Quantum Tunneling of the Magnetic Moment in a Free Particle

M. F. O’Keeffe, E. M. Chudnovsky, and D. A. Garanin
Physics Department, Lehman College, City University of New York,
250 Bedford Park Boulevard West, Bronx, New York, 10468-1589, USA
(Dated: April 28, 2013)

We study tunneling of the magnetic moment in a particle that has full rotational freedom. Exact energy levels are obtained and the ground-state magnetic moment is computed for a symmetric rotor. The effect of the mechanical freedom on spin tunneling manifests itself in a strong dependence of the magnetic moment on the moments of inertia of the rotor. Energy of the particle exhibits quantum phase transitions between states with different values of the magnetic moment. Particles of various shapes are investigated and quantum phase diagram is obtained.

PACS numbers: 75.45.+j, 36.40.Cg, 75.50.Tt, 85.25.Dq

I. INTRODUCTION

There has been much recent interest in quantum mechanics of nanoscopic magnets that possess mechanical freedom. Experimental work in this area focused on free magnetic clusters, magnetic particles that are free to move inside solid nanocavities, magnetic microresonators, and magnetic molecules bridged between conducting leads. Theoretical research on free magnetic particles has been scarce. The generic problem is that of a rigid quantum rotor with a spin. Without a spin this problem is tractable by analytical methods only for a symmetric rotor. Complications resulting from spin degrees of freedom make even symmetric cases significantly more difficult.

First attempt to understand how mechanical freedom of a small magnetic particle affects tunneling of the magnetic moment was made in Ref. where it was noticed that tunneling of a macrospin in a free particle must be entangled with mechanical rotations in order to conserve the total angular momentum (spin + orbital). Similar situation occurs for tunneling of a superconducting current between clockwise and counterclockwise directions in a SQUID. Recently, it was demonstrated that the problem of a rigid rotor with a spin can be solved exactly in the laboratory frame when mechanical rotation is allowed only about a fixed axis and the spin states are reduced to spin-up and spin-down due to strong magnetic anisotropy. The latter is typical for magnetic molecules and small ferromagnetic clusters. The reduction to two spin states in a system rotating about a fixed axis also allows one to obtain simple solution of the problems of a magnetic molecule embedded in a microcantilever, magnetic molecule vibrating between conducting leads, and of a macrospin tunneling inside a torsional resonator. However, the problem for arbitrary rotations of a two-state spin system, which is relevant to free magnetic nanoparticles, remained unsolved until now.

In this paper we show that the problem of a two-state macrospin inside a symmetric rigid rotor has rigorous solution for arbitrary rotations in the coordinate frame that is rigidly coupled to the rotor. Magnetic moment of the electrically neutral rotor is entirely due to spin. It depends on the relative contribution of the up and down spin states. When a nanoparticle is embedded in a solid, tunneling of the spin results in a zero ground-state magnetic moment. This situation changes for a free particle due to a complex interplay between spin and mechanical angular momentum that conserves the total angular momentum. We show that the energy of the particle exhibits first- or second-order quantum phase transitions between states with different values of the total angular momentum when the latter is treated as a continuous variable. The order of the transition depends on the shape of the particle. The ground-state magnetic moment of a free particle with a total spin $S$ can be anything between zero and $g\mu_B S$, depending on the principal moments of inertia (with $\mu_B$ being the Bohr magneton and $g$ being the gyromagnetic factor associated with the spin).

The structure of the article is as follows. Quantum theory of a rigid rotator is briefly reviewed in Sec. Theory of a tunneling macrospin is reviewed in Sec. Quantum states of a rigid rotator containing a tunneling macrospin are constructed in Sec. Ground state of a symmetric rotor with a spin is analyzed in Sec. Ground-state magnetic moment is studied in Sec. Our conclusions are presented in Section.

