Rotational states of a nanomagnet

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We study a nanomagnet that exhibits spin tunneling and is free to rotate about its anisotropy axis. Hamiltonian of a rotated two-state spin system is derived and exact low-energy eigenstates of the nanomagnet that are superpositions of spin and rotational states are obtained. We show that parameter $\alpha=2(\hbar S)^2/(I\Delta)$ determines the ground state of the magnet. Here $\hbar S$ is the spin, I is the moment of inertia, and Δ is the tunnel splitting. The ground-state magnetic moment is zero at $\alpha<\alpha_c=[1-1/(2S)^2]^{-1}$ and nonzero at $\alpha>\alpha_c$. At $\alpha\to\infty$ the spin of the nanomagnet localizes in one of the directions along the anisotropy axis.

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I. INTRODUCTION

This paper deals with quantum spin states of a nanomagnet that is free to rotate. Free magnetic clusters in beams have been studied in the past.[1–6] They exhibit a number of interesting phenomena some of which have been attributed to the interaction between spin and mechanical degrees of freedom. Same is true for nanomagnets confined within solid nanocavities.[7] General analytical solution for the rotational quantum levels of a rigid body does not exist.[8] Spin degree of freedom further complicates the problem. However, as we shall demonstrate below, the exact eigenstates and exact energy levels can be obtained analytically for a nanomagnet that, due to a large magnetic anisotropy, can be described as a two-state spin system and is free to rotate about its anisotropy axis.

Very small magnets exhibit quantum tunneling between spin-up and spin-down magnetic states.[9] The prospect of using them as qubits[10] has inspired recent experiments with molecular nanomagnets deposited on surfaces[11–14] and with single magnetic molecules bridged between metallic electrodes.[15–19] At first glance, partial or total decoupling of a nanomagnet from the environment appears desirable to achieve low decoherence. It was noticed,[20,21] however, that such a decoupling may prohibit spin tunneling altogether due to conservation of the total angular momentum, $\mathbf{J}=\mathbf{S}+\mathbf{L}$, with $\mathbf{S}$ being the total spin of the nanomagnet and $\mathbf{L}$ being its orbital angular momentum. The latter is due to both electrons and nuclei. In our treatment it is associated with the mechanical rotation of the nanomagnet. This situation can be relevant to all experiments with nanomagnets in which they maintain some degree of freedom with respect to rotations.

In this paper we demonstrate that the ground state of a nanomagnet that is free to rotate depends crucially on the parameter $\alpha=2(\hbar S)^2/(I\Delta)$. Here $\hbar S$ is the spin, I is the moment of inertia, and Δ is the tunnel splitting arising from quantum tunneling between spin-up and spin-down states. Qualitatively, this can be understood from the following argument. $\Delta/2$ is the energy gain due to quantum delocalization in the spin space. However, to conserve the total angular momentum $\mathbf{J}$ in a free nanomagnet, spin transitions between spin-up and spin-down states must be accompanied by rotations, with a rotational energy of order $(\hbar S)^2/I$. If α is large, rotations that are needed to conserve $\mathbf{J}$ require more energy than the energy gained due to spin tunneling. In other words, if the nanomagnet is very light, it cannot absorb the change in the angular momentum. In this case the spin cannot tunnel and localizes in one of the up/down states.

Note that rotational states of molecules have been studied from the inception of quantum mechanics[22,23] until present days.[24] These studies either require computation of spin-orbit constants or they choose a symmetry-based Hamiltonian with phenomenological constants that are later determined from experiment. The approach developed in this paper differs from the conventional physics of molecules in that we consider tunneling of a large spin and we treat nanomagnet as a mechanically rigid two-state spin system. Under this assumption the low-energy rotational spectra of the nanomagnet are expressed entirely in terms of the parameters S, Δ, and I. In that low-energy limit all unknown constants of spin-orbit interactions are absorbed into the tunnel splitting Δ. The latter, as well as S and I, can be independently measured, thus, providing a perfect playground for comparison between theory and experiment.

The structure of the paper is as follows. The origin of tunnel splitting for a large spin is reviewed in Sec. II. Spin-rotation coupling for a two-state spin system is introduced in Sec. III. The effect of the magnetic field is studied in Sec. IV. Section V contains conclusions and suggestions for experiment.

