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Multilevel Spin Dynamics in Time-Dependent External Magnetic Field

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Abstract. We investigate the dynamics of a 'giant spin' with 21 levels ($S = 10$) in time dependent external magnetic field. The model can describe the time evolution of the spin degree of freedom in molecular nanomagnets, and our 'exact numerical' treatment of the problem reflects the staircase-like behavior of the experimentally observed magnetization curves. This effect is explained in terms of the level structure, which, at certain values of the external magnetic field, exhibits avoided crossings where the probability of the transitions increases. We show that the multilevel nature of the problem causes these transition probabilities to deviate significantly from the predictions of the traditional Landau–Zener–Stückelberg model.

Keywords: spin dynamics, Landau–Zener model, molecular nanomagnets
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1. Introduction

Parameter values where two energy levels in a quantum system come close to each other, or even cross, are of special interest because of the appearance of fundamental which-way interference effects [1]. For a two-level system with a linearly time-dependent Hamiltonian, the analytically solvable Landau–Zener–Stückelberg model [2–4] reflects the most important properties of this phenomenon. It can describe the adiabatic limit, when the system follows the instantaneous eigenstates of the Hamiltonian, as well as the case when a sudden transition takes place. However, like in the case of a vibrating molecule [5–7], where the level crossings appear

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as a function of the interatomic distance, the parameter that governs the level structure is usually beyond experimental control. In this paper we investigate a model that can describe molecular nanomagnets [8], a physical system where the energy eigenvalues are functions of the applied external magnetic field, thus there is no technical difficulty in the observation of dynamical effects around level crossings.

High-spin molecules such as Mn_{12}-Ac and Fe_8O contain transition metal atoms with strongly exchange-coupled spins, which causes the individual molecules to behave as a single, large spin ($S = 10$ in both cases above). These 'giant spins' or molecular nanomagnets represent a transition between macroscopical magnetism, where domains are responsible for the observable magnetization of the sample, and the case when the behavior of single electrons determines the magnetic properties. In crystals consisting of these molecules there is a weak dipolar interaction that can play an important role [9], but most of the observed effects can be described in terms of a single molecule. Experiments on the magnetization dynamics of crystals of nanomagnets have shown the presence of a series of steps in the hysteresis curve at sufficiently low temperatures [10–13]. This behavior is a consequence of the transitions around level crossings that are consecutively reached by the system as the external magnetic field tunes the level structure via Zeeman interaction. From a different point of view, as we shall see, the relevant spin Hamiltonian for these systems represents an energy barrier between oppositely magnetized states, and, in this sense, the observed steps in the magnetization are signatures of a resonant tunneling effect. The term 'quantum tunneling of magnetization' reflects the fact that no spatial degrees of freedom are involved in this macroscopically observable quantum process.

Additionally, it has been demonstrated that the magnetic tunneling could be accompanied by emitting of electromagnetic pulses, both emission [14–16] and absorption [17,18] of microwave radiation have been observed in recent experiments. It has been proposed [19–21] that the physical mechanism responsible for this radiation is a collective quantum effect known as superradiance [22, 23]. This interpretation has been questioned and it was argued that when one includes the time scale of relaxation, a maser-like effect is more likely responsible for the observations [24]. Furthermore, the change in magnetization can be described in terms of avalanches, which were recently shown to propagate through the crystal in an analogous way to that of a flame front in a flammable chemical substance (deflagration) [25, 26]. It has also been suggested [27] that these molecules can be used for implementing a quantum computational algorithm.

In this work we study the dynamics of the multilevel system corresponding to the 21 spin states of the Mn_{12}-Ac molecule in a time-dependent magnetic field. By solving the relevant time-dependent Schrödinger equation, we show the role of the consecutive avoided level crossings in the formation of the magnetization curves. It will be demonstrated that the energy levels that do not take part in a certain transition directly, still can modify the dynamics in such a way that the resulting transition probabilities deviate significantly from the predictions of the Landau–Zener–Stückelberg (LZS) model.