II. QUANTIZATION OF RIGID BODY ROTATIONS

Consider first the problem without a spin. We choose the coordinate frame that is rigidly coupled with the rotating body and direct the axes of that frame $x, y,$ and $z$ along the principal axes of the tensor of moments of inertia of the body. In such coordinate frame the Hamiltonian of mechanical rotations is given by.

$$\hat{H}_R = \frac{\hbar^2}{2} \left( \frac{L_x^2}{I_x} + \frac{L_y^2}{I_y} + \frac{L_z^2}{I_z} \right). \quad (1)$$

Here $I_x, I_y, I_z$ are the principal moments of inertia and $L_x, L_y, L_z$ are projections of the operator of the mechanical angular momentum, defined in the fixed laboratory frame.
coordinate frame, onto the body axes \( x, y, z \). Such a choice of coordinates and operators results in the anomalous commutation relations\(^2\), \( [I_k, L_j] = -i\epsilon_{ijk}L_k \) (notice the minus sign in the right-hand side), but does not affect the relations \( \textbf{L}^2 = L(L+1), \) \( [\textbf{L}^2, L_\pm] = 0 \).

For a symmetric rotor two of the moments of inertia are the same, \( I_x = I_y \), and the Hamiltonian can be written as

\[
\hat{H}_R = \frac{\hbar^2}{2I_x} L_x^2 + \frac{\hbar^2L_y^2}{2} \left( \frac{1}{I_z} - \frac{1}{I_x} \right).
\]

The corresponding eigenstates are characterized by three quantum numbers \( L, K, \) and \( M \),

\[
L_x|L, K\rangle = L(L + 1)|L, K\rangle, \quad L = 0, 1, 2, \ldots
\]

\[
L_y|L, K\rangle = K|L, K\rangle, \quad K = -L, -L + 1, \ldots, -1, L
\]

\[
L_z|L, K\rangle = M|L, K\rangle, \quad M = -L, -L + 1, \ldots, L - 1, L,
\]

where \( L_z \) is the angular momentum operator defined with respect to the laboratory coordinate frame \( (X, Y, Z) \). The eigenvalues of \( (2) \) are degenerate on \( M \):

\[
E_{L,K} = \frac{\hbar^2 L(L+1)}{2I_x} + \frac{\hbar^2 K^2}{2} \left( \frac{1}{I_z} - \frac{1}{I_x} \right).
\]

The general form for the energy levels of a rotating asymmetric rigid body, \( I_x \neq I_y \neq I_z \), does not exist, although it is possible to calculate matrix elements of the Hamiltonian for a given \( L \).

### III. Tunneling of a Large Spin

Let \( \textbf{S} \) be a fixed-length spin embedded in a stationary body. Naturally, the magnetic anisotropy is defined with respect to the body axes. The general form of the crystal field Hamiltonian is

\[
\hat{H}_S = \hat{H}_\parallel + \hat{H}_\perp,
\]

where \( \hat{H}_\parallel \) commutes with \( S_z \) and \( \hat{H}_\perp \) is a perturbation that does not commute with \( S_z \). The states \( |\pm S\rangle \) are degenerate ground states of \( \hat{H}_\parallel \), where \( S \) is the total spin of the nanomagnet. \( \hat{H}_\perp \) slightly perturbs these states, adding to them small contributions from other \( |m_S\rangle \) states. We will call these degenerate perturbed states \( |\pm S\rangle \). Physically they describe the magnetic moment aligned 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 \( |\pm S\rangle \) states for integer \( S \). The ground state and first excited state are symmetric and antisymmetric combinations of \( |\pm S\rangle \), respectively,

\[
\Psi_+ = \frac{1}{\sqrt{2}}(|\psi_+\rangle + |\psi_-\rangle)
\]

\[
\Psi_- = \frac{1}{\sqrt{2}}(|\psi_+\rangle - |\psi_-\rangle),
\]

which satisfy

\[
\hat{H}_S \Psi_\pm = E_\mp \Psi_\pm,
\]

where

\[
E_+ - E_- = \Delta.
\]

The tunnel splitting \( \Delta \) is generally many orders of magnitude smaller than the distance to other spin energy levels, which makes the two-state approximation very accurate at low energies. For example,

\[
\hat{H}_S = -DS_y^2 + dS_y^2
\]

with \( d \ll D \) describes the biaxial anisotropy of spin-10 molecular nanomagnet Fe-8, where the tunnel splitting in the limit of large \( S \) is given by

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

The distance to the next excited spin level is \( (2S - 1)D \), which is large compared to \( \Delta \).