II. TUNNELING OF A LARGE SPIN

We begin with a nanomagnet of a fixed-length spin S, rigidly embedded in a solid. The general form of the spin Hamiltonian that corresponds to strong easy-axis magnetic anisotropy is

$$\hat{H}_S=\hat{H}_\parallel+\hat{H}_\perp, \tag{1}$$

where $\hat{H}_\parallel$ commutes with S_z and $\hat{H}_\perp$ is a perturbation that does not commute with S_z. Presence of the magnetic anisotropy axis means that the $|\pm S\rangle$ eigenstates of S_z are degenerate ground states of $\hat{H}_\parallel$. Operator $\hat{H}_\perp$ slightly perturbs the $|\pm S\rangle$ states, adding to them small contributions of other $|m_S\rangle$ states. We shall call these degenerate normalized perturbed

states $|\psi_{\pm S}\rangle$. Physically they describe the magnetic moment of the nanomagnet looking in one of the two directions along the anisotropy axis. Full perturbation theory with account of the degeneracy of $\hat{H}_S$ provides quantum tunneling between the $|\psi_{\pm S}\rangle$ states. The ground state and the first excited state are even and odd combinations of $|\psi_{\pm S}\rangle$, respectively,

$$\Psi_- = \frac{1}{\sqrt{2}}(|\psi_S\rangle + |\psi_{-S}\rangle),$$

$$\Psi_+ = \frac{1}{\sqrt{2}}(|\psi_S\rangle - |\psi_{-S}\rangle). \tag{2}$$

They satisfy

$$\hat{H}_S\Psi_\pm = E_\pm\Psi_\pm \tag{3}$$

with

$$E_+ - E_- \equiv \Delta \tag{4}$$

being the tunnel splitting. The latter is typically many orders of magnitude smaller than the distance to other spin energy levels, making the two-state approximation very accurate at low energies. For example,

$$\hat{H}_S = -DS_z^2 + dS_y^2 \tag{5}$$

with $d \ll D$, which is the case of Fe_8 molecular nanomagnet, one obtains[25] in the limit of large S

$$\Delta = \frac{8S^{3/2}}{\pi^{1/2}}\left(\frac{d}{4D}\right)^S D. \tag{6}$$

The distance to the next excited spin energy level is $(2S-1)D$, which is very large compared to Δ.

Since the low-energy spin states of the nanomagnet are superpositions of $|\psi_{\pm S}\rangle$, it is convenient to describe such a two-state system by a pseudospin 1/2. Components of the corresponding Pauli operator $\boldsymbol{\sigma}$ are

$$\sigma_x = |\psi_{-S}\rangle\langle\psi_S| + |\psi_S\rangle\langle\psi_{-S}|,$$

$$\sigma_y = i|\psi_{-S}\rangle\langle\psi_S| - i|\psi_S\rangle\langle\psi_{-S}|,$$

$$\sigma_z = |\psi_S\rangle\langle\psi_S| - |\psi_{-S}\rangle\langle\psi_{-S}|. \tag{7}$$

The projection of $\hat{H}_S$ onto $|\psi_{\pm S}\rangle$ states is

$$\hat{H}_\sigma = \sum_{m,n=\psi_{\pm S}} \langle m|\hat{H}_S|n\rangle|m\rangle\langle n|. \tag{8}$$

Expressing $|\psi_{\pm S}\rangle$ via $\Psi_\pm$ according to Eq. (2), it is easy to see from Eq. (3) that

$$\langle\psi_{\pm S}|\hat{H}_S|\psi_{\pm S}\rangle = 0, \quad \langle\psi_{-S}|\hat{H}_S|\psi_S\rangle = -\Delta/2. \tag{9}$$

With the help of these relations one obtains from Eq. (8)

$$\hat{H}_\sigma = -(\Delta/2)\sigma_x. \tag{10}$$

To conclude this section, we notice that our spin Hamiltonian $\hat{H}_S$ does not possess the full invariance with respect to rotations. Consequently, $\Psi_\pm$ should not be the eigenstates of $\mathbf{J}$. A closed system consisting of a spin embedded in a solid and the solid itself does possess the full rotational invariance. Through conservation of the total angular momentum (spin +crystal) the spin states become entangled with elastic twists.[26,27] The spin ground state, however, remains unchanged as long as the nanomagnet is rigidly coupled with the solid. This situation is going to change as we turn to a nanomagnet that is free to rotate.

