, \tag{17}$$

the same as Eq. (1). This result shows that P_{kk} does not depend on nuclear spins, i.e., there is no isotope effect. However, since we are interested in transitions of the electronic spin alone, the relevant quantity is

$$P = \sum_{kk'} n_k P_{kk'}, \tag{18}$$

where n_k are populations of the nuclear levels in the initial state. This formula assumes that initially nuclear spins are in a state described by a diagonal density matrix, e.g., a thermal equilibrium state. With account of the no-go theorem[32,34,35] and Eq. (17), the result reduces to

$$P = e^{-\varepsilon} + \sum_{k>k'} n_k P_{kk'}. \tag{19}$$

If all nuclear spins are initially in the ground state ($n_k = \delta_{k,1}$), there are no terms in the sum and the standard LZ result is reproduced. Otherwise P exhibits an isotope effect and increases above $e^{-\varepsilon}$, i.e., coupling to nuclear spins is hampering spin transitions. For not too low temperatures, nuclear spins are equidistributed in the initial state, i.e., $n_k = (2I+1)^{-N}$.

The effect of hampering spin transitions is especially strong at slow sweep. Indeed, at slow sweep in the case of a standard LZ effect, the system practically follows the lower adiabatic level, so that the probability P of a transition to the upper adiabatic level (i.e., of staying on the ascending diabatic level) is exponentially small. For the model with nuclear spins, the starting level of the system is in general not the lowest level because nuclear spins are thermally distributed over their energy levels. In addition, splittings $\Delta_{kk'}$ are widely distributed so that there are very small splittings and the adiabatic limit is practically never reached. As a result, there are a lot of transitions between ascending and descending levels in both directions, so that the electronic spin per-

forms a complicated motion on the Landau-Zener grid.

Consideration in this section suggests that interaction between N nuclear spins does not change the situation qualitatively. Indeed, Eq. (10) has the same form with and without interaction, so that the topology of the LZ grid is not affected. Numerical results of Ref. 27 show only a moderate effect of interaction between nuclear spins. Anyway, all feasible types of interactions between nuclear spins, such as the direct dipole-dipole interaction and indirect interactions via the electronic spins, are much weaker than the interaction of nuclear spins with the electronic spin and interaction of nuclear spins with the external magnetic field or with the gradients of the microscopic electric field[6,7] due to the quadrupole moment of nuclei.

In the next section we will consider our basic model of an electronic spin interacting with one nuclear spin in an effective field that can be easily diagonalized. Generalization for the case of many nuclear spins will be done later in Sec. V.

III. THE MODEL HAMILTONIAN AND ITS DIAGONALIZATION

Consider the Hamiltonian for an electronic spin coupled to a single environmental spin

$$\hat{H} = -\frac{1}{2}W(t)\sigma_z - \frac{1}{2}\Delta\sigma_x - A\sigma_z I_z - \Lambda_z I_z - \Lambda_x I_x \tag{20}$$

that is a particular form of Eq. (2). Terms with $A'\sigma_z I_x$, $A''\sigma_z I_y$, and $\Lambda_y I_y$ can be added to the Hamiltonian but such terms can be eliminated by choosing its own system of axes x', y', z' for the nuclear spin. A stands for the contact hyperfine interaction or for NDDI between the electronic spin and protons, as said above. In Eq. (20) Λ_z and Λ_x are energy-dimensional components of the field acting on nuclear spins, e.g., an external magnetic field, $\Lambda_\alpha = g_n\mu_n H_\alpha$, where $\alpha = x, y$, μ_n is the nuclear magneton, and g_n is the nuclear Landé factor. A Mn^{55} nucleus in the molecular magnet Mn_{12} has $I = 5/2$ and the magnetic moment $\mu_{Mn^{55}} = 3.45\mu_n$, so that $g_{n,Mn^{55}} \simeq 3.45/I \simeq 1.38$. A proton has $I = 1/2$ and the magnetic moment $\mu_p = 2.79\mu_n$, so that $g_{n,p} \simeq 2.79/I \simeq 5.58$. For the contact hyperfine interaction with the Mn^{55} nuclear spins in Mn_{12} one has $A/k_B = 0.02$ K. This interaction is very strong and equivalent to a magnetic field of 40 T applied to nuclear spins.

For the description of the states of the nuclear spin it is convenient to use the basis of its eigenstates corresponding to the states $|\downarrow\rangle$ and $|\uparrow\rangle$, or $\xi = \pm$, of the electronic spin. Fixing the electronic spin in the state ξ creates an effective field $\xi A_z \mathbf{e}_z$ on the nuclear spin then gives the effective nuclear Hamiltonian

$$\hat{H}_{\xi,n,\text{eff}} = -\mathbf{F}_\xi \cdot \mathbf{I}, \tag{21}$$

where

$$\mathbf{F}_\xi = (\xi A + \Lambda_z)\mathbf{e}_z + \Lambda_x \mathbf{e}_x \tag{22}$$

is the total field acting on the nuclear spin. This nuclear Hamiltonian can be diagonalized by choosing the z'_ξ axis for the nuclear spin in the direction of $\mathbf{F}_\xi$. The details of the

procedure that is an implementation of the general method of Sec. II can be found in Appendix. Elements of the Hamiltonian matrix in the new basis have the form

$$H'_{\xi,m_I;\xi',m'_I} = E_{\xi,m_I}\delta_{\xi'\xi}\delta_{m'_I m_I} - \frac{1}{2}\Delta_{\xi,m_I,m'_I}\delta_{\xi',-\xi}, \quad (23)$$

where

$$E_{\xi,m_I} = -\frac{1}{2}\xi W(t) - F_\xi m_I \quad (24)$$

are the diagonal elements of $\mathbb{D}_\pm$ of Eq. (8). For $\Lambda_z=0$ one obtains

$$\Delta_{\xi,m_I,m'_I} = \Delta\xi^{m_I-m'_I}d^{(I)}_{m_I m'_I}\left(2\arcsin\frac{A}{F}\right), \quad (25)$$

where $d^{(I)}_{m_I m'_I}(\beta)$ is the spin rotation matrix and $F=\sqrt{A^2+\Lambda_x^2}$. In Eq. (23) E_{ξ,m_I} describes $2I+1$ ascending ($\xi=-1$) and $2I+1$ descending ($\xi=1$) lines. All crossings are avoided crossings, because all $d^{(I)}_{m_I m'_I}\neq 0$. The sum rule

$$\sum_{m'=-I}^{I}[d^{(I)}_{m'm}(\beta)]^2 = 1 \quad (26)$$

leads to Eq. (17) in our particular case.