It is convenient to describe these lowest energy spin states \( \Psi_\pm \) with a pseudospin-1/2. Components of the corresponding Pauli operator \( \sigma \) are

\[
\sigma_x = |\psi_+\rangle\langle\psi_+| + |\psi_-\rangle\langle\psi_-|
\]

\[
\sigma_y = i|\psi_+\rangle\langle\psi_-| - i|\psi_-\rangle\langle\psi_+|
\]

\[
\sigma_z = |\psi_+\rangle\langle\psi_+| - |\psi_-\rangle\langle\psi_-|.
\]

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

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

Expressing \( |\psi_\pm S\rangle \) in terms of \( \Psi_\pm \) one obtains

\[
\langle \psi_\pm S | \hat{H}_S | \psi_\pm S \rangle = 0,
\]

\[
\langle \psi_\pm S | \hat{H}_S | \psi_\mp S \rangle = -\frac{\Delta}{2},
\]

which gives the two-state Hamiltonian

\[
\hat{H}_\sigma = -\frac{\Delta}{2} \sigma_x
\]

having eigenvalues \( \pm \Delta/2 \).

In the absence of tunneling a classical magnetic moment is localized in the up or down state. It is clear that delocalization of the magnetic moment due to spin tunneling reduces the energy by \( \Delta/2 \). In a free particle, however, tunneling of the spin must be accompanied by mechanical rotations in order to conserve the total angular momentum. Such rotations cost energy, so it is not a priori clear whether the tunneling will survive in a free particle and what the ground state is going to be. This problem is addressed in the following Section.
IV. RIGID ROTOR CONTAINING TUNNELING MACROSPIN

Consider now a tunneling macrospin embedded in a free particle having the body z-axis as the magnetic anisotropy direction. Such a particle is characterized by the total angular momentum, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. In the body frame this operator may appear unconventional due to the different sign of commutation relations for $\mathbf{L}$ and $\mathbf{S}$. However, this problem can be easily fixed by the transformation $\mathbf{S} \rightarrow -\mathbf{S}$ that changes the sign of the commutation relation for $\mathbf{S}$. Such a transformation does not change the results of the previous Section because the crystal field Hamiltonian contains only even powers of $\mathbf{S}$. It is interesting to notice that while in the laboratory frame $[J_z, S_j] = i\epsilon_{ijk} S_k$, components of the operators $\mathbf{J}$ and $\mathbf{S}$ defined in the body frame commute with each other. In addition, operator $J^2$ is the same in the body and laboratory frames. This permits description of quantum states of the particle in terms of quantum numbers associated independently with the total angular momentum and spin.

The full Hamiltonian is given by the sum of the rotational energy and magnetic anisotropy energy

$$\hat{H} = \frac{\hbar^2 L_z^2}{2I_z} + \frac{\hbar^2 L_y^2}{2I_y} + \frac{\hbar^2 L_z^2}{2I_z} + \hat{H}_S. \quad (15)$$

Expressing the mechanical angular momentum $\mathbf{L}$ in terms of the total angular momentum $\mathbf{J}$ and the spin $\mathbf{S}$, we get

$$\hat{H} = \frac{\hbar^2}{2} \left( \frac{J_z^2}{I_z} + \frac{J_y^2}{I_y} + \frac{J_z^2}{I_z} \right) + \frac{\hbar^2}{2} \left( \frac{S_x^2}{I_x} + \frac{S_y^2}{I_y} + \frac{S_z^2}{I_z} \right) - \hbar^2 \left( \frac{J_z S_x}{I_z} + \frac{J_y S_y}{I_y} + \frac{J_z S_z}{I_z} \right) + \hat{H}_S. \quad (16)$$

For a symmetric rigid rotor with $I_x = I_y$ this Hamiltonian reduces to

$$\hat{H} = \frac{\hbar^2 J_z^2}{2I_z} + \frac{\hbar^2 J_z^2}{2I_z} \left( \frac{1}{I_z} - \frac{1}{I_z} \right) - \hbar^2 \left( \frac{J_z S_x}{I_z} + \frac{J_y S_y}{I_z} + \frac{J_z S_z}{I_z} \right) + \hat{H}_S', \quad (17)$$

where

$$\hat{H}_S' = \hat{H}_S + \frac{\hbar^2}{2} \left( \frac{1}{I_z} - \frac{1}{I_z} \right) S_z^2 + \frac{\hbar^2 S_z^2}{2I_z}. \quad (18)$$