III. SPIN-ROTATION COUPLING

So far we have not considered mechanical rotations of the nanomagnet. Rotation by angle ϕ about the anisotropy axis Z transforms the spin Hamiltonian into[27]

$$\hat{H}'_S = e^{-iS_z\phi}\hat{H}_S e^{iS_z\phi}. \tag{11}$$

Noticing that

$$S_z|\psi_{\pm S}\rangle \cong S_z|\pm S\rangle \cong \pm S|\psi_{\pm S}\rangle, \tag{12}$$

it is easy to project Hamiltonian (11) onto $\psi_{\pm S}$. Simple calculation yields the following generalization of Eq. (10):

$$\hat{H}'_\sigma = \sum_{m,n=\psi_{\pm S}} \langle m|\hat{H}'_S|n\rangle|m\rangle\langle n|$$

$$= -\frac{\Delta}{2}[e^{-2iS\phi}\sigma_+ + e^{2iS\phi}\sigma_-]$$

$$= -\frac{\Delta}{2}[\cos(2S\phi)\sigma_x + \sin(2S\phi)\sigma_y], \tag{13}$$

where $\sigma_\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y)$. The argument $2S\phi$ in the above expressions is nontrivial. It does not correspond to a simple rotation in a spin space but is related to the tunneling of a spin in which S_z changes by $2S$.

The full Hamiltonian of a nanomagnet rotating about its anisotropy axis is

$$\hat{H} = \frac{(\hbar L_z)^2}{2I} - \frac{\Delta}{2}[\sigma_x\cos(2S\phi) + \sigma_y\sin(2S\phi)] \tag{14}$$

with $L_z = -i(d/d\phi)$. Notice that for a freely rotating nanomagnet one can no longer separate the spin Hamiltonian from mechanical rotation, making the problem nonperturbative. We are now in a position to find the eigenstates of the rotating magnet. It is easy to check that Hamiltonian (14) commutes with $J_z = L_z + S_z$ and that their common eigenstates are

$$|\Psi_J\rangle = \frac{1}{\sqrt{2}}(C_S|\psi_S\rangle \otimes |J-S\rangle_l + C_{-S}|\psi_{-S}\rangle \otimes |J+S\rangle_l). \tag{15}$$

Here $J \equiv m_J$ while index l denotes states in the mechanical space, with

$$|m\rangle_l \equiv |m_L\rangle = \exp(im_L\phi). \tag{16}$$

Solution of $\hat{H}|\Psi_J\rangle = E_J|\Psi_J\rangle$ gives the following expression for the energy levels:

$$E_{J\pm} = \frac{\Delta}{2}\left[\left(1+\frac{J^2}{S^2}\right)\frac{\alpha}{2} \pm \sqrt{1+\frac{J^2}{S^2}\alpha^2}\right], \tag{17}$$

where

$$\alpha \equiv 2(\hbar S)^2/(I\Delta). \tag{18}$$

For $J \neq 0$ each state is degenerate with respect to the sign of J. For $J=0,1,2,\ldots$ coefficients $C_{\pm}$ are given by

$$C_S = \sqrt{1+\alpha J/\sqrt{S^2+(\alpha J)^2}},$$

$$C_{-S} = \mp\sqrt{1-\alpha J/\sqrt{S^2+(\alpha J)^2}}, \tag{19}$$

where $\mp$ correlates with $\pm$ in Eq. (17).

