Many-spin effects and tunneling splittings in Mn$_{12}$ magnetic molecules

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We calculate the tunneling splittings in a Mn$_{12}$ magnetic molecule taking into account its internal many-spin structure. We discuss the precision and reliability of these calculations and show that restricting the basis (limiting the number of excitations taken into account) may lead to significant error (orders of magnitude) in the resulting tunneling splittings for the lowest energy levels, so that an intuitive picture of different decoupled energy scales does not hold in this case. Possible routes for further development of the many-spin model of Mn$_{12}$ are discussed.

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I. INTRODUCTION

Molecular magnets have proven to be very suitable systems for the study of mesoscopic tunneling effects in magnetic materials. A number of impressive experimental results have been obtained recently, such as thermally-assisted tunneling of ground state - to - ground state tunneling and topological phase effects in spin tunneling. Among others, the molecular magnet Mn$_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ (below referred to as Mn$_{12}$) has received special attention. The effect of resonant magnetization tunneling has been first observed and studied in detailed experiments on Mn$_{12}$, and, at present, a substantial amount of reliable experimental data has been collected. Quantitative analysis of these experiments is a challenging theoretical problem involving fundamental issues about tunneling phenomena in mesoscopic magnetic systems. The basic prerequisite for solving this problem is our ability to evaluate accurately and reliably the energy splittings occurring as a result of tunneling between two (quasi)degenerate levels. At present, carefully designed magnetic relaxation experiments at low and ultralow temperatures (tens or hundreds of milliKilvins) can determine the changes in relaxation time caused by the splittings of order $10^{-2}$ - $10^{-4}$ K, and even smaller of order $10^{-6}$ - $10^{-7}$ K. The relaxation time data obtained in these experiments give information (although indirect) about the splitting values, so that predictions of the theoretical models can be compared with experimental results.

Conventionally, the molecular magnet Mn$_{12}$ is considered as a large single spin $S = 10$ with quasidegenerate levels $S_z = +M$ and $S_z = -M$ split because of tunneling. However, the single-spin Hamiltonian is a phenomenological construct; in reality, this is a many-spin system, consisting of 12 manganese ions coupled by exchange interactions. Here, using Mn$_{12}$ as a well-studied example, we address the problem of reliable many-spin calculation of the tunneling splittings in molecular magnets. Such a calculation is a very complicated task. For example, the Hilbert space of the spin Hamiltonian describing a molecule of Mn$_{12}$ consists of $10^8$ levels, while the smallest tunneling splittings in Mn$_{12}$ are of order of $10^{-10}$ Kelvin (as measured in Ref. for $m = \pm 10$). The brute-force direct calculation of tiny tunneling splittings in this system, even for several low-lying states, is beyond the capabilities of modern computers. The general strategy to solve this problem is to truncate the full Hilbert space thus reducing consideration to a much smaller number of relevant energy levels. This idea, implemented in a rather sophisticated way, forms a basis of several approaches for the evaluation of tunneling phenomena, such as quantum Monte-Carlo methods, stochastic diagonalization, and instanton calculations.

To our knowledge, all calculations of the tunneling splittings in molecular magnets starting from realistic Hamiltonians have employed truncation of the Hilbert space in a much more straightforward, and much less justified manner. High-energy basis states, assumed to be irrelevant, are being explicitly excluded from consideration, and only the low-energy part of the spectrum is being taken into account. In the present paper, we calculate tunneling splittings using the many-spin model of Mn$_{12}$, examining the accuracy and reliability of this straightforward scheme. We demonstrate that, because of strong Dzyaloshinsky-Morya interactions present in Mn$_{12}$, the splitting values obtained in this way are unreliable. We also consider the sensitivity of the calculated splitting values to variation in the Hamiltonian parameters, and determine the accuracy needed for reliable splittings calculation.

The paper is organized as follows. In Section II, we discuss the 8-spin model of Mn$_{12}$ and the methods used to calculate tunneling splittings based on this model. We also consider the stability of the results with respect to possible limitations of the model Hamiltonians. In Section III we consider the reasons for the failure of the energy-based truncation scheme in the splittings calculations. Our conclusions can be found in the Summary.
II. 8-SPIN MODEL OF Mn$_{12}$ AND CALCULATIONS OF THE TUNNELING SPLITTINGS