The last term in $\hat{H}_S'$ is an unessential constant, $\hbar^2 S(S + 1)/(2I_z)^2$. The second term provides renormalization of the crystal field in a freely rotating particle. For, e.g., the biaxial spin Hamiltonian given by Eq. (9) it leads to

$$D \rightarrow D - \frac{\hbar^2}{2} \left( \frac{1}{I_z} - \frac{1}{I_z} \right). \quad (19)$$

This, in turn, renormalizes the tunnel splitting given by Eq. (10). For a particle that is allowed to rotate about the Z-axis only (that is, in the limit of $I_z \rightarrow \infty$) these results coincide with the results obtained by the instanton method in Ref. 26 where it was shown that, in practice, the renormalization of the magnetic anisotropy and spin tunnel splitting by mechanical rotations is small. Eq. (10) provides generalization of this effect for arbitrary rotations of a symmetric rotor with a spin. According to this equation and Eq. (9), when rotations are allowed the effective easy-axis magnetic anisotropy and the tunnel splitting can decrease or increase, depending on the ratio $I_z/I_z$.

Projection of Eq. (17) on the two spin states along the lines of the previous Section gives

$$\hat{H} = \frac{\hbar^2 J_z^2}{2I_z} + \frac{\hbar^2 J_z^2}{2I_z} \left( \frac{1}{I_z} - \frac{1}{I_z} \right) - \frac{\Delta}{2} + \frac{\hbar^2 S}{I_z} J_z \sigma_z. \quad (20)$$

where we have used

$$\langle \psi \pm | S_z | \psi \pm \rangle = \pm S, \quad \langle \psi \pm | S_{xy} | \psi \pm \rangle = 0. \quad (21)$$

We construct eigenstates of this Hamiltonian according to

$$| \Psi_{JK} \rangle = \frac{1}{\sqrt{2}} (| C_+ S \psi \rangle + C_- S | \psi \rangle ) | JK \rangle \quad (22)$$

where

$$J^2 | JK \rangle = J(J + 1) | JK \rangle, \quad J = 0, 1, 2, \ldots$$

$$J_z | JK \rangle = K | JK \rangle, \quad K = -J, \ldots, J. \quad (23)$$

Solution of $\hat{H} | \Psi_{JK} \rangle = E | \Psi_{JK} \rangle$ gives energy levels as

$$E_{JK}^{(\pm)} = E_{JK} \pm \sqrt{\frac{\Delta}{2}^2 + \left( \frac{\hbar^2 KS}{I_z} \right)^2}, \quad (24)$$

where $E_{JK}$ is provided by Eq. (14) with $L$ replaced by $J$. The upper (lower) sign in Eq. (24) corresponds to the lower (upper) sign in Eq. (22). For $K \neq 0$ each state is degenerate with respect to the sign of $K$. For $K = 0, 1, 2, \ldots$ the coefficients in Eq. (22) are given by

$$C_{\pm} = \sqrt{1 \pm \alpha K/\sqrt{S^2 + \langle K \rangle^2}}, \quad (25)$$

where $\alpha$ is a dimensionless magneto-mechanical ratio,

$$\alpha = \frac{2(\hbar S)^2}{I_z \Delta}. \quad (26)$$

Energy levels in Eq. (24) can be given a simple semiclassical interpretation. Indeed, the last term in this equation is the tunnel splitting of the levels in the effective magnetic field that appears in the body reference frame due to rotation about the spin quantization axis at the angular velocity $\hbar K/I_z$. When $S = 0$ (which also means $\Delta = 0$) Eq. (24) with $J = L$ gives the energy of the quantum symmetric rigid rotor without a spin, Eq. (1). In the case of a heavy body (large moments of inertia) the ground state and the first excited state correspond to
$J = K = 0$, and we recover the tunnel-split spin states in a non-rotating macroscopic body, $E_{00 \pm} = \pm \Delta / 2$. In the general case, spin states of the rotator are entangled with mechanical rotations.

