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Rotational States of Magnetic Molecules

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We study a magnetic molecule that exhibits spin tunneling and is free to rotate about its anisotropy axis. Exact low-energy eigenstates of the molecule 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 molecule. Here $\hbar S$ is the spin, I is the moment of inertia, and Δ is the tunnel splitting. The magnetic moment of the molecule is zero at $\alpha < \alpha_c = [1 - 1/(2S)^2]^{-1}$ and non-zero at $\alpha > \alpha_c$. At $\alpha \rightarrow \infty$ the spin of the molecule localizes in one of the directions along the anisotropy axis.

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Crystals of high-spin magnetic molecules came to the attention of physicists after Sessoli et al. [1] discovered that they behave as regular arrays of identical superparamagnetic particles [2]. The remarkable property of magnetic molecules is that their spin can tunnel between up and down directions [3]. This leads to a characteristic step-wise magnetization curve discovered by Friedman et al. in Mn₁₂-Acetate [4] and later observed in hundreds of other molecular magnets. More recently, experiments were performed with magnetic molecules deposited on surfaces [5] and with single molecules bridged between metallic electrodes [6]. The interest to such studies has been driven in part by the prospect of using magnetic molecules as qubits [7]. At first glance, partial or total decoupling of the molecule from the environment appears desirable to achieve low decoherence. It was noticed [8, 9], 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 spin of the molecule and \mathbf{L} being the orbital angular momentum associated with the mechanical rotation. This situation can be relevant to recent experiments with single magnetic molecules if the molecules maintain some degree of freedom with respect to rotations.

Consider first a high-spin molecule in a crystal. The general form of the spin Hamiltonian of the molecule is

$$\hat{H}_S = \hat{H}_{\parallel} + \hat{H}_{\perp}, \quad (1)$$

where \hat{H}_{\parallel} commutes with S_z and \hat{H}_{\perp} is a perturbation that does not commute with S_z . The existence 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 molecule 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

become

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

They satisfy

$$\hat{H}_S \Psi_{\pm} = E_{\pm} \Psi_{\pm} \quad (3)$$

with $E_- - E_+ \equiv \Delta$ being the tunnel splitting. Since the crystal field Hamiltonian \hat{H}_S does not possess the full invariance with respect to rotations, Ψ_{\pm} should not be the eigenstates of \mathbf{J} . However, a closed system consisting of the spin and the crystal does possess such invariance. It has been demonstrated [10, 11] that conservation of the total angular momentum (spin + crystal) dictates entanglement of spin states with elastic twists. This effect contributes to spin decoherence but does not significantly affect the ground state energy.

The situation changes for a free magnetic molecule. A high-spin molecule usually consists of hundreds of atoms, making its mechanical properties similar to the mechanical properties of a tiny solid body. Free magnetic clusters in beams have been studied in the past [12]. They exhibit a number of interesting phenomena some of which have been attributed to the interaction between spin and mechanical degrees of freedom. General analytical solution for the rotational quantum levels of a rigid body does not exist. Spin degree of freedom further complicates the problem. However, as we demonstrate below, the exact eigenstates and exact energy levels can be obtained analytically for the low-energy states of a magnetic molecule that is free to rotate about its anisotropy axis. This could be the case when a free molecule is in a magnetic field or the molecule is bridged between two leads. The eigenstates of such a molecule must be the eigenstates of $J_z = S_z + L_z$. It is then clear that, unless mechanical rotations are involved, conservation of J_z prohibits quantum tunneling of \mathbf{S} . For, e.g., $J_z = 0$ the transitions can only occur between the states $|\psi_S\rangle \otimes |m_L = -S\rangle$ and $|\psi_{-S}\rangle \otimes |m_L = S\rangle$. These are the states in which the angular momentum due to spin is compensated by the angular momentum due to mechanical rotation. For

a superposition of these states to be the ground state of the system, the kinetic energy, $(\hbar S)^2/(2I)$, associated with the rotation cannot significantly exceed the energy gain, $\Delta/2$, due to spin tunneling. Otherwise the ground state will be $|\psi_{\pm S}\rangle \otimes |m_L = 0\rangle$. For a solid particle, the moment of inertia I grows as the fifth power of the size of the particle. Consequently, rotational effects should be less important in large particles. For magnetic molecules, however, the rotational energy $(\hbar S)^2/(2I)$ in many cases will be large enough to cause localization in one of the $|\psi_{\pm S}\rangle$ spin states. Exact analytical solution of this problem is given below.

