Magnetization of $Mn_{12}Ac$ in a slowly varying magnetic field: an ab initio study

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Abstract

Beginning with a Heisenberg spin Hamiltonian for the manganese ions in the $Mn_{12}Ac$ molecule, we find a number of low-energy states of the system. We use these states to solve the time-dependent Schrödinger equation and find the magnetization of the molecule in the presence of a slowly varying magnetic field. We study the effects of the field sweep rate, fourth order anisotropic spin interactions and a transverse field on the weights of the different states as well as the magnetization steps which are known to occur in the hysteresis plots in this system. We find that the fourth order term and a slow field sweep rate are crucial for obtaining prominent steps in magnetization in the hysteresis plots.

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1 Introduction

Recently some magnetic systems have been discovered in which simple quantum mechanical principles lead to some striking macroscopic phenomena. In particular, the observation of discrete steps in the magnetization of single crystals of the compound $Mn_{12}Ac$ in the presence of a time-dependent magnetic field has evoked considerable theoretical interest. This has been termed variously as quantum hysteresis and quantum or resonance tunneling of magnetization.

The basic underlying physics is easy to understand [1]. The system consists of magnetic molecules which interact only weakly with each other. Each molecule is a cluster consisting of a core tetrahedron of four $Mn^{4+}$ ions each with a spin of $\frac{3}{2}$, and an outer crown consisting of eight $Mn^{3+}$ ions each with spin 2. The intracore as well as intracrown magnetic interactions are ferromagnetic, while the interactions between the spins in the core and the crown is antiferromagnetic (see Fig. 1). Thus each molecule is a ferrimagnetic cluster with a ground state spin of 10. In the cluster, the dipolar interaction between the spins leaves only the $M_s = 10$ and $-10$ states degenerate. The application of a magnetic field lifts this degeneracy, resulting in a nonzero magnetization. As the field is increased, different pairs of $M_s$ states become degenerate at certain values of the field. At those particular fields, the presence of matrix elements between the degenerate states, provided either by a weak transverse component in the applied magnetic field or by higher order spin-spin interactions, causes tunneling between the states. This results in a jump in the magnetization. At all other values of the field where there are no energy degeneracies, the plot of magnetization vs field shows plateaus or discrete steps provided the sweep rate of the magnetic field is not too low [3]. This is because, according to the Landau-Zener theory [2], the tunneling amplitude to go from one magnetization state to another is very small unless the sweeping frequency is so low that it is comparable to the matrix element connecting the two states. Such steps in the magnetization are also seen in another magnetic cluster $Fe_8$ [4], although the effect is less dramatic there than in the $Mn_{12}$ cluster.

In recent years, there have been many model calculations which illustrate such steps in the $M$ vs $H$ curves [5, 6]. These models involve either the presence of a transverse magnetic field, or higher order spin couplings which leads to a term of the type $c(S^4_x + S^4_y)$ allowed by the symmetry of the cluster. However, most of these calculations have been restricted to the spin-10 manifold, i.e., a total of 21 states. In contrast, we have carried out an explicit calculation of the low-lying states of a $Mn_{12}Ac$ cluster using a Heisenberg spin model; we then consider 117 of these states which involve several different values of the total spin. We have studied
quantum tunneling between these low-lying states by setting up a Hamiltonian in
this subspace of states which includes, besides the multipolar spin-spin interactions
and a transverse magnetic field, different gyromagnetic ratios for the core and crown
spins. This last interaction, which is reasonable to introduce because of the different
environments around the core and crown spins, has the effect of mixing up the
different spin states of the cluster when a magnetic field is applied; it is therefore
essential to keep states with different values of the total spin in the calculation, rather
than restrict oneself to the spin-10 ground state manifold. We have then evolved an
initial state, which is taken to be the ground state with a specific value of \( M_s = S_z \)
in the absence of the magnetic field, by using the time-dependent formulation of
the problem in the restricted subspace. In the following section, we formulate the
problem and present some numerical details. This will be followed by a section on
the results of our time evolution studies and a discussion of the results.