At $J \approx m_L \gg S$, Eq. (17) gives the energy of the mechanical rotation, $(\hbar m_L)^2/(2I)$. At small α the ground state and the first excited state correspond to $J=0$,

$$E_{0\pm} = \frac{\hbar^2 S^2}{2I} \pm \frac{\Delta}{2}. \tag{20}$$

Here the first term is the energy of the rotation with $m_L = \pm S$. For a nanomagnet rigidly coupled to an infinite mass one has $I \to \infty$ and the energy of the rotation goes to zero. In this case one recovers from Eq. (20) the energies, $\pm\Delta/2$, of the tunnel-split spin states in a macroscopic crystal. As α increases, the ground state switches to higher J. The value of α at which the ground state changes from E_{J-1} to E_J satisfies

$$E_{J-1,-}(\alpha_J) = E_{J,-}(\alpha_J). \tag{21}$$

Solution of this equation for $J=1,2,\ldots,S$ gives

$$\alpha_J = \left[1-\frac{1}{(2S)^2}\right]^{-1/2}\left[1-\frac{(2J-1)^2}{(2S)^2}\right]^{-1/2}. \tag{22}$$

For

$$\alpha < \alpha_1 = [1-1/(2S)^2]^{-1}, \tag{23}$$

the ground state corresponds to $J=0$ and $C_{\pm S}=1$. This is a critical value of α that separates zero and nonzero spin states of the nanomagnet. At $\alpha=\alpha_1$ the transition to the $J=1$ ground state takes place. At $\alpha=\alpha_2$ the ground state changes from $J=1$ to $J=2$ and so on. For any $\alpha > \alpha_S$, with α_S defined as α_J of Eq. (22) at $J=S$, the ground state always corresponds to $J=S$. For example, $S=10$ one obtains $\alpha_1=1.0025$ and $\alpha_{10}=3.2066$. In the limit of $S \to \infty$ one has $\alpha_J \to 1$ for $J \ll S$, and the crossover between zero and nonzero spin can be interpreted as a quantum phase transition. In this limit $\Delta \to 0$ [see Eq. (6)] so that the condition $\alpha=\alpha_1$ can be maintained only if $I \to \infty$. For Δ given by Eq. (6) the crossover value of the moment of inertia grows exponentially with S,

$$I_c = \frac{\pi^{1/2}[(2S)^2-1]}{16S^{3/2}}\left(\frac{4D}{d}\right)^S\frac{\hbar^2}{D}. \tag{24}$$

Our theory, however, is restricted to a monodomain mechanically rigid magnet and, therefore, it applies only to small sizes.

The dependence of the ground-state energy on α for $S=10$ is shown in Fig. 1. While this dependence is smooth, the derivative of the ground-state energy on α shows steps at the critical values of α given by Eq. (22). In the limit of $\alpha \to 0$ the ground-state energy is $-\Delta/2$. This is the gain in energy due to spin tunneling between $|\psi_{\pm S}\rangle$ states in an infinitely heavy particle. In the limit of $\alpha \gg 1$ (light particle) $J=S$ and according to Eq. (17) the ground-state energy approaches zero as $-\Delta/(4\alpha)$. This corresponds to the gradual localization of the spin in one of the $|\psi_{\pm S}\rangle$ states.

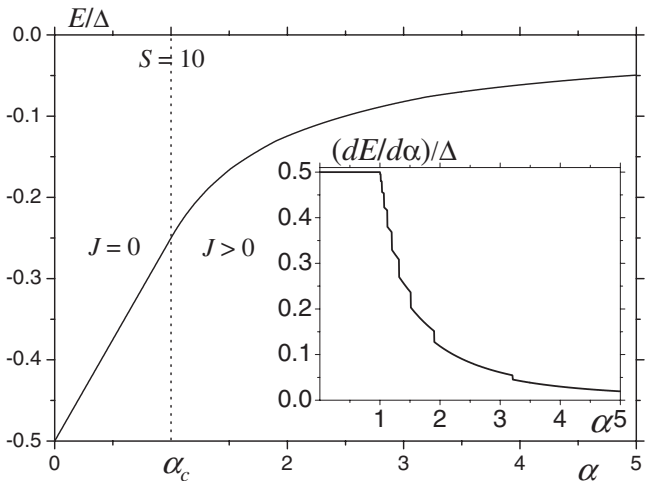

FIG. 1. Zero-field ground-state energy as a function of α. Inset shows the derivative of the ground-state energy on α.