Equations (22)−(25) are our main analytical results for the low-energy states of a free magnetic particle. In general, numerical analysis is needed to find the ground state of the particle. Special cases of the aspect ratio that will be analyzed below include a needle of vanishing diameter (which is equivalent to the problem of the rotation about a fixed axis treated previously in the laboratory frame by two of the authors [15]), a finite-diameter needle, a sphere, and a disk.

V. GROUND STATE

Minimization of the energy in Eq. (24) on $J$ with the account of the fact that $J$ cannot be smaller than $K$ immediately yields $J = K$, that is, the ground state always corresponds to the maximal projection of the total angular momentum onto the spin quantization axis. In semiclassical terms this means that the minimal energy states in the presence of spin tunneling always correspond to mechanical rotations about the magnetic anisotropy axis. This is easy to understand by noticing that the sole reason for mechanical rotation is the necessity to conserve the total angular momentum while allowing spin tunneling to lower the energy. To accomplish this the particle needs to oscillate between clockwise and counterclockwise rotations about the spin quantization axis in unison with the tunneling spin. If such mechanical oscillation costs more energy than the energy gain from spin tunneling, then both spin tunneling and mechanical motion need to oscillate between clockwise and counterclockwise rotations about the spin quantization axis in unison. This is easy to understand by noticing that the sole reason for mechanical rotation is the necessity to conserve the total angular momentum while allowing spin tunneling to lower the energy. To accomplish this the particle needs to oscillate between clockwise and counterclockwise rotations about the spin quantization axis in unison.

For further analysis it is convenient to write Eq. (24) in the dimensionless form,

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

(27)

in terms of dimensionless parameters $\alpha$ and the aspect ratio for the moments of inertia

$$
\lambda = \frac{I_z}{I_x}.
$$

(28)

The range of $\lambda$ for a symmetric rotator is $0 \leq \lambda \leq 2$. For, e.g., a symmetric ellipsoid with semiaxes $a = b \neq c$, one has $\lambda = 2a^2/(a^2 + c^2)$.

The dependence of the energy levels (24) on $J$ at $K = J$ is shown in figures 1 and 2. It exhibits quantum phase transition on the parameter $\alpha$ between states with different values of $J$. Only for a needle of vanishing diameter, $I_z/I_x \to 0$, which corresponds to $a \to 0$ in the case of an ellipsoid, the transition is second order, see Fig. 1. It occurs at $\alpha = [1 - 1/(2S)^2]^{-1}$. This case is equivalent to the rotation about a fixed axis studied in Ref. 16. For any finite ratio $I_z/I_x$ the transition is first order, see Fig. 2. It occurs at the value of $\alpha$ that depends on $I_z/I_x$. The origin of the transfer from a second-order transition at $\lambda = 0$ to the first-order transition at $\lambda \neq 0$ can be traced to the term $[J(J+1) - K^2]S^{-2} \lambda$ in Eq. (27). We should notice that for a finite-size nanomagnet the analogy with first- and second-order phase transition is, of course, just an analogy. To talk about real phase transitions one has to take the limit of $S \to \infty$, $I_{x,z} \to \infty$ when the distances between quantum levels go to zero and the energy becomes quasi-continuous function of $J$. 

FIG. 1: Dependence of energy on $J$ at $K = J$ and $I_z/I_x = 0$ for different values of $\alpha$. The plot shows second-order quantum phase transition on $\alpha$.

FIG. 2: Dependence of energy on $J$ at $K = J$ and $I_z/I_x = 2$ for different values of $\alpha$. The plot shows first-order quantum phase transition on $\alpha$. 

[15] V. GROUND STATE

Minimization of the energy in Eq. (24) on $J$ with the account of the fact that $J$ cannot be smaller than $K$ immediately yields $J = K$, that is, the ground state always corresponds to the maximal projection of the total angular momentum onto the spin quantization axis. In semiclassical terms this means that the minimal energy states in the presence of spin tunneling always correspond to mechanical rotations about the magnetic anisotropy axis. This is easy to understand by noticing that the sole reason for mechanical rotation is the necessity to conserve the total angular momentum while allowing spin tunneling to lower the energy. To accomplish this the particle needs to oscillate between clockwise and counterclockwise rotations about the spin quantization axis in unison with the tunneling spin. If such mechanical oscillation costs more energy than the energy gain from spin tunneling, then both spin tunneling and mechanical motion must be frozen in the ground state as, indeed, happens in very light particles (see below). Rotations about axes other than the spin quantization axis can only increase the energy and, thus, should be absent in the ground state.