Since the low-energy spin states of the molecule 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 σ are

$$\begin{aligned}\sigma_x &= |\psi_{-S}\rangle\langle\psi_S| + |\psi_S\rangle\langle\psi_{-S}| \\ \sigma_y &= i|\psi_{-S}\rangle\langle\psi_S| - i|\psi_S\rangle\langle\psi_{-S}| \\ \sigma_z &= |\psi_S\rangle\langle\psi_S| - |-\psi_S\rangle\langle\psi_{-S}|.\end{aligned}\quad (4)$$

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

$$\hat{H}_\sigma = \sum_{m,n=\psi_{\pm S}} \langle m|\hat{H}_S|n\rangle|m\rangle\langle n|. \quad (5)$$

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

$$\langle\psi_{\pm S}|\hat{H}_S|\psi_{\pm S}\rangle = 0, \quad \langle\psi_{-S}|\hat{H}_S|\psi_S\rangle = -\Delta/2. \quad (6)$$

With the help of these relations one obtains from Eq. (5)

$$\hat{H}_\sigma = -\frac{\Delta}{2}\sigma_x. \quad (7)$$

So far we have not considered mechanical rotations of the molecule. Rotation by angle ϕ about the anisotropy axis Z , transforms the spin Hamiltonian into

$$\hat{H}'_S = e^{-iS_z\phi}\hat{H}_S e^{iS_z\phi}. \quad (8)$$

Noticing that

$$S_z|\psi_{\pm S}\rangle \cong S_z|\pm S\rangle = \pm S|\psi_{\pm S}\rangle, \quad (9)$$

it is easy to project Hamiltonian (8) onto $\psi_{\pm S}$. Simple calculation yields the following generalization of Eq. (7):

$$\begin{aligned}\hat{H}'_\sigma &= \sum_{m,n=\psi_{\pm S}} \langle m|\hat{H}'_S|n\rangle|m\rangle\langle n| \\ &= -\frac{\Delta}{2} [\cos(2S\phi)\sigma_x + \sin(2S\phi)\sigma_y].\end{aligned}\quad (10)$$

The full Hamiltonian of the magnetic molecule rotating about its anisotropy axis is

$$\hat{H} = \frac{(\hbar L_z)^2}{2I} - \frac{\Delta}{2} [\sigma_x \cos(2S\phi) + \sigma_y \sin(2S\phi)], \quad (11)$$

with $L_z = -i(d/d\phi)$.

We are now in a position to find the eigenstates of the rotating molecule. By construction, the Hamiltonian (11) is invariant with respect to rotations about the Z -axis. Consequently, its eigenstates must be the eigenstates of $J_z = L_z + S_z$:

$$\Psi_J = \frac{1}{\sqrt{2}} (C_S|\psi_S\rangle \otimes |J-S\rangle_l + C_{-S}|\psi_{-S}\rangle \otimes |J+S\rangle_l). \quad (12)$$

Here $J \equiv m_J$ while index l denotes states in the mechanical space, with $|m\rangle_l \equiv |m_L\rangle = \exp(im_L\phi)$. Solution of $\hat{H}\Psi_J = E_J\Psi_J$ gives the following expression for the energy levels:

$$E_{J\pm} = \frac{\Delta}{2} \left[\left(1 + \frac{J^2}{S^2}\right) \frac{\alpha}{2} \pm \sqrt{1 + \frac{J^2}{S^2} \alpha^2} \right], \quad (13)$$

where

$$\alpha \equiv \frac{2(\hbar S)^2}{I\Delta}. \quad (14)$$

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

$$\begin{aligned}C_S &= \sqrt{1 + \frac{\alpha J}{\sqrt{S^2 + (\alpha J)^2}}} \\ C_{-S} &= \mp \sqrt{1 - \frac{\alpha J}{\sqrt{S^2 + (\alpha J)^2}}},\end{aligned}\quad (15)$$

where \mp correlates with \pm in Eq. (13).