2. Model

Experimental [11, 12, 28–31] studies on crystals of Mn_{12}-Ac suggest that the spin Hamiltonian for this systems can be written as a sum

$$H_S(t) = H_0(t) + H_1(t)\,, \tag{1}$$

where H_0 is diagonal in the eigenbasis $\{|m\rangle\}$ of the z component of the (dimensionless) spin operator, S_z:

$$H_0(t) = -DS_z^2 - FS_z^4 - g\mu_B B(t) S_z\,. \tag{2}$$

Here the last (Zeeman) term in the right-hand side describes the coupling to an external magnetic field applied along the z direction, which is parallel to the easy axis of the crystal. This external field is time-dependent, in this work we assume sweep rates on the kT/s scale [15]. H_1 in the Hamiltonian represents a small correction to H_0, but it contains terms [12, 29] that do not commute with S_z:

$$H_1 = C(S_+^4 + S_-^4) + E(S_+^2 + S_-^2)/2 + L(S_+ + S_-)/2\,. \tag{3}$$

In the present paper we will concentrate on Mn_{12}-Ac, which can be considered as a representative example of molecular nanomagnets. In this case the values of the parameters in H_0 are $D/k_B = 0.56$ K, and $F/k_B = 1.1 \cdot 10^{-3}$ K. The coefficients in H_1, which are essential for the determination of the transition probabilities, can be obtained by fitting the theoretical results to experimental magnetization curves [24]. In the following we use $L = 0.025 g\mu_B B$ (representing a weak misalignment in the external field B), $E/k_B = -4.48 \cdot 10^{-3}$ K, $C/k_B = 1.7 \cdot 10^{-5}$ K. Let us note that our results do not change qualitatively by choosing different constants, thus the effects presented here are general in that sense.

The magnetic field dependence of the energy levels is shown in Fig. 1. As a guiding line, these eigenvalues can be labeled by m, i.e. the index of the S_z eigenstates. This assignment is based on the fact that H_1 is a relatively weak perturbation to H_0, thus the eigenstates of the full spin Hamiltonian are close to that of H_0. The values of the external field B for the top part of Fig. 1 have been chosen in such a way, that there are certain states $|m\rangle$ and $|m'\rangle$ for which $\langle m|H_0|m\rangle = \langle m'|H_0|m'\rangle$. (In fact, for $B = 0$ this holds for all pairs m and m' satisfying $|m| = |m'|$, while nonzero external field can bring only a single level pair into resonance.) Note that the approximate parabolas shown in the top part of Fig. 1 resemble a double well potential and inspired the notion of magnetic tunneling. However, the exact energy eigenvalues $\{E_n\}$ corresponding to the instantaneous eigenstates of the complete time-dependent Hamiltonian

$$H_S(t)\,|E_n(t)\rangle = E_n(t)\,|E_n(t)\rangle \tag{4}$$

never cross, the term H_1 always introduces a coupling between these states resulting in a level splitting shown schematically by the inset in Fig. 1. Having this in mind,