For further analysis it is convenient to write Eq. (24) in the dimensionless form,

$$
\frac{E_{J,K}^{(\pm)}}{\Delta} = \frac{\alpha}{4} \left[ J(J+1) - \frac{K^2}{S^2} \lambda + \frac{K^2}{S^2} \right] \pm \frac{1}{2} \sqrt{1 + \frac{K^2}{S^2} \alpha^2},
$$

(27)

in terms of dimensionless parameters $\alpha$ and the aspect ratio for the moments of inertia

$$
\lambda = \frac{I_z}{I_x}.
$$

(28)

The range of $\lambda$ for a symmetric rotator is $0 \leq \lambda \leq 2$. For, e.g., a symmetric ellipsoid with semiaxes $a = b \neq c$, one has $\lambda = 2a^2/(a^2 + c^2)$.

The dependence of the energy levels (24) on $J$ at $K = J$ is shown in figures 1 and 2. It exhibits quantum phase transition on the parameter $\alpha$ between states with different values of $J$. Only for a needle of vanishing diameter, $I_z/I_x \to 0$, which corresponds to $a \to 0$ in the case of an ellipsoid, the transition is second order, see Fig. 1. It occurs at $\alpha = [1 - 1/(2S)^2]^{-1}$. This case is equivalent to the rotation about a fixed axis studied in Ref. 16. For any finite ratio $I_z/I_x$ the transition is first order, see Fig. 2. It occurs at the value of $\alpha$ that depends on $I_z/I_x$. The origin of the transfer from a second-order transition at $\lambda = 0$ to the first-order transition at $\lambda \neq 0$ can be traced to the term $[J(J+1) - K^2]S^{-2} \lambda$ in Eq. (27). We should notice that for a finite-size nanomagnet the analogy with first- and second-order phase transition is, of course, just an analogy. To talk about real phase transitions one has to take the limit of $S \to \infty$, $I_{x,z} \to \infty$ when the distances between quantum levels go to zero and the energy becomes quasi-continuous function of $J$. 

FIG. 1: Dependence of energy on $J$ at $K = J$ and $I_z/I_x = 0$ for different values of $\alpha$. The plot shows second-order quantum phase transition on $\alpha$.

FIG. 2: Dependence of energy on $J$ at $K = J$ and $I_z/I_x = 2$ for different values of $\alpha$. The plot shows first-order quantum phase transition on $\alpha$. 

[15]
The quantum number $K$ determines the ground state, as the energy, Eq. (27), no longer formally depends on $J$. However, the values of $\alpha_J$ at $\lambda = 0$, for which ground state transitions occur, are the same as those for which $E_{J,-K-1}^{(-)} = E_{J,K}^{(+)}$, and we will use $J$ to describe the ground state of the axial rotor as well. The first ground state transition occurs from $J = 0$ to $J = 1$ at $\alpha(\lambda) = \alpha_1(0) = \alpha_1^0(0)$, because $J_c = 1$ for $\lambda \lesssim 0.01$. At $\alpha = \alpha_2(0)$ the ground state switches from $J = 1$ to $J = 2$, and so on. The final transition is to a completely localized spin state $J = S$ in which spin tunneling is frozen for all $\alpha > \alpha_S(0)$. For example, when $S = 10$, $\alpha_1(0) = \alpha_1^0(0) = 1.0025$ and $\alpha_{10} = 3.2066$.