To compute the magnetic moment we notice that L_z in our formalism describes the mechanical rotation of the nanomagnet as a whole, not the orbital states of the electrons. Consequently, the magnetic moment of a free magnet should be entirely due to its spin,

$$\mu = -g\mu_B\langle\Psi_J|S_z|\Psi_J\rangle = -g\mu_B S\frac{\alpha J}{\sqrt{S^2+(\alpha J)^2}}. \tag{25}$$

Here g is the spin gyromagnetic factor. The minus sign reflects negative gyromagnetic ratio, $\gamma=-g\mu_B/\hbar$, for the electron spin. If the ground state corresponds to $J=0$, spin-up and spin-down states contribute equally to the wave function and the magnetic moment is zero. When J in the ground state is nonzero, spin-up and spin-down states contribute with different weights and the nanomagnet has a nonzero magnetic moment. Which J corresponds to the ground state depends on the parameter α. The dependence of the ground-state magnetic moment on α is shown in Fig. 2.

IV. EFFECT OF THE MAGNETIC FIELD

The above results can be easily generalized to take into account the effect of the external magnetic field B applied along the Z axis. Such a field adds a Zeeman term, $g\mu_B S_z B$, to Hamiltonian (1). This term is invariant with respect to the rotation by the angle ϕ. Its projection onto $\psi_{\pm S}$ simply adds $g\mu_B SB\sigma_z$ to Eq. (14). The full projected Hamiltonian becomes

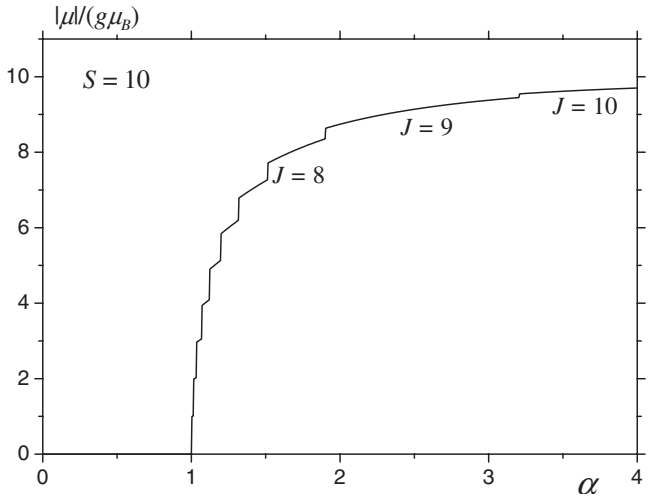

FIG. 2. Dependence of the ground-state magnetic moment on parameter α.

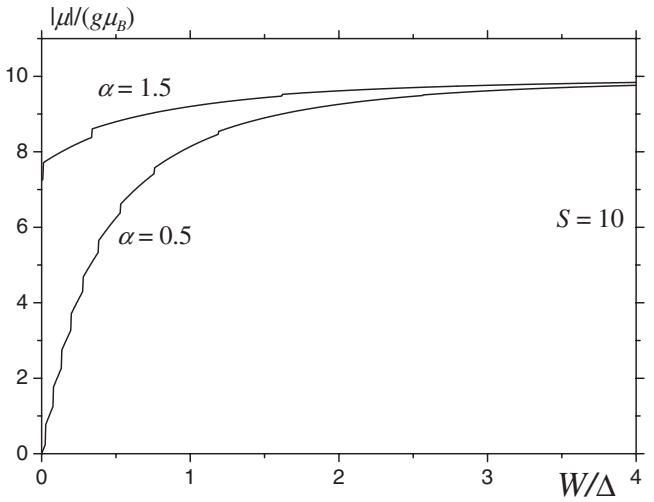

FIG. 3. Field dependence of the magnetic moment. Note the jumps at $W=W_J$.

