Quantum Fluctuations in Large-Spin Molecules

A. K. Zvezdin

Institute of General Physics, Moscow 117942, Russia

V. V. Dobrovitski and B. N. Harmon

Ames Laboratory, Iowa State University, Ames, Iowa 50011

M. I. Katsnelson

Institute of Metal Physics, Ekaterinburg 620219, Russia

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A new type of mesoscopic quantum effect in large-spin molecules possessing easy-axis anisotropy, such as Mn$_{12}$, is predicted. The response of such a system to an external field applied perpendicular to the easy axis is considered. It is shown that the susceptibility of this system exhibits a peculiar peak of purely quantum origin. This effect arises from very general properties of quantum fluctuations in spin systems. We demonstrate that the effect is entirely accessible for contemporary experimental techniques. Our studies show that the many-spin nature of the Mn$_{12}$ clusters is important for a correct description of this quantum peak.

Quantum fluctuations in spin systems receive much attention at present, being important in applied as well as fundamental fields of physics. As an example, mention can be made of attempts to explain the superconductivity in high-$T_c$ cuprates in terms of electron interaction with quantum spin fluctuations [1]. Another example is the analysis of implementations of algorithms for quantum computations, quantum cryptography and quantum searching [2], where quantum spin fluctuations enter into consideration. And, finally, quantum fluctuations are one of basic concepts underlying mesoscopic quantum effects in spin systems [3].

For experimental study of quantum fluctuations, molecular magnets, such as Mn$_{12}$, Fe$_8$, Fe$_{17}$ etc. [4], are very suitable. They belong to a new class of magnetic materials that has been receiving increasing attention, being promising for fundamental studies as well as for practical applications. An adequate understanding of their properties is important.

At present, the phenomenon of magnetization tunneling in these magnets has attracted much attention [5,6]. But, as we show in this work, quantum fluctuations in molecular magnets can reveal themselves also in another, very interesting way, different from magnetization tunneling and exhibiting a new type of mesoscopic quantum effect.

We consider a mesoscopic magnetic system possessing an anisotropy of easy-axis type, such as the Mn$_{12}$ molecule, subjected to an external magnetic field directed perpendicular to the easy axis. We show that the susceptibility of this system as a function of the magnetic field has a clearly visible peak in the vicinity of the spin-reorientation transition. This peak is of purely quantum origin and differs significantly from what is expected for classical spins, thus demonstrating a fundamental difference between classical and quantum fluctuations in spin systems.

Our results demonstrate that the magnitude of the susceptibility peak noticeably depends on whether we account for the internal structure of the cluster or use the single-spin description. This fact can be useful for elaboration of an adequate many-spin Hamiltonian for Mn$_{12}$. It is an important issue now, since recent experiments [7] show that the single-spin model, long used for description of the Mn$_{12}$ cluster, is deficient and a model accounting for the constituent many-spin nature of these clusters is necessary.

To clarify the matter, let us consider a single-spin model (see inset in Fig. 1). Choosing the $z$-axis as the easy axis of the system and the $x$-axis to coincide with the field direction, the Hamiltonian $\mathcal{H}$ of the system is

$$\mathcal{H} = -D S_z^2 - g \mu_B H_z S_z,$$

where $D$ is the easy-axis anisotropy constant, $g$ is the gyromagnetic ratio, $\mu_B$ — the Bohr magneton, $H_z$ is the field applied along the $x$-axis, $S_z$ and $S_x$ are the spin operators. Here and below, the following numerical procedure has been used. The Hamiltonian of the system under consideration has been diagonalized numerically and the expectation value of the $x$-projection of the spin $\langle S_x \rangle$ has been obtained by quantum-statistical averaging over the Gibbs canonical ensemble. The normalized susceptibility $\chi$ in the $x$-direction

$$\chi(H_z) = d\langle S_x \rangle/dH_x,$$

has been calculated by numerical differentiation. Since we are interested in quantum fluctuations only, we restrict ourselves to the low-temperature region.

If we treat the system [1] as a classical spin at zero temperature, the dependence $\chi(H_z)$ has a step-like form (see Fig. 1, dashed line). But if we account for quantum fluctuations, i.e. if we consider the quantum spin
described by the Hamiltonian $H$, the peak in the magnetic susceptibility appears. In Fig. 2 (solid line) we show the result for the case of the spin $S = 10$ with $g = 2$ and the anisotropy constant $D = 0.53 \text{ cm}^{-1}$ (or, equivalently, $D/k_B = 0.76 \text{ K}$); these parameters correspond to the single-spin model of Mn$_{12}$.