**Needle of finite diameter:** The ground state of a needle of finite diameter ($a \ll c$ for an ellipsoid) with $\lambda = 0.1$, that is free to rotate about any axis, shows qualitatively different behavior. As $\alpha$ increases, the ground state changes from $J = 0$ to $J = 3$ at $\alpha = \alpha_3^0(0)$, as the smallest value of $\alpha_J^0(0.1)$ for $1 \leq J \leq S$ occurs for $J_c = 3$. The $J = 1, 2$ states never become the ground state. After this, transitions occur to successively higher $J$, beginning with $J = 4$ at $\alpha = \alpha_4(0.1)$, and eventually localizing the spin with $J = S$ for $\alpha > \alpha_S(0.1)$. For $S = 10$, $\alpha_5^0(0.1) = 1.0588$ and $\alpha_{10} = 3.3935$.

**Sphere:** As $\lambda$ increases towards unity, the particle becomes more symmetric with the moment of inertia having (prolate) ellipsoidal symmetry, until it reaches spherical symmetry at $\lambda = 1$. The first ground state transition occurs from $J = 0$ to $J = J_c = 3$ at $\alpha = \alpha_3^0(1)$, and subsequent transitions occur at $\alpha = \alpha_4(1)$. However, the spin never localizes in the $J = S$ state even for very large $\alpha$, as $\alpha_J(1)$ has a pole at $J = S$, so the last transition occurs to the $J = S - 1$ state at $\alpha = \alpha_{S-1}(1)$. For $S = 10$, $\alpha_5^0(1) = 1.3187$ and $\alpha_{10}(1) = 2.4325$.

**Disk:** With $\lambda$ increasing from unity, the symmetry of the body becomes that of an oblate ellipsoid, and begins to flatten in the plane perpendicular to the anisotropy axis. It is easy to check from Eq. (27) that for $1 < \lambda \leq 2$ the state with $J = S$ always has higher energy than the state with $J = S - 1$, even in the limit of $\alpha \to \infty$. This means that for an oblate particle some spin tunneling (accompanied by mechanical rotations) survives in the ground state no matter how light the particle is. This purely quantum-mechanical result has no semi-classical analogue. In the case of a disk of vanishing thickness, $\lambda = 2$, the first ground state transition occurs from $J = 0$ to $J = J_c = 6$ at $\alpha = \alpha_6^0(2)$, and subsequent transitions occur at $\alpha = \alpha_J(2)$ up through $J = S - 1$. For $S = 10$, $\alpha_6^0(2) = 1.5873$ and $\alpha_9(2) = 3.5849$.

VI. GROUND-STATE MAGNETIC MOMENT

As has been already mentioned, the magnetic moment is due entirely to the spin of the particle, as $L_z$ represents mechanical motion of the particle as a whole, and not
electron orbital angular momentum. Thus,

$$\mu = -g\mu_B \langle \Psi_J | S_z | \Psi_J \rangle = -g\mu_B S \frac{\alpha K}{\sqrt{S^2 + (\alpha K)^2}}.$$  \hfill (34)$$

Here $g$ is the spin gyromagnetic factor, and the minus sign reflects the negative gyromagnetic ratio $\gamma = -g\mu_B/\hbar$. The ground state always corresponds to $J = K$, so these are used interchangeably in descriptions of the ground state.

FIG. 4: Ground state magnetic moment for a needle of vanishing diameter ($\lambda = 0$), finite-diameter needle ($\lambda = 0.1$), sphere ($\lambda = 1$), and a disk of vanishing thickness ($\lambda = 2$).

FIG. 5: Quantum phase diagram for the ground-state magnetic moment and the total angular momentum.

The dependence of the magnetic moment on $\alpha$ for different aspect ratios of the particle is shown in Fig. 4. For $\alpha < \alpha_J(\lambda)$ the ground state corresponds to $J = K = 0$, so the spin-up and spin-down states are in an equal superposition which produces zero magnetic moment. At greater values of $\alpha$ the spin states contribute in unequal amounts which leads to a non-zero magnetic moment. As $\alpha$ becomes large, the magnetic moment approaches its maximal value $|\mu_{\text{max}}| = g\mu_B S$. Note that the magnetic moment approaches its maximum value even for values of $\lambda$ that do not admit transitions to $J = S$ states.