At $J \approx m_L \gg S$, Eq. (13) 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 $J = 0$,

$$E_{0\pm} = \frac{\hbar^2 S^2}{2I} \pm \frac{\Delta}{2}. \quad (16)$$

Here the first term is the energy of the rotation with $m_L = \pm S$. For a molecule rigidly coupled to an infinite mass one has $I \rightarrow \infty$ and the energy of the rotation goes to zero. In this case one recovers from Eq. (16) 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

$$E_{J-1,-(\alpha J)} = E_{J,-(\alpha J)}. \quad (17)$$

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

$$\alpha_J = \left[1 - \frac{1}{(2S)^2}\right]^{-1/2} \left[1 - \frac{(2J-1)^2}{(2S)^2}\right]^{-1/2}. \quad (18)$$

For α smaller then

$$\alpha_1 = [1 - 1/(2S)^2]^{-1} \quad (19)$$

the ground state corresponds to $J = 0$, $C_{\pm S} = 1$. 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. At α greater than

$$\alpha_S = \left[1 - \frac{1}{(2S)^2} \right]^{-1/2} \left[1 - \left(1 - \frac{1}{2S} \right)^2 \right]^{-1/2} \quad (20)$$

the ground state always corresponds to $J = S$. For, e.g., $S = 10$ one obtains $\alpha_1 = 1.0025$ and $\alpha_{10} = 3.2066$. 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. (18). In the limit of $\alpha \rightarrow 0$ 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. (13) 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.

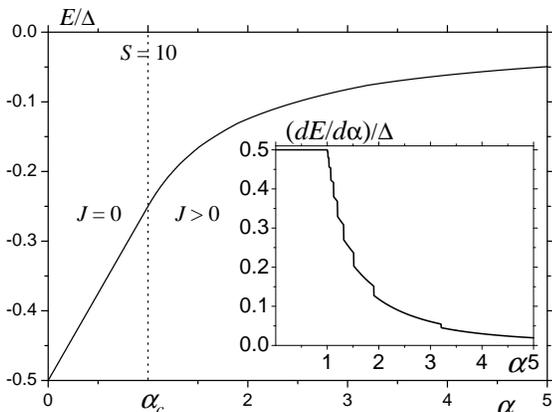


FIG. 1: Zero-field ground state energy as a function of α . Inset shows the derivative of the ground state energy on α .

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

$$\mu = -g\mu_B \langle \Psi_J | S_z | \Psi_J \rangle = -g\mu_B S \frac{\alpha J}{\sqrt{S^2 + (\alpha J)^2}}. \quad (21)$$

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 non-zero, spin-up and spin-down

states contribute with different weights and the molecule has a non-zero 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.

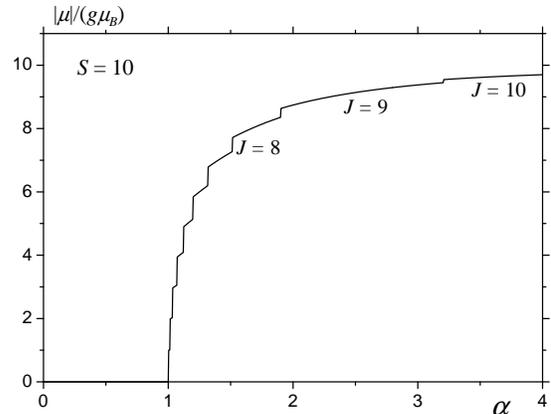


FIG. 2: Dependence of the ground-state magnetic moment on parameter α .