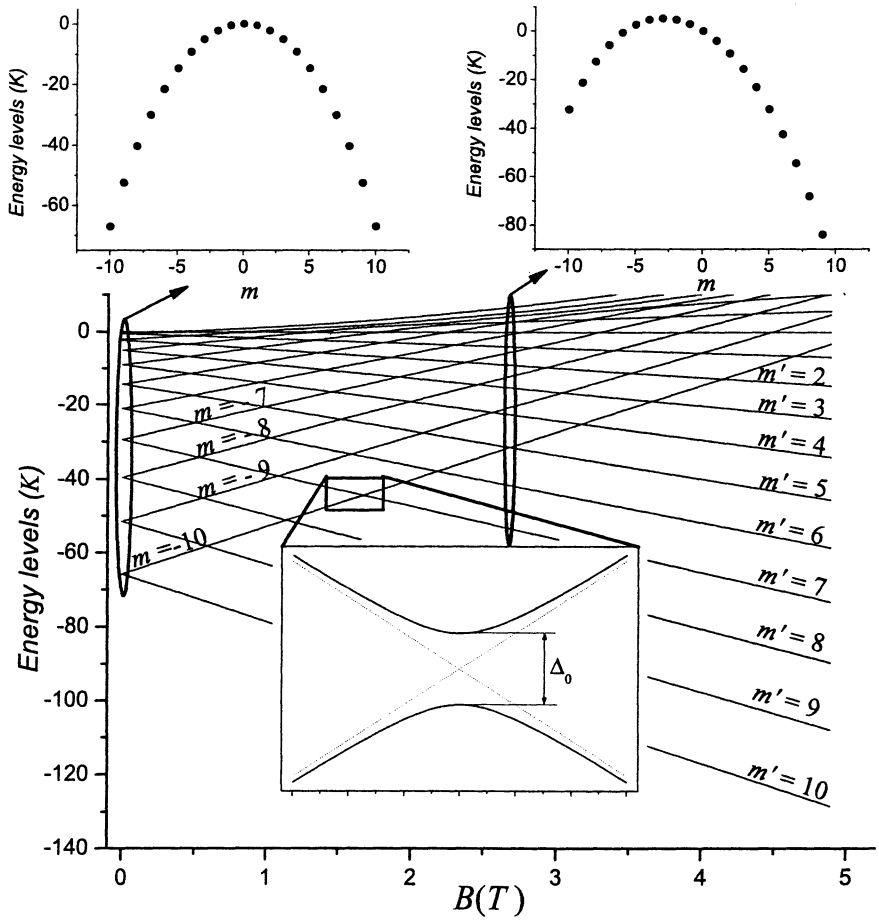

Fig. 1. The energy levels of the spin Hamiltonian (1) as a function of the magnetic field B (bottom). For two specific values of B (denoted by the ellipses in the bottom part of the figure) the expectation values $\langle m|H_0|m\rangle$ are also shown, which are close to the exact energy eigenvalues (top)

it is tempting to treat the problem as a sequence of two-level transitions, and, additionally, use the Landau–Zener–Stückelberg model to estimate the Hamiltonian reduced to the relevant level pair at a given junction:

$$H_{\mathrm{red}}(t) = \hbar \begin{pmatrix} \Omega t & \Delta/2 \\ \Delta/2 & -\Omega t \end{pmatrix}. \tag{5}$$

In this framework, if the system is initially in the lower adiabatic level, the probability of staying there long after the avoided crossing is given by $P_{\mathrm{LZS}} = 1 - \exp(-\pi\Delta^2/2\Omega)$. Formulating it in terms of the eigenstates of S_z, we see that small

values of $P_{\rm LZS}$ means no appreciable change either in the population of these states, or the magnetization $\langle S_z \rangle$; $P_{\rm LZS} \approx 1$ is observable as a step in the magnetization, while the populations of the adiabatic levels are practically unchanged. Note that the formula for $P_{\rm LZS}$ has been used in several interesting experiments [32,33] related to various molecular nanomagnets when analyzing the data. It is important to emphasize that $P_{\rm LZS}$ depends on the ratio $\Delta/\sqrt{\Omega}$, i.e. on a single parameter (which, in appropriate dimensionless units, is simply the level splitting). In the next section we show that the dynamics in the whole spin Hilbert space, governed by the

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H_S |\Psi\rangle \tag{6}$$

Schrödinger equation, can no longer be described by a single parameter. Consequently the exact transition probabilities can be significantly different from $P_{\rm LZS}$.

3. Multilevel Dynamics

Now we calculate the dynamics described by Eq. (6). Initially the external magnetic field is zero, and we assume that it raises to its maximal value of $B_{\rm max}$ according to

$$B(t) = \frac{B_{\rm max}}{2} \left[\tanh\left(\frac{2wt - \delta}{B_{\rm max}} \right) + 1 \right], \tag{7}$$

where the shift δ has to be chosen such that at $t = 0$ the external magnetic field is negligible. The maximal magnetic field sweep rate $w = \max(dB/dt)$ falls in the kT/s range.

The results obtained by the numerical solution of Eq. (6) is compared to the predictions of the LZS model in Fig. 2, where the initial state was $|\Psi\rangle_0 = |m = -10\rangle$, representing a completely magnetized molecule. Note that due to the time scales (roughly 10^9 Bohr oscillations corresponding to the time window shown in Fig. 2), a rather sophisticated integration method was needed, the details of which can be found in Ref. [34]. On the other hand, for the LZS results only the level splitting Δ and the sweep rate (related to Ω in Eq. (5)) had to be determined for all the relevant avoided crossings.

The steps seen in Fig. 2 are very similar to the experimental curves, but differ from the result that can be obtained by using the LZS theory (also plotted in this figure). Faster sweep rates mean smaller transition probabilities between the eigenstates of S_z. Although the exact dynamics is different from the LZS result, in the investigated sweep rate range we found that $\langle S_z \rangle$ scales with the sweep rate almost exactly the same way as one could deduce from $P_{\rm LZS}$. Additionally, Fig. 2 also shows that, since the states $|m\rangle$ are not exact eigenstates of the complete spin Hamiltonian H_S, there are rapid oscillations in $\langle S_z \rangle$ for higher external fields, which are clear indications of the Rabi-like oscillations corresponding to different eigenenergies of H_S. We note that if we take relaxation effects into account [34], these oscillations disappear on a very short timescale.