2 Theoretical Model and Computational Details

The dimension of the Fock space spanned by the magnetic cluster \( Mn_{12}Ac \) is exactly
a hundred million. When specialized to the states of interest in the low energy sector,
the dimensionalities reduce considerably even though they are still large. Table 1
gives the dimensionalities of the Hilbert spaces corresponding to the various \( M_s \)
values of interest. These states can be represented by 32 bit integers by associating
two bits with each of the core spins of \( s = \frac{3}{2} \) (namely, \( M_s = \frac{3}{2} \rightarrow 00 \), \( M_s = -\frac{1}{2} \rightarrow 
01 \), \( M_s = +\frac{1}{2} \rightarrow 10 \), and \( M_s = +\frac{3}{2} \rightarrow 11 \)), and three bits with each of the outer spins
with \( s = 2 \) (\( M_s = -2 \rightarrow 000 \), \( M_s = -1 \rightarrow 001 \), \( M_s = 0 \rightarrow 010 \), \( M_s = +1 \rightarrow 011 \)
and \( M_s = +2 \rightarrow 100 \)); these states are generated in an ascending order of the 32 bit
integers that represent them.

The Hamiltonian describing the spin interactions in the cluster is given by
\[
\hat{H} = -J \sum_{\langle ij \rangle \text{core}} \hat{S}_i \cdot \hat{S}_j - J' \sum_{\langle ij \rangle \text{crown}} \hat{S}_i \cdot \hat{S}_j + J'' \sum_{\langle \text{core} \rangle \langle \text{crown} \rangle} \hat{S}_i \cdot \hat{S}_j,
\]
where \( J \) is ferromagnetic, \( J' \) is antiferromagnetic, and the summations are taken
over nearest neighbors. We have taken \( J = 1.0 \) and \( J' = 0.2 \) in our calculations.
Every crown spin has two nearest neighbors in the crown while every core spin has
three nearest neighbors in the core corresponding to the tetrahedral geometry of the
core spin. Every core spin also has three nearest neighbor crown spins.

The Hamiltonian matrix is set-up in the desired \( M_s \) space, which in our case is
restricted to \( M_s = 9, 10 \) and 11. In each subspace we have obtained a few low-lying
states using the Davidson algorithm [7]. We have also calculated the spin densities
and the spin-spin correlation functions in each of the states. Using the spin-spin
correlation functions, we have computed the expectation value of $S_{total}^2$ operator,
from which we have identified the total spin of the state. We also compute the total
spin density of the core and crown spins in each of these states. From the total spin
and the spin density of the core and crown spins in the given $M_s$ state, we have
used the spin ladder operators to obtain the spin densities in the core and crown
of the cluster in all the allowed $M_s$ states. These are later used in computing the
magnetization response of the system. We find that the lowest five states with the
above values of $M_s$ belong to $S_{total} = 10, 11, 12, 10$ and 13; their energies are given
in Table 2. We therefore have a total of 117 low-lying states.

To study quantum tunneling we have considered all these low-lying states and
the following Hamiltonian,

$$\hat{H} = E_s - D \hat{S}_{z,\text{total}}^2 + c (\hat{S}_{x,\text{total}}^4 + \hat{S}_{y,\text{total}}^4) - g_{\text{crown}} h(t) \hat{S}_{z,\text{crown}} - g_{\text{core}} h(t) \hat{S}_{z,\text{core}}.$$  \hspace{1cm} (2)

Here $D$ is the quadratic anisotropy factor, $g_{\text{crown}}$ and $g_{\text{core}}$ are the Landé $g$-factors
for the crown and core spin respectively, and $h(t)$ is the time-dependent magnetic
field. We have chosen $D = 10^{-3}$ and $c = 10^{-3}$ (in units of J) in accordance with the
experimental values [8, 9]. We take $g_{\text{crown}} = 1.85$ and $g_{\text{core}} = 2.0$ in order to keep
the average $g$ value equal to the experimental value of 1.9. The constants $E_s$ in (2)
correspond to the five lowest energies obtained from Eq. (1) and given in Table 2.
The fourth order anisotropy term allows transition between states with $\Delta M_s = \pm 4$.
To study the evolution of the magnetization as a function of the applied magnetic
field, we start from an axial field equal to $-1$ (in units of $J/\hbar$) and then slowly
increase it in steps till it equals +1; the exact procedure for sweeping the field is
described below.