$$\hat{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2} - \frac{\Delta}{2}[\sigma_x \cos(2S\phi) + \sigma_y \sin(2S\phi)] - \frac{W}{2}\sigma_z, \tag{26}$$

where

$$W \equiv -2g\mu_B SB. \tag{27}$$

Since this Hamiltonian is invariant with respect to rotations, its eigenfunctions are still given by Eq. (15) with the coefficients $C_{\pm S}$ now depending on B. Solving $\hat{H}|\Psi_J\rangle = E_J|\Psi_J\rangle$ one obtains

$$E_{J\pm} = \frac{\Delta}{2}\left[\left(1+\frac{J^2}{S^2}\right)\frac{\alpha}{2} \pm \sqrt{1+\left(\frac{W}{\Delta}+\frac{J}{S}\alpha\right)^2}\right] \tag{28}$$

for the energy levels. Here W can be positive or negative depending on the orientation of the field. Positive W corresponds to the magnetic field in the direction of the magnetic moment, which provides the lower energy. At $B \neq 0$ coefficients $C_{\pm S}$ can be presented in the form

$$C_S = \sqrt{1+\frac{\bar{W}}{\sqrt{\Delta^2+\bar{W}^2}}}, \quad C_{-S} = \mp\sqrt{1-\frac{\bar{W}}{\sqrt{\Delta^2+\bar{W}^2}}} \tag{29}$$

with

$$\bar{W} \equiv W + \alpha J\Delta/S. \tag{30}$$

Notice that Eq. (29) coincides with the form of $C_{\pm S}$ for a motionless nanomagnet in the magnetic field $\bar{B}=B-\hbar J/(\gamma I)$. The magnetic moment of the magnet that is free to rotate is given by

$$\mu = -g\mu_B S\bar{W}/\sqrt{\Delta^2+\bar{W}^2}. \tag{31}$$

In the absence of the magnetic field, quantum number J corresponding to the ground state is determined by α. For example, magnetic molecules this parameter is fixed. On the contrary, in the presence of the field, J can be manipulated by changing B. Solving Eq. (21) with $E_{J\pm}$ of Eq. (28), one obtains the following expression for $W=W_J$ at which the ground state switches from $J-1$ to J:

$$\frac{W_J}{\Delta} = \frac{2J-1}{2S}\left\{\sqrt{\left[1-\left(\frac{2J-1}{2S}\right)^2\right]^{-1}+\left(\frac{\alpha}{2S}\right)^2}-\alpha\right\}. \tag{32}$$

Here $J=1,2,\ldots,S$. The dependence of the ground-state magnetic moment on W is shown in Fig. 3. The jumps at critical values of the field must show as sharp maxima in the differential susceptibility.

V. CONCLUSIONS

We have obtained exact low-energy quantum states of a nanomagnet that exhibits spin tunneling and is free to rotate about its anisotropy axis. The ground state depends on the parameter $\alpha=2(\hbar S)^2/(I\Delta)$. At $\alpha<[1-1/(2S)^2]^{-1}$ the spin tunneling produces superposition of spin-up and spin-down states, resulting in a zero magnetic moment. At $\alpha>[1-1/(2S)^2]^{-1}$ the nanomagnet develops a finite magnetic moment. The spin localizes in one of the two directions along the magnetic anisotropy axis in the limit of $\alpha\to\infty$.

Various limits discussed above are physically accessible in magnetic molecules and atomic clusters. A high-spin molecule usually consists of hundreds of atoms, making its mechanical properties similar to the mechanical properties of a tiny solid body. Molecule of a nanometer size has the moment of inertia in the ballpark of 10^{-35} g cm^2. The energy of the rotation induced by a spin transition may be comparable to Δ but it is small compared to the energy of the excited states with $|m_S|<S$. For Mn_{12} and Fe_8 with $\hat{H}_{\|}\approx -DS_z^2$ these excited states are separated from the ground state by $(2S-1)D$, which is 13 K and 5 K for the above molecules, respectively. In the low-energy limit, the only relevant spin transitions coupled to rotations are tunneling transitions be-

tween $|S\rangle$ and $|-S\rangle$ in which the spin angular momentum changes by $2S$.

Our theory can apply to small clusters of ferromagnetic materials. In this case the parameter α can be controlled by the magnetic anisotropy and the size of the cluster. For Mn_{12} and Fe_8 molecules $\alpha \gg 1$. Thus, when free to rotate, the spin tunneling in these molecules must be strongly suppressed. Such a behavior would be very different from their behavior in a crystal. This effect may be important in designing qubits based on magnetic molecules. It can be studied experimentally same way as it has been done for beams of atomic clusters.

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