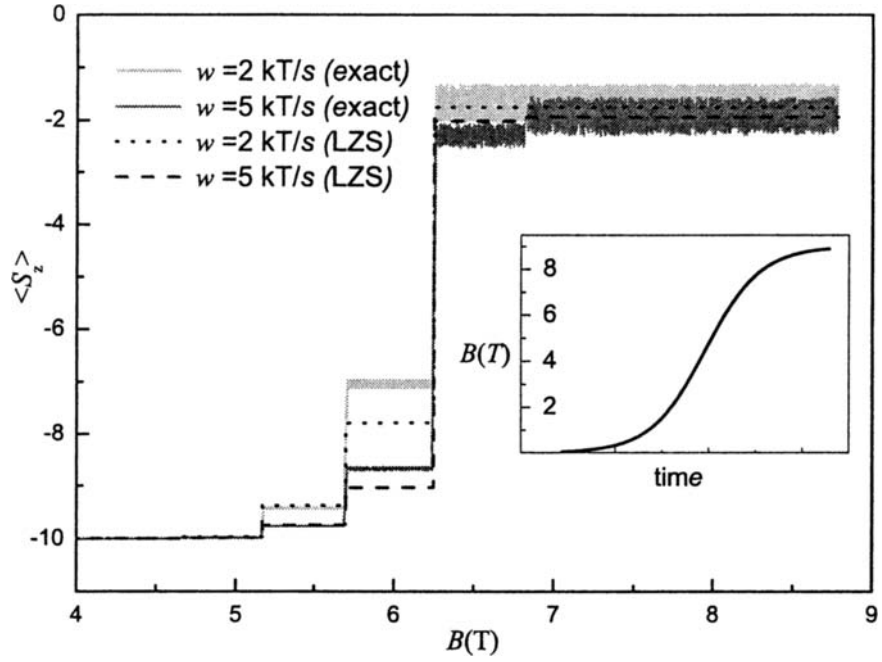

Fig. 2. The expectation value of $\langle S_z \rangle$ (solid lines) as a function of the external magnetic field B for different maximal sweep rates. The exact results are compared with the predictions of the LZS approximation (dashed and dotted lines). The pulse shape corresponding to this figure is given by Eq. (7) and shown in the inset. Above 5.7 T rapid oscillations appear, see the text for more details

As we can see, the LZS result is quantitatively different from the exact $\langle S_z \rangle(t)$ curve that was calculated by taking all the 21 levels into account. The position of the steps (determined by the avoided crossings) are the same, but their heights are different, and this difference can be as large as 30%.

In order to understand the physical reason for this effect, the first important point to take into account is that, to a very good approximation, the transitions seen in Fig. 2 take place between two neighboring adiabatic levels. For sweep rates in the kT/s range the characteristic time of the transitions [35, 36] at the avoided level crossings neither overlap nor influence each other. This suggests that a model estimating the dynamics as a sequence of two-level transitions may turn out to be accurate. Indeed, the exact results shown in Fig. 2 can be reproduced to a very good approximation by the proper reduction of H_S to the relevant level pairs [24]. However, in this way we can observe that the time dependence of each reduced two-level Hamiltonian is not exactly the same as that of an LZS matrix given by Eq. (5). The origin of this difference is simply the eigenvalue equation, where all the 21 levels play their role. Additionally, it can be shown that there is a continuous

set of parameters in H_S that can lead to the same value of $\Delta/\sqrt{\Omega}$ for a given transition. In the LZS model P_{LZS} is the same for all of these Hamiltonians, but the reduced two-level Hamiltonians are different, resulting in the fact that the exact transition probabilities will also be different. This shows that that the dynamics is also influenced by the levels that do not take part in the relevant transition.

4. Conclusions

We studied the time evolution of a multilevel spin system being the model of the molecular nanomagnet Mn_{12}-Ac in the presence of time-dependent magnetic field. Using an appropriate 'exact numerical' method, we followed the time evolution from zero external magnetic field until the saturation of the magnetization is reached. We found that for sweep rates in the kT/s range, steps in the magnetization originate from two-level transitions which cannot be described within the framework of the Landau–Zener–Stückelberg (LZS) model, but an efficient and accurate approximation based on two-level non-LZS transitions is feasible. This introduces the possibility of performing long term dynamical calculations that can directly be related to experiments.

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