We have studied the time evolution of the system by solving the time-dependent
Schrödinger equation

$$i\hbar \frac{d\psi}{dt} = \hat{H}(t) \psi.$$  \hspace{1cm} (3)

We assume the system to be in the state with $S = 10, M_s = -10$ (all-spins-down
state) at time $t = 0$. This is the initial state which is time evolved according to the
equation

$$\psi(t + \delta t) = e^{-i\hat{H}(t+\frac{\delta t}{2})\delta t/\hbar} \psi(t).$$  \hspace{1cm} (4)

The evolution is carried out by explicit diagonalization of the Hamiltonian matrix
$H(t+\frac{\delta t}{2})$, and using the resulting eigenvalues and eigenvectors to evaluate the matrix
of the time evolution operator $e^{-i\hat{H}(t+\frac{\delta t}{2})\delta t/\hbar}$. Since the Hamiltonian matrix is in a
truncated basis of 117 eigenstates of the magnetic cluster, it is possible to repeatedly
carry out the time evolution in small time steps of size $\Delta t$. 

4
3 Results and Discussion

We have carried out a systematic investigation of the dependence of the magnetization steps on the field sweep rate, the fourth order anisotropy term, and the presence of a transverse field. Before doing that, it is useful to have an idea of the energy levels of the system as a function of the magnetic field.

Fig. 2 shows the the energy levels of the Hamiltonian in Eq. (2) with a constant axial magnetic field \( h(t) = H_z \). We can see from that figure that there are at least three values of the axial field where level crossings occur. In the case of interacting spins with exchange constant \( J \) and field value \( H_z = 0 \), levels with opposite magnetizations \( \pm M_s \) are degenerate. But when we introduce quantum fluctuations, such as the fourth order anisotropy term, then the magnetization is no longer conserved. Crossings occur around \( H_z = \pm 0.25, \pm 0.4 \) and \( \pm 0.5 \) (in units of \( J/h \)). The energy spectrum is symmetric about \( H_z = 0 \). We should expect to see jumps in the magnetization value at those values of the field where the crossings occur. Besides, as we will see, the occurrence and widths of plateaus in the magnetization are strongly dependent on the field sweep rate. The number of plateaus and their locations and widths depend on the probability of tunneling from one magnetization state to another. This probability increases when the time scale of sweeping matches with the time scale of tunneling. In that case, the probability of staying in the same eigenstate is small; the state is scattered into another eigenstate which produces a step in the magnetization plot.

Following the technique used by De Raedt et al. [4], we now study the behavior of the magnetization as the field is changed with time. The magnetic field \( H_z \) is increased from \(-1\) to \(1\) in steps of \(0.02\). At each value of the field, the state is evolved for 300 time steps of size \( \Delta t \). We have considered two different time step values given by \( \Delta t = 0.01 \, h/J \) and \( 0.1 \, h/J \); thus each value of the field is kept fixed for a time equal to \( 3 \, h/J \) and \( 30 \, h/J \) respectively. The field sweep rate is given by \( 0.02/(300\Delta t) \); we therefore have two sweep rates differing by a factor of 10. At each time step, the time evolved state is used to compute the magnetization \( M \) given by

\[
M(t) = \langle \psi(t) | \hat{S}_{z,total} | \psi(t) \rangle .
\]  

The magnetization at each value of the field is then taken to be the average of the magnetization computed over all the time steps for which the field is held fixed.

In Fig. 3, we show the step behavior of the magnetization with the applied field. The upper curve is for a time step equal to \( 0.1 \) (in units of \( h/J \)), while the lower curve is for a time step of \( 0.01 \). We observe jumps and steps in the magnetization plot at field values of approximately \( H_z = 0.25, 0.4 \) and \( 0.5 \). Before the first jump
in the magnetization the magnetization value remains almost constant at $-10$. The reason why we do not see any jumps at $H_z = -0.25$, $-0.4$ or $-0.5$ is because of the significant energy difference between the spin-10 ground state and the higher spin excited states; this makes the scattering probability extremely small. We observe a remarkable thing that the magnetization value seems to saturate after a certain time evolution, but it never approaches the state with all spins up. We can argue that in our model the system can only gain or loose energy by interacting with the time-dependent field, and there is no interaction with the environment through, for example, spin-phonon or nuclear spin-electron spin interactions. So even for very large $H_z$ the magnetization does not reach the saturation value in a finite time. However, the magnetization does reach a higher value for large fields if the sweep rate is lower, since there is more time to tunnel to the lowest energy states in that case. The inset of Fig. 3 shows the result obtained when the field is held fixed for a longer time equal to 300 $\bar{h}/J$ corresponding to 3000 time steps of size $0.1 \bar{h}/J$ each. Note that the plateau in the inset occurs at a different value of the magnetization compared to the plateaus in the two curves in the main figure where the sweep rates were faster. This is due to tunneling to nearly degenerate states with different values of the magnetization.