For $\Lambda_z=0$, one obtains the matrix $\mathbb{V}'$ in Eq. (10) ($\xi=-1$, $\xi'=1$) in the form

$$\mathbb{V}' = -\frac{\Delta}{2}\begin{pmatrix} \dfrac{\Lambda_x}{F} & \dfrac{A}{F} \\ -\dfrac{A}{F} & \dfrac{\Lambda_x}{F} \end{pmatrix} \quad (27)$$

for $I=1/2$,

$$\mathbb{V}' = -\frac{\Delta}{2}\begin{pmatrix} \dfrac{\Lambda_x^2}{F^2} & \sqrt{2}\dfrac{\Lambda_x A}{F^2} & \dfrac{A^2}{F^2} \\ -\sqrt{2}\dfrac{\Lambda_x A}{F^2} & \dfrac{\Lambda_x^2-A^2}{F^2} & \sqrt{2}\dfrac{\Lambda_x A}{F^2} \\ \dfrac{A^2}{F^2} & -\sqrt{2}\dfrac{\Lambda_x A}{F^2} & \dfrac{\Lambda_x^2}{F^2} \end{pmatrix} \quad (28)$$

for $I=1$, etc. The matrix elements depend only on the relation between Λ_x and A in Eq. (20). For $\Lambda_x\gg A$ the matrix $\mathbb{V}'$ becomes nearly diagonal, that results from $\beta_\xi\approx\beta_{-\xi}$ thus $\beta\approx 0$. In the opposite case $\Lambda_x\ll A$ matrix $\mathbb{V}'$ becomes nearly antidiagonal, that results from $\beta=\beta_{-\xi}-\beta_\xi\approx\pi$. For $\Lambda_x\gg A$ level splittings $\Delta_{\xi,m_I,m'_I}=2|V'_{\xi,m_I,m'_I}|$ are large between the levels having the same m_I, other splittings are small, as shown in Fig. 1(b). This means that transitions of the electronic spin mostly leave nuclear spins at their initial levels, a natural result for a small coupling to spins. For $\Lambda_x\ll A$, the maximal splittings are those between the levels with nuclear indices related by $m'_I=-m_I$, while other splittings are small, as shown in Fig. 1(a). In the original basis with the quantization axis z, this means that the states of nuclear spins do not change, too, similarly to the other limiting case. Indeed, for
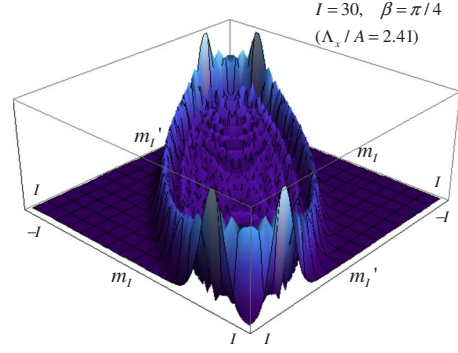

FIG. 2. (Color online) Squares of splittings, $(\Delta'_{m_I m_I})^2 \propto [d^{(I)}_{m_I m_I}(\beta)]^2$ on the LZ grid for a large "nuclear spin" $I=30$ and $\beta=\pi/4(\Lambda_x/A=2.41)$.

$\Lambda_x=0$ there are no transitions of nuclear spins since the latter have no dynamics. For $\Lambda_z\neq 0$, matrix $\mathbb{V}'$ is cumbersome but has the same properties: Nearly diagonal for $\beta\approx 0$ (small A) and nearly antidiagonal for $\beta\approx\pi$ (large A).

For large I the distribution of splittings in the plane (m_I,m'_I), defined by the spin rotation matrix $d^{(I)}_{m_I m'_I}(\beta)$, becomes more interesting, see Fig. 2. The splittings become very small outside an ellipse and maximal on the ellipse. Inside the ellipse, $d^{(I)}_{m_I m'_I}(\beta)\sim 1$ but changes abruptly if the indices change by one. For $\beta=\pi/2$ the ellipse becomes a circle of radius I. For $\beta\to 0$ or $\beta\to\pi$ the ellipse degenerates into a vertical ($m'_I=m_I$) or horizontal ($m'_I=-m_I$) lines, respectively. For large I, even if β is close to 0 ($\Lambda_x/A\gg 1$) or π ($\Lambda_x/A\ll 1$), there are many crossings inside the ellipse where splittings are comparable to Δ.

In particular, for $\beta\ll 1$ the matrix $d^{(I)}_{m'm}(\beta)$ of Eq. (A8) becomes nearly diagonal and can be expanded directly as

$$d^{(I)}_{m'm}(\beta) \cong \delta_{m'm} - \beta\langle m'|iI_y|m\rangle$$

$$= \delta_{m'm} - \frac{\beta}{2}(\delta_{m',m+1}l_{m,m+1} - \delta_{m',m-1}l_{m,m-1}), \quad (29)$$

where $l_{m,m+1}=\sqrt{I(I+1)-m(m+1)}$. This is the case realized for $\Lambda_x\gg A$, where from Eq. (A10) with $\xi=-1$ follows $\beta\cong -2A/F\cong -2A/\Lambda_x$ and in Eq. (A7)

$$\frac{\Delta_{-1,m_I,m'_I}}{\Delta} = \delta_{m_I m'_I} + \frac{A}{\Lambda_x}(\delta_{m'_I,m_I-1}l_{m_I,m_I-1} - \delta_{m'_I,m_I+1}l_{m_I,m_I+1}), \quad (30)$$

in accordance with Eqs. (27) and (28) in this limit. Similarly, the case $\Lambda_x\ll A$ corresponds to β close to π, so that $d^{(I)}_{m'm}(\beta)$ becomes nearly anti-diagonal. The elements adjacent to the antidiagonal are proportional to $(\Lambda_x/A)l_{m_I,m_I+1}$. In both cases, diagonal or anti-diagonal form of $d^{(I)}_{m'm}(\beta)$ requires $IA/\Lambda_x \ll 1$ or $I\Lambda_x/A\ll 1$, respectively.