The cluster Mn$_{12}$ consists of eight Mn$^{3+}$ ions having spin 2 and four Mn$^{4+}$ ions having spin 3/2, coupled by exchange interactions. The total number of spin states in Mn$_{12}$ is $10^5$, and a corresponding Hamiltonian matrix is rather large to be treated by modern computers. To overcome this difficulty, we can employ the natural hierarchy of interactions present in Mn$_{12}$. The antiferromagnetic exchange interactions $J_1 \simeq 220$ K between Mn$^{3+}$ and Mn$^{4+}$ ions are significantly stronger than all the other, so corresponding pairs of Mn$^{3+}$ and Mn$^{4+}$ ions can be considered as stiff dimers with the total spin $S = 1$. Thus, giving rise to the 8-spin model of Mn$_{12}$. The range of validity of the 8-spin model, and the corresponding 8-spin Hamiltonian of Mn$_{12}$ have been considered in Ref. [14]. After examination of different possible interactions, the following Hamiltonian has been proposed:

$$\mathcal{H} = -J \left( \sum_i s_i \right)^2 - J' \sum_{(i,j)} s_i s_j - K_z \sum_{i=1}^4 \left( S_i^z \right)^2 \quad (1)$$

Here, $s_i$ and $s_j$ are the spin operators for the large spins $S = 2$ and small dimer spins $s = 1/2$, correspondingly (the subscript $i$ indexes the spins). The first two terms describe isotropic Heisenberg exchange between the spins. The third term describes the single-ion easy-axis anisotropy of large spins. The fourth term represents the antisymmetric Dzyaloshinsky-Morya (DM) interactions in Mn$_{12}$, where $D^{i,j}$ is the Dzyaloshinsky-Morya vector describing the DM-interaction between $i$-th small spin and $j$-th large spin. Existence of DM-interactions in Mn$_{12}$ has been suggested in Ref. [14], and their magnitude has been estimated in Ref. [14] based on the neutron scattering data. The molecules of Mn$_{12}$ possess a fourfold rotational-reflection axis (symmetry $S_4$) imposing restrictions on the DM-vectors $D^{i,j}$, so that Dzyaloshinsky-Morya interactions can be described by only three parameters $D_x \equiv D_x^{1,8}$, $D_y \equiv D_y^{1,8}$, and $D_z \equiv D_z^{1,8}$.

It has been demonstrated [14] that the above model satisfactorily describes a rather wide range of experimental data, such as the splitting of the neutron scattering peaks, results of EPR measurements and the temperature dependence of magnetic susceptibility. Here, for calculations we use the parameter set A from Ref. [14],

$$\begin{align*}
    & A: \quad J = 0, \quad J' = 105 \text{ K}, \quad K_z = 5.69 \text{ K} \\
    & D_x = 25 \text{ K}, \quad D_y = 0, \quad D_z = -1.2 \text{ K}.
\end{align*}$$

which also gives a good description of the response of Mn$_{12}$ molecules to a transverse magnetic field (external field applied perpendicular to the easy axis of the molecule). However, this set of parameters should not be considered as being accurately determined, since the amount of the experimental information available is not yet sufficient to achieve particularly reliable parameters. In the Hamiltonian [14], only the fourth term, representing the Dzyaloshinsky-Morya (DM) interactions, can lead to tunneling [14] the first three terms conserve the $z$-projection of the total spin $S_z$ and can not induce tunneling between levels with different $S_z$, while the DM-term mixes levels with different $S_z$. In what follows, we will label the energy levels by the value of $S_z$. Although it is not an exact quantum number, we can formally consider the DM-interaction as a perturbation, and use perturbation theory terminology.

The following values of the tunneling splittings corresponding to the parameter set [14] have been obtained by the diagonalization of the full Hamiltonian matrix (of the size $10^4 \times 10^4$) using quadruple precision arithmetics:

$$\begin{align*}
    \Delta E(\pm 10) &= 1.18 \cdot 10^{-15} \text{ K}, \quad \Delta E(\pm 8) = 1.06 \cdot 10^{-11} \text{ K} \\
    \Delta E(\pm 6) &= 3.87 \cdot 10^{-8} \text{ K}, \quad \Delta E(\pm 4) = 2.08 \cdot 10^{-6} \text{ K}, \\
    \Delta E(\pm 2) &= 4.17 \cdot 10^{-2} \text{ K}.
\end{align*}$$

The splittings for odd values of $S_z$ are not shown: they constantly remain at the level of the numerical precision of the calculations (of order of $10^{-19}$ K). In Mn$_{12}$, these splittings should be zero since the fourfold symmetry of the molecule imposes certain restrictions on the symmetry of the spin Hamiltonian and makes some matrix elements vanish. In the single-spin model of Mn$_{12}$ this property of the spin Hamiltonian is introduced explicitly, by retaining only those operators which possess the required fourfold symmetry. In the many-spin simulations, we obtain the same result independently.

