Many-spin calculation of tunneling splittings in Mn_{12} magnetic molecules

H. A. De Raedt and A. H. Hams
Institute for Theoretical Physics and Materials Science Centre, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

V. V. Dobrovitski, M. Al-Saqer, M. I. Katsnelson, and B. N. Harmon[a)]
Ames Laboratory, Iowa State University, Ames, Iowa 50011

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. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1452703]

Molecular magnets are 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[1,2] and ground-state tunneling,[3] and topological phase effects.[3] Among others, the molecular magnet $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ (referred to as Mn_{12}) has received special attention, and a substantial amount of reliable experimental data has been collected. Quantitative analysis of these experiments is a challenging theoretical problem, requiring the ability to accurately evaluate the energy splittings occurring as a result of tunneling between two (quasi) degenerate levels.[4] At present, the experiments can detect[1–3] the changes in relaxation time caused by the splittings of the order of $10^{-6}-10^{-7}$ K. The relaxation time data obtained in these experiments give information (although indirect) about the splitting values.

Conventionally, the molecular magnet Mn_{12} is considered as a large single spin $\mathcal{S}=10$ with quasidegenerate levels $\mathcal{S}_z=+M$ and $\mathcal{S}_z=-M$ 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 reliably calculating the tunneling splittings in molecular magnets. Such a calculation is a very complicated task: 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^{-12} K. The general strategy is to truncate the full Hilbert space to a much smaller number of relevant energy levels. This idea, implemented in a rather sophisticated way, forms the basis of several approaches for the evaluation of tunneling phenomena, such as quantum Monte Carlo methods,[5] stochastic diagonalization,[6] and instanton calculations.[7]

However, 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 manner. High-energy states, assumed to be irrelevant, are being excluded from consideration, and only the low-energy part of the spectrum is being taken into account.[8] In the present article, we calculate tunneling splittings using the many-spin model of Mn_{12}, examining the accuracy and reliability of this straightforward scheme. We demonstrate that the splitting values obtained in this way are unreliable. We also consider the sensitivity of the calculated splitting values to variations in the Hamiltonian parameters, and determine the accuracy needed for reliable splittings calculation.

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 rather large (10^8), so we employ the hierarchy of interactions present in Mn_{12}. The antiferromagnetic exchange $J_1 \simeq 220$ K between Mn^{3+} and Mn^{4+} ions is significantly stronger than all the others,[9] so the pairs of Mn^{3+} and Mn^{4+} ions can be considered as stiff dimers with the total spin $s=1/2$, thus giving rise to the eight-spin model of Mn_{12}. The range of validity of the eight-spin model, and the corresponding eight-spin Hamiltonian of Mn_{12} have been considered in Ref. 10. After an examination of different eight possible interactions, the following Hamiltonian has been proposed:

$$\mathcal{H}=-J\left(\sum_i \mathbf{s}_i\right)^2-J'\sum_{\langle k,l\rangle}\mathbf{s}_k\mathbf{S}_l-K_z\sum_{i=1}^{4}(S_i^z)^2 + \sum_{\langle i,j\rangle}\mathbf{D}^{i,j}\times[\mathbf{s}_i\times\mathbf{S}_j]. \quad (1)$$

Here, $\mathbf{S}_i$ and $\mathbf{s}_i$ are the spin operators for the large spins $S=2$ and small dimer spins $s=1/2$, correspondingly. The first two terms describe an 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 between i-th small spin and j-th large spin, where $\mathbf{D}^{i,j}$ is the DM vector. Due to the symmetry of the molecule, all DM 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[10] that the aforementioned model satisfactorily describes a rather wide range of experi-