IV. TRANSITIONS ON THE LANDAU-ZENER GRID

Quantum evolution of the system accompanying the sweeping across the Landau-Zener grid consists in LZ transitions at avoided crossings and a free evolution between them. The latter leads to accumulation of quantum-mechanical phases that leads to the interference in the staying probability P. The calculation is a straightforward matrix algebra that can be found in the Appendix. The final result is the full scattering matrix of Eq. (B20) that transforms the initial state of the system $\mathbf{c}^{\mathrm{in}}$ into the final state $\mathbf{c}^{\mathrm{out}}$. If in the initial state the nuclear spin is in its ground state, application of Eq. (B17) and calculation of the staying probability yields the result of Eq. (1), no effect of nuclear spins.

For $I=1/2$ the problem can be solved analytically. If the nuclear spin is in its excited state, then the result is

$$P = e^{-\varepsilon} + \exp\left(-\frac{\varepsilon A^2}{F^2}\right)\left[1 - \exp\left(-\frac{\varepsilon A^2}{F^2}\right)\right]$$
$$\times \left[1 - \exp\left(-\frac{\varepsilon \Lambda_x^2}{F^2}\right)\right] 4 \sin^2\frac{\varepsilon F^2}{\pi \Delta^2}. \quad (31)$$

In the fast-sweep limit $\varepsilon \ll 1$ this formula simplifies to

$$P \cong e^{-\varepsilon} + \varepsilon^2 \left(\frac{A\Lambda_x}{F^2}\right)^2 4 \sin^2\frac{\varepsilon F^2}{\pi \Delta^2}, \quad (32)$$

i.e., at the linear order in ε Eq. (1) is robust. For $A \ll \Lambda_x$ the envelope of Eq. (31) has a local maximum at $\varepsilon \sim \Lambda_x^2/A^2$ with $P_{\max} \sim 1$. The asymptotic $\varepsilon \gg 1$ behavior Eq. (31) is determined by the factor $\exp(-\varepsilon A^2/F^2)$ that is slowly decaying for $A \ll \Lambda_x$. The factor A^2/F^2 in the exponential is the square of the antidiagonal elements of the matrix in Eq. (27) and it corresponds to the splitting that is much smaller than Δ. To the contrary, for $A \gg \Lambda_x$ the result is close to $P=e^{-\varepsilon}$. This means that the influence of nuclear spins strongly coupled to the electronic spin is small.

In fact, analytical expressions, although too cumbersome, can be obtained for any I. The common feature of the solutions for all I is a standard decay of $P(\varepsilon)$ for $\varepsilon \gg 1$ in the case $A \gg \Lambda_x$ and an extremely slow decay in the case $A \ll \Lambda_x$. This becomes clear from the analysis of the LZ grids in both limiting cases, shown in Fig. 1. For $A \gg \Lambda_x$ the large splittings in Fig. 1(a) line up horizontally, and in the slow-sweep limit the system cannot cross the dotted line moving along the ascending levels from left to right. It follows the exact levels and adiabatically turns down to the descending levels that leads to a full LZ transition, $P \approx 0$. On the contrary, for $A \ll \Lambda_x$ the large splittings in Fig. 1(b) line up vertically. Although at slow sweep transitions at these crossings are adiabatic, there are smaller crossings at $W<0$ and $W>0$ where transitions are non-adiabatic, so that the electronic spin can end up in its both states. As a result, $P(\varepsilon)$ vanishes only at extremely slow sweep, $\varepsilon \ggg 1$, at which the smallest crossings become adiabatic.

Next we present figures illustrating the dependence of the asymptotic staying probability P on the sweep-rate parameter ε for the model with one nuclear spin. Figure 3 shows the results for $I=1/2$ and different ratios between Λ_x and the electron-nuclear coupling A. The effect of nuclear spins is
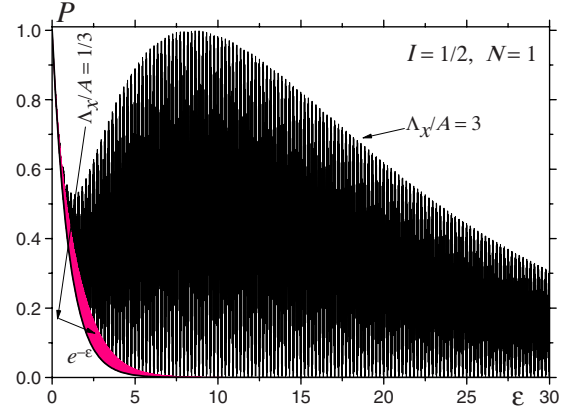

FIG. 3. (Color online) Asymptotic staying probability P for an electronic spin coupled to one nuclear spin $I=1/2$, initially in its excited state. The influence of strongly coupled nuclear spins becomes small, the curve $\Lambda_x/A = 1/3$.

large for $\Lambda_x \gtrsim A$, in accordance with Eq. (31).

With increasing I the number of crossings in the LZ grid and thus the effect of the coupling to the nuclear spin on P increases, as one can see in Fig. 4. On the other hand, the effect is maximal for the nuclear spin initially in the mostly excited state and decreases in the case of the thermal distribution ($T=\infty$) in the initial state. For $I=5/2$ the effect is large even for $\Lambda_x/A = 1/3$. This suggests that Λ_x/A is not a proper parameter to describe relative strength of different terms in the Hamiltonian. As commented upon below Eq. (30), the ratio between the sub-anti-diagonal to the dominant antidiagonal terms is

$$l_{m,m+1}\Lambda_x/A \sim I\Lambda_x/A \quad (33)$$

that is close to 1 in Fig. 4. Still in Mn_{12} the hyperfine coupling A is very strong, see comment below Eq. (20). External transverse field of 2 T creates $\Lambda_x/A \simeq 2/40=0.05$, so that with $I=5/2$ one has $I\Lambda_x/A \simeq 0.12$. Since this parameter en-
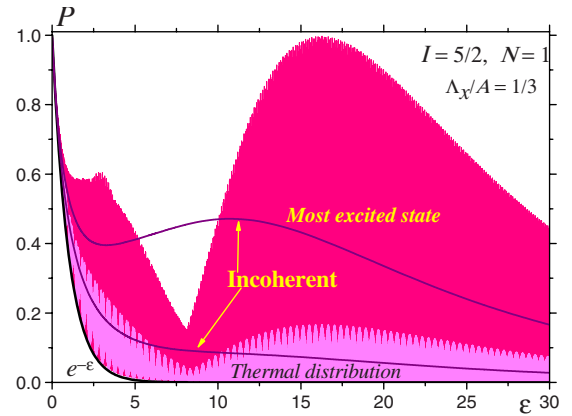