Experimentally we see transitions between states for which $\Delta m = \pm 1$ [9]. This is because, even in a single crystal of $Mn_{12}Ac$, all the clusters do not have exactly the same orientation. This would imply that the magnetic field seen by a cluster would also have a transverse component due to a slight misalignment of the axial field. To account for this fact we have added a term $-gH_x\hat{S}_x$ to the Hamiltonian in Eq. (2). In Fig. 4, we show the magnetization plateaus in the presence of a fixed and small transverse field equal to 0.01 $J/\hbar$ when the axial field is applied in the same manner as before. For the lower sweep rate, we do see one more plateau here than in Fig. 3 where there was only a fourth order term and no transverse field.

In Fig. 5, we show the magnetization when there is only a transverse field equal to 0.05 and no fourth order term. On comparing this with Fig. 4, we can see that in the presence of a higher transverse field the magnetization is much larger for positive values of the axial field; in fact, the magnetization almost reaches the maximum possible value of 10 for the lower sweep rate. This is because excited states start getting populated more easily when the magnitude of the leaking term is larger. We also note that there are no intermediate plateaus for the lower sweep rate in Fig. 5 because the system has more time to evolve to the lowest energy state at each field.

It is instructive to contrast the effects of the fourth order term vs. a transverse field on the dispersion of the low-lying energy levels. In Fig. 6, we show the energy
levels for two different axial fields equal to 0 and 0.26. The two figures on the left have the fourth term but no transverse field, while the two figures on the right have a transverse field of 0.05 but no fourth order term. (For ease of comparison, we have subtracted out appropriate constants to make the ground state energy equal to zero in all the four figures). It is clear that the energy levels have a much greater dispersion in the presence of the fourth order term; this means that the gaps are larger, the tunneling amplitudes will be smaller and the magnetization plateaus would be more prominent in that case. With a transverse field present, the energy levels almost form a continuum with very small gaps; hence the system can easily make transitions from one state to another and the plateaus would be smaller. This emphasizes that the fourth order term is essential for observing magnetization plateaus, and explains why there are more plateaus in Fig. 3 than in Fig. 5.

To study the populations of different $M_s$ states at the different plateau regions, we show histograms in Figs. 7 (a) and (b). $|C|^2$ is the sum of the squares of the modulus of the coefficients for each value of $M_s$ in the time evolved state $\psi(t)$ averaged over the time for which the field is held constant. We have followed the changes in $|C|^2$ for different $M_s$ states at three values of the axial fields where the plateaus begin in Fig. 3. In Fig. 7 (a), we show the change of weights of different $M_s$ values at the three onset values of the field. We can clearly see that the $\hat{S}_x^4 + \hat{S}_y^4$ term connects states with $\Delta M_s = \pm 4$. This plot also explains why the saturation magnetization value never reaches $+10$. The $M_s = -10$ state has a considerable weight in all three plateaus although it decreases gradually at higher magnetic fields. In Fig. 7 (b), we have studied the case when the system is experiencing a transverse field in addition to the fourth order term. In the presence of the leaking term $-gH_s\hat{S}_x$, the population distribution changes completely. Here we see transitions between states with $\Delta m = \pm 1$. The population of the $M_s = -10$ state decreases drastically from the first plateau to the third plateau. We do not see any weight for $M_s = 10$ state in this case also.

In Figs. 8 (a) - (c), we show the time evolution of the magnetization at a constant axial field equal to 0.74 $J/\hbar$. The oscillations are most complex when we have both a transverse field and a fourth order term as in Fig. 8 (b). The oscillations are somewhat simpler when we have only the fourth order anisotropy term and no transverse field as in Fig. 8 (a); we see a beat structure superimposed on regular oscillations. Finally, when we only have a small transverse field equal to 0.05 and no fourth order term, the magnetization evolves as a smooth cosine function with time as shown in Fig. 8 (c); the behavior is just like that of a two-level system. Note also that the ranges of the magnetization oscillations change considerably with the sweep rate in all the three figures.
Finally, in Fig. 9, we present the weights of the different $M_s$ states when there is a constant axial field equal to 0.74 and a transverse field equal to 0.05, but no fourth order term. The weights are dramatically different for the two sweep rates; for the lower sweep rate shown in the lower panel, the system has sufficient time to reach states with higher magnetization.