The first question to pose concerns the accuracy of the level splitting evaluation. Parameters of the Hamiltonian are determined with some finite precision, and a small error (say, of the order of several Kelvin) affects the level energy by an amount of order of Kelvin, which is much larger than the very small value of tunneling splitting (of order of $10^{-12}$ K). Does it deprive the calculation results of all meaning? To answer this question, we note that the levels $|S_z = +M\rangle$ and $|S_z = -M\rangle$ are degenerate due to exact symmetry properties of the spin Hamiltonian, and, in the absence of the DM-term, would be degenerate at any value of parameters. Therefore, the tunneling splittings $\Delta E_{+M,-M}$ are governed only by the strength of the interaction which breaks the symmetry, i.e. the DM-interaction. If the parameters of the Hamiltonian are determined with reasonably small relative error, and if the numerical calculation is done with sufficient precision, then the relative error of the level splittings will also be small. This conclusion is supported by our calculations: a 10% variation in the Hamiltonian parameters leads to the variation in the splitting values at most by a factor of ten, so that accurate determination of the Hamiltonian parameters is necessary for reliable calculation of the tunneling splittings. If only a logarithmic
accuracy in the splitting values is needed, then the 10% uncertainty in the Hamiltonian parameters is sufficient.

However, there is another, much more important source of possible error. The description of the Mn$_{12}$ molecule by the 8-spin model requires a full, high-precision diagonalization of the Hamiltonian matrix with dimensions $10^4 \times 10^4$. Solving this problem is rather time-consuming. Matrices of that size can be processed very effectively using Lanczos-type methods, but the application of these methods to the tunneling splitting calculations constitutes quite a difficult problem by itself. A very large number of iterations is needed to achieve the necessary precision and in addition the precision is hard to control when the level separation is very small, so that special techniques are necessary.

Therefore it is natural first to explore another approach, namely, to omit high-energy basis states, retaining only the low-lying part of the spectrum where basis levels have energies less than some threshold value $E_{\text{cut}}$. This approach has been adopted extensively and in fact, we are not aware of any calculations of tunnel-splitting of magnetic molecules done in a different way: calculations based on both the single-spin and the many-spin model have employed this method. In this paper, we assess the validity of this energy-based truncation approach by considering the dependence of the tunneling splittings $\Delta E_{+M,-M}$ for different pairs of degenerate levels $|S_z = +M\rangle$ and $|S_z = -M\rangle$ on the number of lowest levels $N_{\text{low}}$ actually used in calculations (or, in other words, their dependence on the energy threshold $E_{\text{cut}}$).

A brief description of the basis states is in order. We first consider the first two exchange terms in the Hamiltonian of Eq. (1) and diagonalize within the manifold of all the 8-spin configurations yielding states with $S_z = 0$; there are 1286 energy eigenvalues corresponding to eigenvectors with $S$ ranging from 0 to 10. The distribution of states is: (10,1), (9,7), (8,24), (7,56), (6,104), (5,164), (4,220), (3,248), (2,232), (1,168), (0,62), where the first number in parenthesis is the value of $S$ and the second is the number of levels with this value of $S$. With the $2S + 1$ degeneracies included, there are exactly 10000 states. These are the basis states which are then used to diagonalize the full Hamiltonian, including anisotropy and DM terms.

The initial increase in the number of basis states considered, $N_{\text{low}}$, leads to an overall increase in $\Delta E_{+M,-M}$ accompanied by oscillations (see Fig. 1). After $N_{\text{low}}$ achieves the value of about 700, the oscillations have become small and $\Delta E_{+M,-M}$ versus $N_{\text{low}}$ exhibits a plateau. This saturation lead in Ref. 11 to the conclusion that the resulting values give the actual splittings with sufficient accuracy. But this conclusion is wrong. A further increase of the number of levels leads to a resurgence of the oscillations at $N_{\text{low}} \sim 1200$, with a quite pronounced jump in $\Delta E_{+M,-M}$ for $N_{\text{low}} \sim 1700$. For a larger number of levels, the situation repeats itself: the values of the splittings reach another plateau, then oscillations appear again with a subsequent jump, etc. We have traced this behavior up to $N_{\text{low}} \sim 3000$, which is already $1/3$ of the total number of levels. The observed behavior of $\Delta E_{+M,-M}$ is, in our opinion, a very clear signal that energy-based truncation of the Hilbert space is not a good strategy for the computation of tunneling splittings: it gives unreliable results.

The rather sharp jumps in the tunneling splittings as discussed above and illustrated in Fig. 1 are associated with the inclusion of basis states with large $S$ values. Because of the selection rule for the DM term ($S \rightarrow S \pm 1$), the $S = 10$ ground state only couples with $S = 9$ states. States with smaller $S$ values affect the splittings more indirectly by coupling with other states which eventually couple to the ground state. While the states with large $S$ cause jumps in the splitting values, there are few of them, and the smaller coupling of smaller $S$ states still is significant because of the cumulative effect of so many states (see the distribution given above). Therefore, the evaluation of tunneling splittings for a general system possessing strong DM interactions requires consideration of sufficiently large portion of Hilbert space.