a)Electronic mail: harmon@ameslab.gov

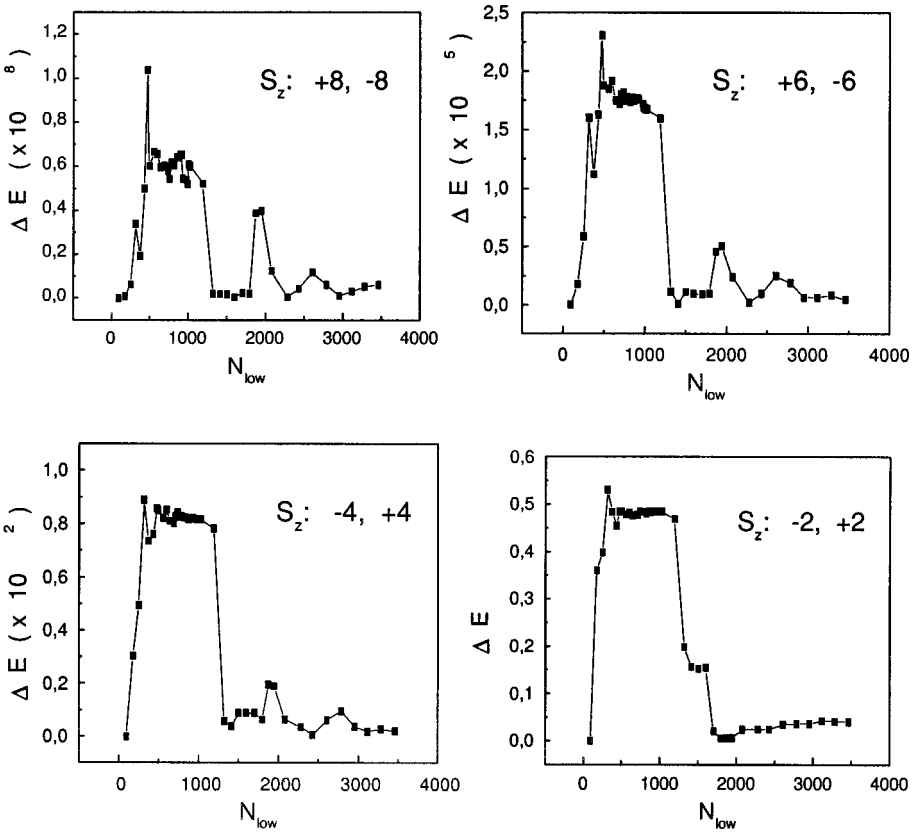

FIG. 1. Dependence of the tunneling splittings $\Delta E_{+M,-M}$ (in Kelvins) versus the number of levels taken into account in the many-spin calculations. The parameter set A has been used for calculations. The results for $M=8$, 6, 4, and 2 are presented. Tunneling splittings for the levels with odd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

mental data, such as the splitting of the neutron scattering peaks, results of electron paramagnetic resonance measurements and the temperature dependence of magnetic susceptibility. Here, for calculations, we use the parameter set A from Ref. 10: set **A**: $J=0$, $J'=105$ K, $K_z=5.69$ K $D_x=25$ K, $D_y=0$, $D_z=-1.2$ K. However, this set of parameters should not be considered as being final, since the amount of the experimental information is not yet sufficient. In what follows, we will label the energy levels by the value of the total spin $\boldsymbol{\mathcal{S}}$ and its z-projection $\boldsymbol{\mathcal{S}}_z$. Although these are not exact quantum numbers, we can formally consider the DM interaction as a perturbation, and use perturbation theory terminology.

In our calculations, we first consider the first two exchange terms in the Hamiltonian of Eq. (1) and diagonalize them within the manifold of the states with $\boldsymbol{\mathcal{S}}_z=0$; there are 1286 such states with $\boldsymbol{\mathcal{S}}=0...10$. These basis states are then used to diagonalize the full Hamiltonian (of the size $10^4\times10^4$), including the anisotropy and DM terms. This gives values of $\sqrt{\langle \boldsymbol{\mathcal{S}}_z^2\rangle}$ for the manifold $\boldsymbol{\mathcal{S}}=10$ as follows: ±9.758, ±8.755, ±7.765, ±6.786, ±5.817, ±4.855, ±3.902, ±2.029, ±1.171, and ±0.670. The following values of the tunneling splittings have been obtained by the diagonalization of the full Hamiltonian matrix using quadruple precision arithmetics: $\Delta E(\pm10)=1.18\times10^{-15}$ K, $\Delta E(\pm8)=1.06\times10^{-11}$ K, $\Delta E(\pm6)=3.87\times10^{-8}$ K, $\Delta E(\pm4)=2.08\times10^{-6}$ K, $\Delta E(\pm2)=4.17\times10^{-2}$ K. The splittings for odd values of $\boldsymbol{\mathcal{S}}_z$ constantly remain at the level of the numerical precision (of order of 10^{-19} K);[11] these splittings vanish due to four-fold symmetry of the molecule. 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 symmetry. Fitting our energy levels of the $S=10$ states with the single spin model $E=-\alpha\ S_z^2-\beta\ S_z^4$ (Ref. 10) yields $\alpha=0.617$ K and $\beta=-0.79$ mK.