FIG. 4. (Color online) P for one nuclear spin $I=5/2$ with $\Lambda_x/A = 1/3$. The nuclear spin is prepared (i) in its mostly excited state and (ii) in thermal distribution. In the latter case oscillations of $P(\varepsilon)$ are reduced. The results of the incoherent approximation (defined in the next section) are shown by smooth lines in the two cases.

ters squared the effective sweep parameter $\varepsilon_{mm'}$ at sub-primary crossings, the direct effect of Mn^{55} spins on the LZ transitions in Mn_{12} should be small for not too strong magnetic fields. The physical reason for this is that nuclear spins do not have a sufficient dynamics to undergo transitions together with the electronic spin. The only thing that they can do is to create a static bias on the electronic spin, random because of the thermal distribution of nuclear spins. The latter becomes very important in combination with the dipole-dipole interaction between the electronic spins.[18]

V. MANY NUCLEAR SPINS AND INCOHERENT APPROXIMATION

Let us now consider the model of many nuclear spins coupled to the electronic spin. The simplest way to generalize the results of the preceding section is to assume the equivalence of nuclear spins and the same coupling to the central electronic spin. In this case Eq. (20) is replaced by

$$\hat{H} = -\frac{1}{2}W(t)\sigma_z - \frac{1}{2}\Delta\sigma_x - (A\sigma_z + \Lambda_z)I_{\text{tot},z} - \Lambda_x I_{\text{tot},x},$$

$$(34)$$

where $\mathbf{I}_{\text{tot}} = \Sigma_{i=1}^{N}\mathbf{I}_i$ is the total nuclear spin. In fact, 12 nuclear spins in Mn_{12} couple to the atomic spins with somewhat different coupling constants[5] but this will be ignored for a moment. The length of the total nuclear spin is dynamically conserved, $[\hat{H}, (\mathbf{I}_{\text{tot}})^2] = 0$. Thus the states of the nuclear subsystem can be classified by the value of the total spin $I_{\text{tot}} \leq NI$ and its projection m_I on some axis. This reduces the problem to the one studied in the preceding section. In particular, for all nuclear spins in the ground state the nuclear subsystem will evolve as a single spin $I_{\text{tot}} = NI$. In the realistic case of thermal distribution of nuclear spins one has to average the solutions for particular values of I_{tot} and m_I in the initial state over the distribution of I_{tot} and m_I.

The number of realizations $\mathcal{N}(I_{\text{tot}})$ of I_{tot} can be computed recurrently.[40] If the total spin of a system of N nuclei is I_{tot}, the total spin of its subsystem of $N-1$ nuclei I'_{tot} assumes the values $|I_{\text{tot}} - I| \leq I'_{\text{tot}} \leq \min\{I_{\text{tot}} + I, (N-1)I\}$. Thus for the number of realizations $\mathcal{N}(I_{\text{tot}}, N)$ one can write

$$\mathcal{N}(I_{\text{tot}}, N) = \sum_{I'_{\text{tot}} = |I_{\text{tot}} - I|}^{\min\{I_{\text{tot}} + I, (N-1)I\}} \mathcal{N}(I'_{\text{tot}}, N-1). \quad (35)$$

The initial condition for this recurrence relation is $\mathcal{N}(I'_{\text{tot}}, 2) = 1$ for $0 \leq I'_{\text{tot}} \leq 2I$. The quantity $\mathcal{N}(I_{\text{tot}})$ obeys the normalization condition

$$\sum_{I_{\text{tot}} = \text{frac}(NI)}^{NI} (2I_{\text{tot}} + 1)\mathcal{N}(I_{\text{tot}}) = (2I+1)^N. \quad (36)$$

For $NI \gg 1$, the quantity $(2I_{\text{tot}} + 1)\mathcal{N}(I_{\text{tot}})/(2I+1)^N$ is the high-temperature distribution function of the magnitude of I_{tot} and it is well approximated by $4\pi I_{\text{tot}}^2 F(\mathbf{I}_{\text{tot}})$, where $F(\mathbf{I}_{\text{tot}})$ is a normalized Gaussian function with respect to the three components of $\mathbf{I}_{\text{tot}}$.[41] Thus for the asymptotic $NI \gg 1$ form of the distribution function of I_{tot} normalized by 1 one has
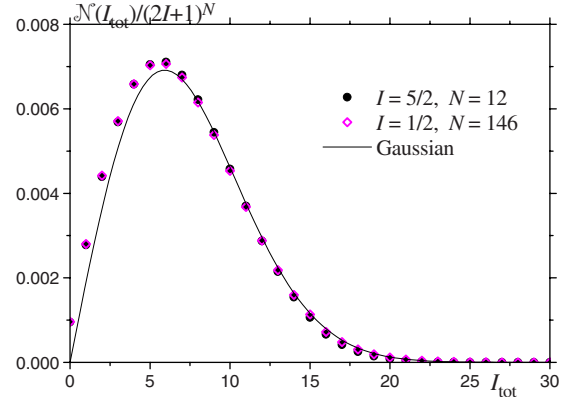

FIG. 5. (Color online) Normalized distribution function for the total nuclear spin I_{tot}.

$$\frac{\mathcal{N}(I_{\text{tot}})}{(2I+1)^N} \cong \frac{2\pi I_{\text{tot}}}{(2\pi\sigma_I)^{3/2}}\exp\left(-\frac{I_{\text{tot}}^2}{2\sigma_I}\right). \quad (37)$$

where $\sigma_I = (N/3)I(I+1)$. It has a maximum at $I_{\text{tot}} = \sqrt{\sigma_I}$ which is about 6 for Mn_{12} ($I=5/2$, $N=12$). Figure 5 shows an agreement between the exactly computed $\mathcal{N}(I_{\text{tot}})/(2I+1)^N$ and its Gaussian approximation for $I=5/2$ and $N=12$. This agreement improves for higher values of NI. One can see that practically the same result for $\mathcal{N}(I_{\text{tot}})/(2I+1)^N$ can be achieved with $I=1/2$ and $N=146$. Thus in the model described by Eq. (34), the effect of 12 Mn^{55} spins is the same as that of about 150 protons.