The essentially quantum nature of the effect can be demonstrated as follows. If $S_z$ commutes with the Hamiltonian, as for classical spins, the susceptibility $\chi$ would be governed by classically defined fluctuations of $S_z$: $\langle S_z S_z \rangle - \langle S_z \rangle^2$. Dependence of this quantity on $H_z$ (normalized by the value $S = 10$) is presented in Fig. 3 by the dotted line and shows a monotonic decrease with no peak. But for a quantum spin the quantity $S_z$ does not commute with the Hamiltonian, and the correct measure of fluctuations has to be formulated in terms of Kubo correlators: $\chi = \langle S_z S_z \rangle - \langle S_z \rangle^2$. Dependence of this quantity on $H_z$ is shown in Fig. 4 (solid line) and shows a monotonic decrease with no peak. But for a quantum spin the quantity $S_z$ does not commute with the Hamiltonian, and the correct measure of fluctuations has to be formulated in terms of Kubo correlators: $\chi = \langle S_z S_z \rangle - \langle S_z \rangle^2$. Dependence of this quantity on $H_z$ is shown in Fig. 4 (solid line) and shows a monotonic decrease with no peak.

Now, for a more realistic description of the effect in Mn$_{12}$Ac molecules, we have to go beyond the single-spin model. The core of such a molecule, the cluster Mn$_{12}$, schematically shown in Fig. 5, consists of 4 Mn$^{4+}$ ions with spins 3/2 and 8 Mn$^{3+}$ ions with spins 2. The ions are coupled by exchange interactions; the values of the exchange integrals are not known, but the estimates are given in Table 1: $J_1 = -150 \text{ cm}^{-1}$ (AFM exchange), $J_2 = J_3 = -60 \text{ cm}^{-1}$ and $|J_4| < 30 \text{ cm}^{-1}$. These values are rough, but describe correctly the scale of exchange interactions in Mn$_{12}$. In the ground state the system has a large total spin, $S = 10$. Recent experiments [11] show that the excitations with spin values other than $S = 10$ are rather close to the ground state: the distance is 40–60 K (exact values differ in different models), so an account of these excitations is necessary. The cluster possesses rather strong magnetic easy-axis anisotropy: the zero-field splitting between the levels $M = \pm 10$ and $M = \pm 9$ is 14.4 K.

The total number of spin states in Mn$_{12}$ is large even for modern computers, but we employ the fact that the exchange interactions $J_i$ are much larger than all the others, so corresponding pairs of Mn$^{3+}$ and Mn$^{4+}$ ions form dimers with total spin 1/2. This model has already been successfully used for a description of the spin states of the cluster. Its validity is supported by experiments [11]: the states of dimers with spin higher than 1/2 (excitations of dimers) come into play when the external magnetic field is about 400 T or when temperatures becomes as high as 200–250 K. This scale of energies is completely irrelevant to the effect we are interested in: we consider magnetic fields of order of 7–10 T and temperatures of order of 1–4 K.

Thus, we consider the Mn$_{12}$ cluster as consisting of four "small" dimer spins 1/2 and four "large" spins 2 (corresponding to the four non-dimerized Mn$^{3+}$ ions), coupled by exchange interactions. Moreover, we have to account for anisotropic relativistic interactions in the cluster, so the Hamiltonian of the system is:

$$H = -2J \sum_{\langle i,j \rangle} s_i s_j - J' \sum_{\langle k,l \rangle} s_k S_l + H_{\text{rel}},$$  \hspace{1cm} (3)$$

where $s_i$ are spin operators of small spins 1/2, $S_l$ are spin operators of large spins 2, and $H_{\text{rel}}$ denotes the relativistic Hamiltonian describing the magnetic anisotropy in the cluster. Summations in (3) are over pairs of spins coupled by exchange interactions. In zeroth order of perturbation theory, $J = -J_2$ and $J' = -J_3 + 2J_4$. This Hamiltonian is the basis of the subsequent analysis. Unfortunately, the exchange integrals of the Hamiltonian (3) and an exact form of the anisotropic term $H_{\text{rel}}$ are not known. Therefore, we examined the effect using very different sets of parameters. Below, we show typical cases, which give basic information about the dependence of the effect on the cluster parameters.

In Fig. 6 we show that the account of sufficiently large number of excited states is crucial for a correct description of the $\chi(H_x)$ dependence. If we include only the states belonging to the manifold $S = 10$, the height of the peak becomes considerably smaller. The more excited states we take into consideration, the more prominent the peak. Calculations with different sets of parameters give qualitatively the same results.