It is noteworthy that the same truncation method works rather well for calculations of the energies of well-separated levels. To compare the model against most of the experiments, it suffices to know the positions of the levels with much less precision, usually an error less than 0.1 K is already adequate. This level of precision can be obtained by taking into account $N_{\text{low}} \sim 1000$ levels (i.e., 1/10 of the total Hilbert space). Even using $N_{\text{low}} \sim 500$, the error in the level position is less than 1 K even for the states of energy about 60 K. Therefore, the matrix-truncation approach is adequate for fitting the model parameters to experimental data. But the calculations of the tunneling splittings should be done using the full Hamiltonian matrix.

III. DISCUSSION

We have shown that truncating the Hilbert space leads to large errors in the calculated values of tunneling splittings. But actually, any sensible Hamiltonian is inevitably obtained due to some truncation of the Hilbert space. For example, the Hamiltonian (1) can be considered as a result of the two-step procedure (i) projection of the real many-electron Hamiltonian onto the subspace of suitably chosen single-electron orbital states, yielding a general spin Hamiltonian of the molecule; and (ii) projection of the resulting spin Hamiltonian onto the subspace of the 8-spin model. This procedure is usually justified (at least, at the heuristic level) by invoking some kind of perturbation or WKB-theory arguments, and corresponds to an intuitive idea of different, practically independent energy scales.

However, in the case of the tunneling splittings, we see that very different energy scales significantly affect each other. Why do the same arguments not work if we truncate the 8-spin Hamiltonian? In our opinion, this
takes place because the conditions of the applicability of WKB-reasoning (or similar arguments based on perturbation theory) are not satisfied. The spin of the system \( S = 10 \) is too small, so that the instanton action on the trajectories corresponding to the 8-spin model is not large enough. Indeed, for systems with well-separated levels, the quasiclassical approximation usually already works reasonably for a total spin \( S \sim 2-3 \). However, as has been demonstrated to apply the same type of arguments to the splitting calculations, the (normalized) instanton action \( S_I \) should exceed the value of 12. For the model employed in Ref. 13, this corresponds to the system with a total spin (more exactly, with the total antiferromagnetic vector) of order of several thousand. Thus, the tunneling splittings, in general, appear to be much more sensitive to the method of calculation than the level energies themselves, and conditions for applicability of the conventional WKB-reasoning are considerably more stringent (though for Mn\(_{12}\) they can of course be different from the condition \( S_I > 12 \)). Qualitatively this agrees with our observations (see Section II). Even a rather severe truncation of the Hilbert space has a minor effect on the level energies, while correct values of the tunneling splittings require a diagonalization of the full Hamiltonian.

Briefly, these arguments can be expressed in a rather obvious form: the 8-spin model is not “macroscopic enough” to justify the truncation of the Hilbert space by some WKB or similar perturbation approach. In this case the intuitive picture of different independent energy scales is misleading.

This conclusion raises important questions, namely, is the 8-spin model, being the result of the truncation of, e.g., 12-spin Hamiltonian, sufficient to predict reliably the tunneling splittings (or, in other words, is the 12-spin model “macroscopic enough” to be truncated)? What is the minimal model allowing the splittings to be calculated correctly? We believe that these are key questions, not only for Mn\(_{12}\) but for the whole class of magnetic molecules. For this purpose, ab-initio calculations of the exchange and anisotropic intramolecular interactions in Mn\(_{12}\) could be very useful. Also, reliable experimental data for the tunneling splittings would obviously be of great value for further development.

IV. SUMMARY

We have calculated the tunneling splittings in Mn\(_{12}\) on the basis of the 8-spin model proposed earlier. We have shown that rather accurate knowledge of the Hamiltonian parameters is needed for the accurate splitting calculations; although, for logarithmic accuracy, 10% error in the parameters can be tolerated. Furthermore, we have demonstrated that a reliable calculation of the tunneling splittings for a system with strong DM interactions requires the use of the full Hamiltonian matrix. We have explicitly shown that an energy-based Hilbert space truncation scheme can be successfully used for the determination of the level energies, but leads to erroneous results when applied to the splitting calculations.

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FIG. 1: Dependence of the tunneling splittings $\Delta E_{+M,-M}$ (in Kelvins) versus the number of levels taken into account in the many-spin calculations. The parameter set A (see text) has been used for calculations. The results for $M = 8, 6, 4, \text{ and } 2$ are presented. Tunneling splittings for the levels with odd $M$ are zero because of the symmetry properties of the spin Hamiltonian.

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