Summation over different values of I_{tot} makes calculations lengthier. In addition, there are high values of I_{tot} with a small statistical weight that consume a lot of time but do not change the result. Thus one has to introduce a cut-off on I_{tot}. The results for $I=5/2$ and $N=12$ (or for $I=1/2$ and $N=146$) and $\Lambda_z = 0$ are shown in Fig. 6. Since the most probable value of I_{tot} in this case is between 5 and 6, deviations from the standard LZ effect are noticeable for Λ_x/A down to 0.1 (see discussion at the end of preceding section).
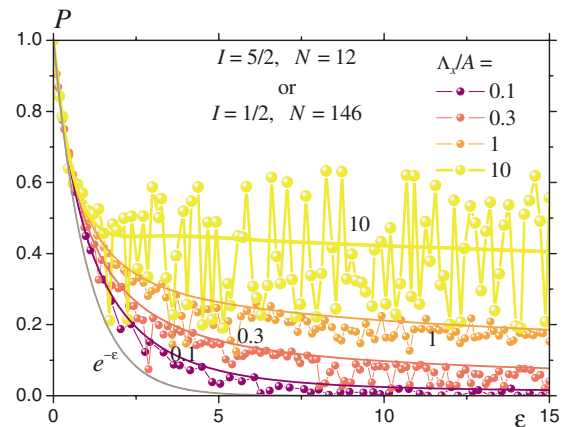

FIG. 6. (Color online) $P(\varepsilon)$ for the electronic spin coupled to $N=12$ nuclear spins $I=5/2$ (initially in a thermal state with $T=\infty$) for different ratios Λ_x/A and $\Lambda_z=0$. Results of the incoherent approximation are shown by solid lines of same color.

One can see in Fig. 6 that summations over both I_{tot} and m_I in the initial state lead to decreasing of quantum-mechanical oscillations in $P(\varepsilon)$. However, averaging out the oscillations is incomplete because for all values of I_{tot} the W intervals in the LZ grid are the same, although the number of crossings change. In real situations the oscillations should be averaged out, mainly because of different couplings A to different nuclear spins that increases the number of crossings from $(2I_{\text{tot}}+1)^2$ to $(2I+1)^{2N}$. To take the phase averaging into account without increasing the size of the problem, one can use the incoherent approximation. In the case of well-separated resonances one can consider the occupation numbers of the states

$$p_{\xi,m_I} = |c_{\xi,m_I}|^2. \tag{38}$$

The change of the state at the kth resonance is described by Eq. (B13). Then for the probabilities one has

$$p^{\text{out}}_{\xi,m_I} = A^{(k)}_{\xi,m_I;\xi',m_I'} A^{(k)*}_{\xi,m_I;\xi'',m_I''} c^{\text{in}}_{\xi',m_I'} c^{\text{in}*}_{\xi,m_I''}. \tag{39}$$

Neglecting interference effects or, in other words, averaging over phases amounts to the aproximation

$$c^{\text{in}}_{\xi',m_I'} c^{\text{in}*}_{\xi'',m_I''} \Rightarrow p_{\xi',m_I'}\delta_{\xi'\xi''}\delta_{m_I'm_I''}. \tag{40}$$

Then the change of the occupation numbers across a resonance is described by

$$p^{\text{out}}_{\xi,m_I} = B^{(k)}_{\xi,m_I;\xi',m_I'} p^{\text{in}}_{\xi',m_I'}, \tag{41}$$

where

$$B^{(k)}_{\xi,m_I;\xi',m_I'} = |A^{(k)}_{\xi,m_I;\xi',m_I'}|^2. \tag{42}$$

Incoherent approximation requires only a slight change of the computational method. Instead of Eq. (B17) one has

$$\mathbf{p}^{\text{out}} = \mathbb{B}^{(2I)}\mathbb{B}^{(2I-1)}\cdots\mathbb{B}^{(-2I+1)}\mathbb{B}^{(-2I)}\mathbf{p}^{\text{in}}. \tag{43}$$

In particular, for one nuclear spin $I=1/2$ one obtains Eq. (31) with $\sin^2(\ldots)\Rightarrow 1/2$.

Results of the incoherent approximation are shown in Figs. 4 and 6 by smooth curves. The results similar to those in Fig. 6 but for large ratios Λ_x/A are shown in Fig. 7 within the incoherent approximation. For very large Λ_x/A, the sub-primary splittings [left and right from the primary splittings at $W=0$ in Fig. 1(b)] are very small, so that for not too slow sweep transitions occur at $W=0$ and they become adiabatic with $P\approx 0$ for $\varepsilon\gtrsim 1$. However, with further increase of ε transitions at crossings with sub-primary splittings begin, and the curve $P(\varepsilon)$ goes up again. Figure 8 gives an idea of the dependence $P(\varepsilon)$ for a large nuclear spin. The apparent overall dependence is $P(\varepsilon)\simeq C_1-C_2\log\varepsilon$, seen in Fig. 8 over several decades in ε. There are slow oscillations for $\Lambda_x/A=100$ that tend to disappear for large I.

VI. DISCUSSION

The model of a two-level system coupled to one or many environmental spins considered above is one of basic models illustrating many-body Landau-Zener effect with many
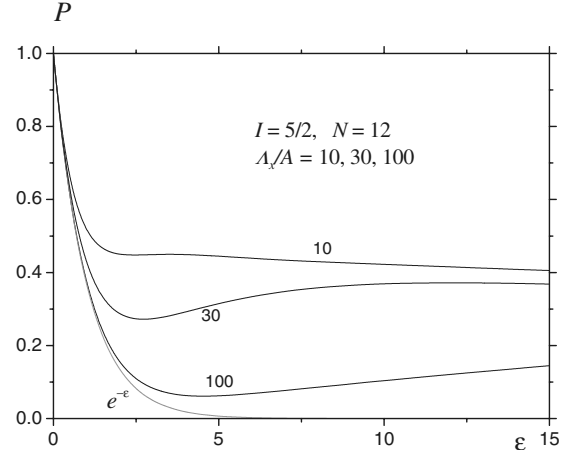

FIG. 7. $P(\varepsilon)$ for the electronic spin coupled to $N=12$ nuclear spins $I=5/2$ for large ratios Λ_x/A and $\Lambda_z=0$ within the incoherent approximation.

avoided level crossings forming a Landau-Zener grid. Exact results of the multilevel LZ effect such as the no-go theorem and DOBE formula apply to this model. In particular, if the environmental spins are initially in their ground states, the asymptotic staying probability is unchanged and given by Eq. (1). Accordingly no isotope effect exists in this case. However, such an effect occurs when preparing nuclear spins e.g., in a thermal ensemble.