The first question concerns the accuracy of the level splitting evaluation. A small error (say, of the order of several Kelvin) in the parameters of the Hamiltonian effects the level of energy by an amount of an order of Kelvin which is much larger than the typical value of tunneling splitting (of the order of 10^{-12} K). To explain why the results still remain meaningful, we note that the levels $|\boldsymbol{\mathcal{S}}_z=+M\rangle$ and $|\boldsymbol{\mathcal{S}}_z=-M\rangle$ are degenerate due to the exact symmetry properties of the spin Hamiltonian, and, in the absence of the DM term, would be degenerate at any value of parameters. 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. 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 eight-spin model requires a high-precision diagonalization of the $10^4 \times 10^4$ Hamiltonian matrix, which is rather time consuming. It is natural to truncate Hilbert space retaining only some smaller number N_{low} of the low-energy basis levels. This approach, to our knowledge, is the only one which has been actually used for Mn_{12}, for both the single-spin and the many-spin calculations.[8] To assess the usefulness of this energy-based truncation scheme, we consider the dependence of the tunneling splittings $\Delta E_{+M,-M}$ on the number of lowest levels N_{low}.

The initial increase in the number N_{low} of basis states leads to an increase in $\Delta E_{+M,-M}$ accompanied by oscillations (see Fig. 1). After N_{low} achieves the value of about 700, the oscillations have become small and $\Delta E_{+M,-M}$ versus N_{low} exhibits a plateau. This saturation lead, in Ref. 8, 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 resurrection of the oscillations at $N_{\mathrm{low}} \sim 1200$, with a pronounced jump in $\Delta E_{+M,-M}$ for $N_{\mathrm{low}} \sim 1700$. For a larger number of levels, the situation repeats itself: we have traced this behavior up to $N_{\mathrm{low}} \sim 3000$. The rather sharp jumps in the tunneling splittings are associated with the account of basis states with large S values. Because of the selection rule for the DM term ($\mathcal{S} \rightarrow \mathcal{S} \pm 1$), the $\mathcal{S}=10$ ground state only couples with $\mathcal{S}=9$ states. States with smaller $\mathcal{S}$ values effect the splittings more indirectly by coupling with other states which eventually couple to the ground state. While the states with large $\mathcal{S}$ cause jumps in the splitting values, there are few of them, and the smaller coupling of smaller $\mathcal{S}$ states is still significant because of the cumulative effect of so many states. 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.

However, any practical Hamiltonian is obtained by the truncation of the Hilbert space. For example, the Hamiltonian (1) is a result of the two-step procedure:[12] (i) projection of the real many-electron Hamiltonian onto the subspace of single-electron orbital states, and (ii) projection of the resulting spin Hamiltonian onto the eight-spin model. This procedure is usually justified by perturbation or Wentzel–Kramers–Brillouin (WKB)-theory arguments, and corresponds to the picture of different and practically independent energy scales. However, in the case of the tunneling splittings, very different energy scales significantly affect each other. In our opinion, this takes place because WKB reasoning (or similar arguments based on perturbation theory) is not applicable since the spin of the system $\mathcal{S}=10$ is too small, and the instanton action[4] is not large enough. Indeed, for well-separated levels, the quasiclassical approximation already works reasonably well for $\mathcal{S} \sim 2-3$. However, as has been demonstrated,[13] for the splitting calculations, the (normalized) instanton action S_I should exceed the value of 12, and for the model of Ref. 13, this corresponds to the total spin (more exactly, the total antiferromagnetic vector) of the order of several thousand. Thus, the tunneling splittings appear to be much more sensitive to the method of calculation than the level energies themselves, and conditions for the applicability of the conventional WKB reasoning are considerably more stringent. This agrees with our observations: truncation of the Hilbert space has a minor effect on the level energies, but correct values of the splittings require a diagonalization of the full Hamiltonian.

Summarizing, we have calculated the tunneling splittings in Mn_{12} on the basis of the eight-spin model proposed earlier.[10] 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. We have demonstrated that a reliable calculation of the tunneling splittings 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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