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 the Hamiltonian (1). This term is invariant with respect to the rotation by the angle ϕ . Its projection onto $\psi_{\pm S}$ simply adds $g\mu_B S B \sigma_z$ to Eq. (11). The full projected Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2I} \frac{d^2}{d\phi^2} - \frac{\Delta}{2} [\sigma_x \cos(2S\phi) + \sigma_y \sin(2S\phi)] - \frac{W}{2} \sigma_z, \quad (22)$$

where

$$W \equiv -2g\mu_B S B. \quad (23)$$

Since this Hamiltonian is invariant with respect to rotations about the Z -axis, its eigenfunctions are still given by Eq. (12) with the coefficients $C_{\pm S}$ now depending on B . Solving $\hat{H}\Psi_J = E_J\Psi_J$ one obtains

$$E_{J\pm} = \frac{\Delta}{2} \left[\left(1 + \frac{J^2}{S^2} \right) \frac{\alpha}{2} \pm \sqrt{1 + \left(\frac{W}{\Delta} + \frac{J}{S} \alpha \right)^2} \right] \quad (24)$$

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

$$C_S = \sqrt{1 + \frac{\bar{W}}{\sqrt{\Delta^2 + W^2}}}, \quad C_{-S} = \mp \sqrt{1 - \frac{\bar{W}}{\sqrt{\Delta^2 + W^2}}}, \quad (25)$$

with

$$\bar{W} \equiv W + \alpha J \Delta / S. \quad (26)$$

Notice that Eq. (25) coincides with the form of $C_{\pm S}$ for a frozen magnetic molecule in the magnetic field $\bar{B} = B - \hbar J / (\gamma I)$. The magnetic moment of the molecule that is free to rotate is given by

$$\mu = -g\mu_B S \frac{\bar{W}}{\sqrt{\Delta^2 + \bar{W}^2}}. \quad (27)$$

In the absence of the magnetic field, quantum number J corresponding to the ground state is determined by α . For a given magnetic molecule this parameter is fixed. On the contrary, in the presence of the field, J can be manipulated by changing B . Solving Eq. (17) with $E_{J\pm}$ of Eq (24), one obtains the following expression for $W = W_J$ at which the ground state switches from $J - 1$ to J :

$$\frac{W_J}{\Delta} = \frac{2J-1}{2S} \left\{ \sqrt{\left[1 - \left(\frac{2J-1}{2S} \right)^2 \right]^{-1} + \left(\frac{\alpha}{2S} \right)^2} - \alpha \right\}. \quad (28)$$

Here $J = 1, 2, \dots, S$. The dependence of the ground state magnetic moment on W is shown in Fig. 3. The jumps

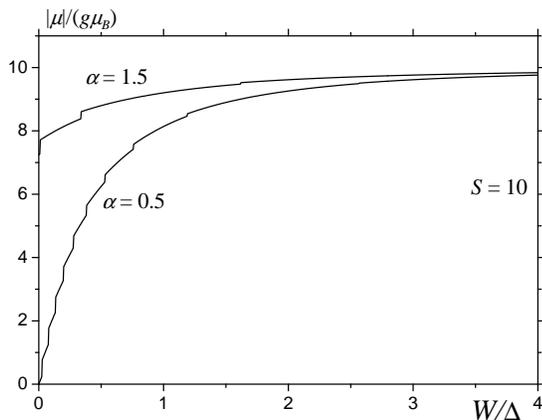


FIG. 3: Field dependence of the magnetic moment. Note the jumps at $W = W_J$.

at critical values of the field must show as sharp maxima in the differential susceptibility.

In conclusion, we have obtained exact low-energy quantum states of a magnetic particle (molecule) that exhibits spin tunneling and is free to rotate about its anisotropy axis. The ground state depends on the parameter $\alpha = 2(\hbar S)^2 / (I \Delta)$. Various limits studied above are physically accessible in magnetic molecules and atomic clusters. At $\alpha \rightarrow \infty$ the spin localizes in one of the two directions along the magnetic anisotropy axis. Magnetic molecule of a nanometer size has the moment of inertia

in the ballpark of 10^{-35} g cm². For $S = 10$ this provides $\alpha \sim 1$ at $\Delta/\hbar \sim 10^{10}$ s⁻¹. The tunnel splitting of, e.g., Mn₁₂ and Fe₈ molecules is much smaller. Thus the spin tunneling in these molecules must be strongly suppressed if they are free to rotate. This effect may be important in designing qubits based upon magnetic molecules.

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