The model under consideration is relevant for spin tunneling in molecular magnets, with coupling to nuclear spins, although direct comparison with experimental results requires taking into account the dipole-dipole interaction between electronic spins at the same time. Ref. 24 studying the effect of nuclear spins only states that the results can be applicable for the sweep fast enough, where the effect of the DDI is weak. In fact, in the fast-sweep limit $\varepsilon\ll 1$ both effects of nuclear spins and DDI on the staying probability P are of order ε^2 and additive, although the DDI contribution is reduced by nuclear spins.[18] For a general sweep $\varepsilon\gtrsim 1$, no analytical or numerical method treating the DDI microscopically is known.

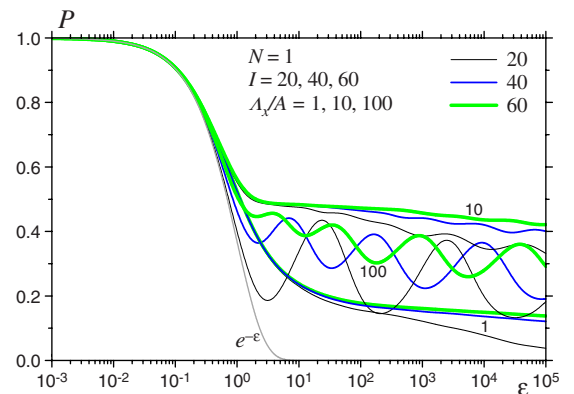Surprisingly, nuclear spins strongly coupled to the electronic spin, such as 12 Mn[55] nuclear spins $I=5/2$ in Mn$_{12}$, do

FIG. 8. (Color online) $P(\varepsilon)$ for the electronic spin coupled to one large "nuclear spin" for different ratios Λ_x/A and $\Lambda_z=0$ within the incoherent approximation.

not significantly change the asymptotic survival probability $P(\varepsilon)$ for the electronic spin. This follows from the analysis of the Landau-Zener grid, Fig. 1(a). In physical terms, nuclear spins in the case $\Lambda_x \ll A$ do not have a sufficient dynamics to undergo transitions together with the electronic spin. They rather act on the latter as static random fields that have no effect by themselves but do significantly reduce the influence of the DDI on the LZ effect.[18]

To the contrast, protons in molecular magnets can influence the LZ effect directly. Although the nuclear magneton μ_n is small, the energy of the dipole-dipole interaction with nuclear spins can exceed tunnel splitting Δ. For instance, the ground-state splitting in Fe_8 in zero field is only $\Delta/k_B \simeq 10^{-7}$ K. The energy bias on the electron spin from a proton at distance r is given by $W \sim 2Sg\mu_B\mu_p/r^3$, where $g = 2$ and $\mu_p = 2.79\mu_n$. One has $\Delta \sim W$ at the distance $r_\Delta \simeq 72$ Å. The volume of a corresponding sphere comprises about 400 unit cells of a molecular magnet. As each molecule, occupying a unit cell, comprises about 120 protons,[23] the number of protons creating bias $W \gtrsim \Delta$ is about $N = 50000$. These protons are typically weakly coupled to the electronic spin ($A \ll \Lambda_x$) since their Zeeman interaction with the external field greatly exceeds their NDDI with electronic spins. Applying an external magnetic field, one can drastically increase Δ and thus reduce N.

Effect of protons in principle could be tackled with the method described in Sec. II. However, as each proton couples to the electronic spin with its own coupling constant A, the number of lines in the LZ grid, 2^N, is too large to implement a working computational algorithm. The first expected effect of so many crossings is complete averaging out of quantum-mechanical phase oscillations that are still seen in Fig. 6. This effect can easily be accounted for by the incoherent approximation of Sec. V. After that different couplings A become less important, and one can get a qualitative idea of the effect of protons from the analysis in the preceding section. The most probable combined nuclear spin I_{tot} in the distribution of Eq. (37) is $\sqrt{\sigma_I} \approx 110$ that is of the same order as the large "nuclear spins" simulated in Fig. 8. The resulting $P(\varepsilon)$ is decaying extremely slowly because of a strong non-adiabaticity at large ε induced by weak avoided crossings outside the ellipse in Fig. 2. As the width of the distribution of I_{tot} is of the same order as the most probable value of I_{tot}, slow oscillations in Fig. 2 should be averaged out after summation over all I_{tot}. One can see that the results for $P(\varepsilon)$ in the case $A \ll \Lambda_x$ slowly approach $1/2$. This is in accord with the results of Ref. 42 where the influence of environment was modeled by a density-matrix equation with dephasing.

It does not make sense, however, to further elaborate on the effect of protons in this paper because in the practical case $A \ll \Lambda_x$ coupling to electronic spins only slightly perturbs protons. This might be an indication of a possibility to solve the problem by another and more efficient method.