Positions of excited levels to a large extent are governed by isotropic exchange interactions, which are not exactly known. Therefore, we performed calculations with different values of exchange integrals, which yield the energies of excitations within the region 30–60 K (cf. above). Some results are shown in Fig. 7; similar results have been obtained for different sets of exchange parameters and different forms of the anisotropic term $H_{\text{rel}}$ (see below). Furthermore, different types of easy-axis anisotropy in Mn$_{12}$ clusters have been checked. Generally, the term $H_{\text{rel}}$ contains a single-site anisotropy of large spins (spins of Mn$^{3+}$ ions) and various kinds of anisotropic exchanges between different spins. We performed calculations for three basic types of the easy-axis anisotropy:

$$H_{\text{rel}}^1 = -K \sum_{i=1}^{4} (S^z_i)^2,$$  \hspace{1cm} (4a)$$

$$H_{\text{rel}}^2 = -J_{zz} \sum_{\langle i,j \rangle} s_i^z s_j^z,$$  \hspace{1cm} (4b)$$

$$H_{\text{rel}}^3 = -J_{zz} \sum_{\langle i,j \rangle} s_i^z S_j^z,$$  \hspace{1cm} (4c)$$
where summations in (4b) and (4c) are over exchange-coupled pairs of spins. Anisotropy parameters ($K$, $J_{zz}$, or $J_{ij}$) have been chosen to give a correct value of the zero-field splitting between the states $M = \pm 10$ and $M = \pm 9$ (14.4 K, see above). All three types of anisotropy give rather close energies of low-lying excitations, and, correspondingly, the curves $\chi(H_z)$ are very close (the difference does not exceed 6%).

Finally, we examined stability of the effect with respect to temperature variations and deviation of the external field direction. The results of our calculations for different temperatures are shown in Fig. 3. The peak shifts to lower field values and broadens. But, until temperature becomes as high as 5 K, the peak is in evidence. Also, as can be seen from Fig. 3, the direction of the external field should be close to the perpendicular to the easy axis. This restriction is not too stringent: the peak is visible until the deflection exceeds 2°. These conclusions has been confirmed by calculations with different cluster parameters.

Our calculations show that the effect is present in systems with very high value of the total spin $S$. E.g., for $S = 100$ the effect is in evidence at temperatures lower than 2–3 K, when the deflection of the field from the perpendicular to the easy axis is less than 0.2°. Thus, this effect could be effective for study of mesoscopic quantum phenomena in systems with very large $S$ (such as barium hexaferrite single particles [3]), where detection of resonant tunneling could be difficult.

Summarizing, we predict a new mesoscopic quantum effect. The spin system possessing easy-axis anisotropy, e.g. the magnetic molecule Mn$_{12}$Ac, subjected to an external magnetic field directed perpendicular to the easy axis, exhibits a peak of susceptibility in the vicinity of spin reorientation transition. It is large and stable enough to be studied experimentally at temperatures about 2–4 K. The external field magnitude should be 7–8 T, and possible deflection of the field direction from the perpendicular to the easy axis has to be not more than 1–2°. These conditions are quite accessible for contemporary experimental techniques.

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[1] D. J. Scalapino, Phys. Reports 250, 329 (1995).
[2] P. W. Shor, SIAM J. Comput. 26, 1484 (1997); N. Gershenson and I. L. Chuang, Science 275, 350 (1997).
[3] For a review, see Quantum Tunneling of Magnetization — QTM’94, ed. by L. Gunther and B. Barbara, (Kluwer, Dordrecht, 1995); P. C. E. Stamp, E. M. Chudnovsky and B. Barbara, Int. J. Mod. Phys. B 6, 1355 (1992).
[4] D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, Science 265, 1054 (1994).
[5] J. R. Friedman, M. P. Sarachik, J. Tejada and R. Ziolo, Phys. Rev. Lett. 76, 3830 (1996); L. Thomas et al., Nature 383, 145 (1996); F. Hartmann-Boutron, P. Politi and J. Villain, Int. J. Mod. Phys. 10, 2577 (1996).
[6] W. Wernsdorfer et al., Phys. Rev. Lett. 79, 4014 (1997).
[7] M. Hennion et al., Phys. Rev. B 56, 8819 (1997); A. M. Gomes et al., Phys. Rev. B 57, 5021 (1998).
[8] D. N. Zubarev, Nonequilibrium Statistical Thermodynamics (Consultants Bureau, New York, 1974).
[9] R. Sessoli et al., J. Am. Chem. Soc. 115, 1804 (1993).
[10] A. L. Barra, D. Gatteschi and R. Sessoli, Phys. Rev. B 56, 8192 (1997).
[11] A. K. Zvezdin and A. I. Popov, Sov. Phys. JETP 82, 1140 (1996).
[12] A. A. Mukhin et al. in Proceedings of ICM’97 Conference, Cairns, Australia, July 1997 (unpublished).
FIG. 5. Temperature dependence of the effect: (i) temperature $T = 2$ K (solid line); (ii) $T = 3$ K (dashed line); (iii) $T = 4$ K (dotted line). The easy-axis anisotropy is of single-site type, the form (4a). The cluster parameters are: $J' = 90$ K, $J = 0$, $K = 5.71$ K.

FIG. 6. Role of the deflection of the field from the normal to the easy axis: (i) no deflection (solid line); (ii) the deflection is $1^\circ$ (dashed line); (iii) the deflection is $2^\circ$ (dotted line). The easy-axis anisotropy is of single-site type, the form (4a). Cluster parameters are: $J' = 90$ K, $J = 0$, $K = 5.71$ K. Temperature $T = 2$ K.
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