4 Summary and Outlook

We have studied the effects of the sweep rate, fourth order anisotropic term and a transverse magnetic field on the quantum tunneling of magnetization in $Mn_{12}Ac$. An effort to reproduce the experimental details will require the introduction of terms which take into account the other degrees of freedom necessary for the spin system to relax back to the ground state after a scattering event. It would also be worthwhile to extend this approach to finite temperatures to investigate the thermodynamic properties of the molecule and to study the phenomenon of thermally assisted tunneling [10]. For models of the Ising kind, a nontrivial response of the magnetization is known for an alternating field [11]. A study of the same in our model is currently in progress. In conclusion, we would like to say that incorporating the spin-phonon [12], hyperfine [13] and dipolar interactions [14] to quantitatively explain the experiments will be a challenge for the future.

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| $M_s$ value | Dimension of Hilbert Space |
|------------|---------------------------|
| ±13        | 139672                    |
| ±12        | 269148                    |
| ±11        | 484144                    |
| ±10        | 817176                    |
| ±9         | 1299632                   |
| ±8         | 1954108                   |
| ±7         | 2785384                   |
| ±6         | 3772176                   |
| ±5         | 4862352                   |
| ±4         | 5974048                   |
| ±3         | 7003944                   |
| ±2         | 7842070                   |
| ±1         | 8390440                   |
| 0          | 8581300                   |

Table 1. Different $M_s$ values and the corresponding Hilbert space dimensions.

| $S_{total}$ | Energies    |
|-------------|-------------|
| 10          | -53.251824  |
| 11          | -52.419914  |
| 12          | -51.512498  |
| 10          | -50.910154  |
| 13          | -50.529748  |

Table 2. Energies (in units of J) of the lowest five states and the corresponding $S_{total}$ values for the Hamiltonian in Eq. (1).
Figure Captions

1. A schematic diagram of the exchange interactions between the $Mn$ ions in the $Mn_{12}Ac$ molecule.

2. Energy spectrum of the Hamiltonian in Eq. (2) in the presence of a time-independent axial field. Only a few low-lying energy levels are shown.

3. Evolution of magnetization at two different sweep rates. The upper curve is for a time step equal to 0.1 (in units of $\hbar/J$), while the lower curve is for a time step of 0.01. The inset shows the result obtained when the field is held fixed for a time equal to 300 $\hbar/J$.

4. Magnetization vs. the axial field for two different sweep rates when there is both a fourth order term and a transverse field equal to 0.01 $J/\hbar$.

5. Magnetization vs. the axial field for two different sweep rates when there is only a transverse field equal to 0.05 and no fourth order term.

6. Energy level distribution of the system for two different axial fields. The two figures on the left have a fourth order term and no transverse field, while the two figures on the right have a transverse field and no fourth order term.

7. Weights of different $M_s$ states at the onset fields of three different plateaus is shown in plot (a), and in the presence of an additional small transverse field $H_x = 0.01$ is shown in plot (b). The fourth order term is present in both cases. Note that $\Delta M_s$ is equal to 4 and 1 in cases (a) and (b) respectively.

8. Evolution of magnetization with time is shown at a constant value of the axial field equal to 0.74. In (a) there is only a fourth order anisotropy term; in (b) there is both a fourth order term and a transverse field equal to 0.01; in (c) there is only a transverse field equal to 0.05. Note that the ranges of the oscillations change considerably with the sweep rate.

9. Weights of different $M_s$ states in the presence of an axial field equal to 0.74 and a transverse field equal to 0.05 for two different sweep rates.
$S = 2 \quad S = 3/2$

J - Ferromagnetic  \quad J' - Antiferromagnetic

Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7 (a)
Fig. 7 (b)
Fig. 8 (a)
Fig. 8 (b)
Fig. 8 (c)
\[ \Delta t = 0.01 \]

\[ \Delta t = 0.1 \]