APPENDIX A: DIAGONALIZATION OF THE NUCLEAR HAMILTONIAN

The nuclear part of the Hamiltonian can be diagonalized for a given direction of the electronic spin ξ by choosing the quantization axis for nuclear spins along the field $\mathbf{F}_\xi$ defined by Eq. (22), i.e.,

$$\mathbf{e}_{z'_\xi} = \frac{\xi A + \Lambda_z}{F_\xi}\mathbf{e}_z + \frac{\Lambda_x}{F_\xi}\mathbf{e}_x, \tag{A1}$$

where

$$F_\xi = \sqrt{(\xi A + \Lambda_z)^2 + \Lambda_x^2}. \tag{A2}$$

The vectors $\mathbf{e}_{z'}$ are rotated away from $\mathbf{e}_z$ by the angles

$$\beta_\xi = \arccos\frac{\xi A + \Lambda_z}{F_\xi}. \tag{A3}$$

For $\Lambda_x \ll A$, Λ_z and $\Lambda_z < A$, β_+ is close to 0 and β_- is close to π. For $\Lambda_x \ll A$, Λ_z and $A < \Lambda_z$, both β_+ and β_- are close to 0. For the transverse nuclear axes we define

$$\mathbf{e}_{y'_\xi} = \mathbf{e}_y, \quad \mathbf{e}_{x'_\xi} = [\mathbf{e}_y \times \mathbf{e}_{z'_\xi}] = \frac{\xi A + \Lambda_z}{F_\xi}\mathbf{e}_x - \frac{\Lambda_x}{F_\xi}\mathbf{e}_z. \tag{A4}$$

The corresponding basis set of states has the form

$$|\xi, m_I\rangle = |\xi\rangle|m_I\rangle_\xi, \tag{A5}$$

where the rotated states $|m_I\rangle_\xi$ depend on ξ. Elements of the Hamiltonian matrix $\mathbb{H}'$ in the new basis, Eq. (10), are defined by

$$H'_{\xi, m_I; \xi', m'_I} = {}_\xi\langle m_I|\langle\xi|\hat{H}|\xi'\rangle|m'_I\rangle_{\xi'}. \tag{A6}$$

With the help of $\mathbf{I} = I_{x'_\xi}\mathbf{e}_{x'_\xi} + I_y\mathbf{e}_y + I_{z'_\xi}\mathbf{e}_{z'_\xi}$ one obtains Eq. (23) in which

$$\Delta_{\xi, m_I, m'_I} = \Delta_\xi\langle m_I|m'_I\rangle_{-\xi} \tag{A7}$$

are the elements of $\mathbb{V}'$ in Eq. (11) for $\xi = -1$, and the elements of $\mathbb{V}'^\dagger$ for $\xi = 1$. Elements of the Hamiltonian matrix are placed in order of ξ changing from -1 to 1 and m_I changing from I to $-I$.

The projector ${}_\xi\langle m_I|m'_I\rangle_{-\xi}$ can be expressed through the spin rotation matrix[43]

$$d^{(I)}_{m'm}(\beta) = \langle m'|e^{-i\beta I_y}|m\rangle$$

$$= \left[\frac{(I-m)!(I-m')!}{(I+m)!(I+m')!}\right]^{1/2}\left(\cos\frac{\beta}{2}\right)^{m+m'}\left(\sin\frac{\beta}{2}\right)^{m-m'}$$

$$\times \sum_n \frac{(-1)^n(I+m+n)!}{(I-m-n)!(m+n-m')!n!}\left(\sin\frac{\beta}{2}\right)^{2n}, \tag{A8}$$

summation going over $\max(0, m'-m) \le n \le I-m$. The final expression is good for $\beta > 0$. In the case $\beta < 0$ one should use the relation $d^{(J)}_{m'm}(\beta) = (-1)^{m'-m}d^{(J)}_{m'm}(-\beta)$. For large I numerical implementation of Eq. (A8) leads to precision problems. In this case it is much more convenient to obtain

$d^{(I)}_{m'm}(\beta)$ numerically by finding eigenstates of the operator $I_z \cos\beta + I_x \sin\beta$ and projecting them on $|m\rangle$, eigenstates of I_z.

Using $|m_I\rangle_\xi = e^{-i\beta_\xi I_y}|m_I\rangle$, where $|m_I\rangle$ are the states of the initial basis, quantized along the z-axis, one obtains

$$_\xi\langle m_I|m_I'\rangle_{-\xi} = \langle m_I|e^{i\beta_\xi I_y}e^{-i\beta_{-\xi}I_y}|m_I'\rangle = d^{(I)}_{m_I m_I'}(\beta),$$

$$\beta = -\beta_\xi + \beta_{-\xi}. \tag{A9}$$

For $\Lambda_z = 0$ from Eq. (A3) one obtains

$$\beta = 2\xi \arcsin\frac{A}{F}, \tag{A10}$$

where $F = \sqrt{A^2 + \Lambda_x^2}$.

APPENDIX B: TRANSITIONS ON THE LANDAU-ZENER GRID

As in the general case considered in Sec. II, the energy levels described by Eq. (24) separate into two families, ascending lines for $\xi = -1$ and descending lines for $\xi = +1$. There are crossings between these families at

$$E_{+,m_I^{(+)}}(t) = E_{-,m_I^{(-)}}(t). \tag{B1}$$

Each ascending line crosses with $2I+1$ descending lines and vice versa. In the case $\Lambda_z = 0$ that will be considered below, crossings are defined by

$$W^{(\text{cross})}_{m_I^{(+)},m_I^{(-)}} = (m_I^{(-)} - m_I^{(+)})F \equiv kF,$$

$$k = m_I^{(-)} - m_I^{(+)} = -2I, -2I+1, \ldots, 2I. \tag{B2}$$

There are total $4I+1$ crossings. For a given k, the values of $m_I^{(-)}$ and $m_I^{(+)}$ satisfy

$$m_I^{(-)} - m_I^{(+)} = k, \quad -I \le m_I^{(-)}, m_I^{(+)} \le I. \tag{B3}$$

For the leftmost crossing with $k = -2I$ there is only one solution, $(m_I^{(-)} = -I, m_I^{(+)} = I)$, i.e., only one pair of lines is crossing here. Similarly, for the rightmost crossing with $k = 2I$ there is only one pair of crossing lines with $(m_I^{(-)} = I, m_I^{(+)} = -I)$. For the crossing with $k = -2I+1$, there are two pairs of crossing lines with $(m_I^{(-)} = -I+1, m_I^{(+)} = I)$ and $(m_I^{(-)} = -I, m_I^{(+)} = I-1)$. For $k = 0$ there are I crossing lines with all possible values of m_I and the corresponding $m_I^{(+)} = m_I$. In general, the allowed values of $m_I^{(-)}$ and $m_I^{(+)}$ are in the intervals

$$\max(-I-k, -I) \le m_I^{(+)} \le \min(I-k, I), \tag{B4}$$

and

$$\max(-I+k, -I) \le m_I^{(-)} \le \min(I+k, I). \tag{B5}$$

In the case $\Delta \ll A, \Lambda_x$ crossings are well separated from each other. In this case the process consists of tunneling transitions at the crossings and free evolution with phase accumulation in the ranges between them. Transition at each crossing is described by the LZ scattering matrix

$$M(\Delta) = \begin{pmatrix} \sqrt{P} & \text{sign}(\Delta)\sqrt{1-P}e^{-i\phi} \\ -\text{sign}(\Delta)\sqrt{1-P}e^{i\phi} & \sqrt{P} \end{pmatrix}, \tag{B6}$$

where P given by Eq. (1) is the Landau-Zener staying probability and

$$\phi = \pi/4 + \text{Arg}\,\Gamma(1 - i\delta) + \delta(\ln\delta - 1) \tag{B7}$$

with $\delta \equiv \varepsilon/(2\pi)$ is the scattering phase and Γ is Gamma function.

Evolution of the wave function between level crossings reduces to the accumulation of the phase factors $\exp[i\Phi_{\xi,m_I}(t)]$, where the phases are given by

$$\Phi_{\xi,m_I}(t) = -\frac{1}{\hbar}\int^t dt' E_{\xi,m_I}(t'). \tag{B8}$$

The change of the phase between the kth and $(k+1)$th crossings is given by

$$\Phi^{(k+1/2)}_{\xi,m_I} = \frac{1}{\hbar}\int_{t_k}^{t_{k+1}} dt'\left[\frac{\xi}{2}vt + Fm_I\right] = \frac{1}{\hbar}\frac{F}{v}\left[\frac{\xi}{4}F(2k+1) + Fm_I\right] \tag{B9}$$

or, finally,

$$\Phi^{(k+1/2)}_{\xi,m_I} = \frac{\varepsilon F^2}{\pi\Delta^2}\left[\xi\left(k + \frac{1}{2}\right) + 2m_I\right]. \tag{B10}$$

Evolution of the state on the interval between the kth and $(k+1)$th crossings is given by

$$c^{\text{out}}_{\xi,m_I} = T^{(k+1/2)}_{\xi,m_I;\xi',m_I'}c^{\text{in}}_{\xi',m_I'} = \exp[i\Phi^{(k+1/2)}_{\xi,m_I}]\delta_{\xi'\xi}\delta_{m_I'm_I}c^{\text{in}}_{\xi',m_I'} \tag{B11}$$

or in the vector-matrix form

$$\mathbf{c}^{\text{out}} = \mathbb{T}^{(k+1/2)}\mathbf{c}^{\text{in}}. \tag{B12}$$

The change of the state across the kth resonance is described by

$$c^{\text{out}}_{\xi,m_I} = A^{(k)}_{\xi,m_I;\xi',m_I'}c^{\text{in}}_{\xi',m_I'}, \tag{B13}$$

or

$$\mathbf{c}^{\text{out}} = \mathbb{A}^{(k)}\mathbf{c}^{\text{in}}, \tag{B14}$$

where for ξ, m_I and ξ', m_I' describing a pair of crossing levels $A^{(k)}_{\xi,m_I;\xi',m_I'}$ is given by the LZ scattering matrix M, otherwise, if there is no crossing, it is $A^{(k)}_{\xi,m_I;\xi',m_I'} = \delta_{\xi,\xi'}\delta_{m_I'm_I}$. To formulate the condition of crossing, one has to consider the cases $\xi' = \pm 1$ separately. For $\xi' = +1$ (descending line) the nuclear quantum number $m_I' = m_I^{(+)}$ should be in the interval given by Eq. (B4), for a crossing to be realized, then in the scattered state one has $m_I = m_I^{(-)} = m_I' + k$. For $\xi' = -1$ (ascending line) the nuclear quantum number $m_I' = m_I^{(-)}$ should be in the interval given by Eq. (B5), for a crossing to be realized, then in the scattered state one has $m_I = m_I^{(+)} = m_I' - k$. Thus in the general case one obtains

$$A^{(k)}_{\xi,m_I;\xi',m'_I} = M_{\xi,\xi'}(\Delta_{\xi,m_I,m_I-k}) \times (\delta_{\xi\xi'}\delta_{m_I m'_I} + \delta_{\xi,-\xi'}\delta_{m_I,m'_I+k}) \tag{B15}$$

for $\xi' = +1$, $\max(-I-k,-I) \leq m'_I \leq \min(I-k,I)$,

$$A^{(k)}_{\xi,m_I;\xi',m'_I} = M_{\xi,\xi'}(\Delta_{\xi,m_I,m_I+k}) \times (\delta_{\xi\xi'}\delta_{m_I m'_I} + \delta_{\xi,-\xi'}\delta_{m_I,m'_I-k}) \tag{B16}$$

for $\xi' = -1$, $\max(-I+k,-I) \leq m'_I \leq \min(I+k,I)$, and $A^{(k)}_{\xi,m_I;\xi',m'_I} = \delta_{\xi,\xi'}\delta_{m'_I m_I}$ in all other cases.

The evolution of the state across the whole grid is given by

$$\mathbf{c}^{\text{out}} = \mathbb{A}^{(2I)}\mathbb{T}^{(2I-1/2)}\mathbb{A}^{(2I-1)}\cdots \times \mathbb{A}^{(-2I+1)}\mathbb{T}^{(-2I+1/2)}\mathbb{A}^{(-2I)}\mathbf{c}^{\text{in}}, \tag{B17}$$

where $\mathbf{c}^{\text{in}}$ is the state of the system before the leftmost crossing. The calculation can be made recurrent introducing the scattering matrix after the kth crossing:

$$\mathbf{c}^{\text{out}}_k = \mathbb{L}^{(k)}\mathbf{c}^{\text{in}}, \tag{B18}$$

where $\mathbf{c}^{\text{in}}$ is the initial state, same as in Eq. (B17). One has $\mathbb{L}^{(-2I)} = \mathbb{A}^{(-2I)}$

$$\mathbb{L}^{(k)} = \mathbb{A}^{(k)}\mathbb{T}^{(k-1/2)}\mathbb{L}^{(k-1)}, \tag{B19}$$

$k = -2I+1, -2I+1, \ldots, 2I$. In the final state it is

$$\mathbf{c}^{\text{out}} = \mathbf{c}^{\text{out}}_{2I} = \mathbb{L}^{(2I)}\mathbf{c}^{\text{in}}, \tag{B20}$$

$\mathbb{L}^{(2I)}$ being the full scattering matrix of the grid.

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