Because the ground state is completely determined by the parameters $\alpha$ and $\lambda$, we can depict the ground state behavior in a quantum phase diagram shown in Fig. 5. The curves separate areas in the $(\alpha, \lambda)$ plane that correspond to different values of $J$ and different values of the magnetic moment. Notice the fine structure of the diagram (lower picture in Fig. 5) near the first critical $\alpha$. This very rich behavior of the ground state on parameters must have significant implications for magnetism of rigid atomic clusters.
VII. CONCLUSIONS

We have studied the problem of a quantum rotator containing a tunneling spin. This problem is relevant to quantum mechanics of free magnetic nanoparticles. It also provides an interesting insight into quantum mechanics of molecules studied from the macroscopic end. The answer obtained for the energy levels of a symmetric rotor, Eq. (24), is non-perturbative and highly non-trivial. It is difficult to imagine how it could be obtained from first principles without the reduction to two spin states. Indeed, for spin $S$ the tunnel splitting itself generally appears in the $S$-th order of perturbation theory, see Eq. (10), so the path from the full crystal-field Hamiltonian like, e.g., Eq. (9) to Eq. (24) must be very long. Equations (22) and (23) represent, therefore, a unique exact solution of the quantum-mechanical problem of a mechanical rotator with a spin. Striking feature of this solution is presence of first- and second-order quantum phase transitions between states with different values of the magnetic moment.

Our results provide the framework for comparison between theory and experiment on very small free magnetic clusters. Our main conclusion for experiment is that rotational states and magnetic moments of such clusters depend crucially and in a predictable way on size and aspect ratio. This dependence results in a complex phase diagram that separates regions in the parameter space, corresponding to different values of the magnetic moment. Broad distribution of the magnetic moments that does not simply scale with the volume, has, in fact, been reported in beams of free atomic clusters of ferromagnetic materials. Our results may shed some additional light on these experiments. They may also apply to free magnetic molecules if one can justify the condition of rigidity. Direct comparison between theory and experiment may be possible for atomic clusters (molecules) in magnetic traps.

To see that the quantum problem studied in this paper may, indeed, be relevant to quantum states of free nanomagnets, consider, e.g., a spherical atomic cluster of radius $R$ and average mass density $\rho$ having spin $S = 10$ that, when embedded in a large body, can tunnel between up and down at a frequency of a few GHz, thus providing $\Delta \sim 0.1 K$. Significant changes in the magnetic moment of such a cluster would occur at $\alpha \sim 1$, which, according to Eq. (20), corresponds to $I = 8 \pi \rho R^2/15 \sim 10^{-42} \text{kgm}^2$ and $R \sim 1 \text{nm}$. For a magnetic molecule like, e.g., Mn$_{12}$, the moments of inertia would also be in the ballpark of $10^{-42} \text{kgm}^2$. However, the natural spin tunnel splitting in Mn$_{12}$ is very small, thus, providing a very large $\alpha$. Same is true for Fe$_8$ magnetic molecules. In this case the spin tunneling in a free molecule must be completely frozen. Even if the molecule cannot be considered as entirely rigid, such effect, if observed, would receive natural interpretation within the framework of our theory.

VIII. ACKNOWLEDGEMENTS

This work has been supported by the U.S. Department of Energy through grant No. DE-FG02-93ER45487.

1. I. M.I. Billas, A. Châtelain, and W. A. de Heer, Science 265, 1682 (1994).
2. X. S. Xu, S. Yin, and W. A. de Heer, Phys. Rev. Lett. 95, 237209 (2005).
3. F. W. Payne, W. Jiang, J. W. Emmert, J. Deng, and L. A. Bloomfield, Phys. Rev. B 75, 094431 (2007).
4. J. Tejada, R. D. Zysler, E. Molins, and E. M. Chudnovsky, Phys. Rev. Lett. 104, 027202 (2010).
5. T. M. Wallis, J. Moreland, and P. Kabos, Appl. Phys. Lett. 89, 122502 (2006).
6. J. P. Davis, D. Vick, D. C. Fortin, J. A. J. Burgess, W. K. Hiebert, M. R. Freeman, Appl. Phys. Lett. 96, 072513 (2010).
7. H. B. Heersche, Z. de Groot, J. A. Folk, H. S. J. van der Zant, C. Romeike, M. R. Wegewijs, L. Zobbi, D. Barreca, E. Tondello, and A. Cornia, Phys. Rev. Lett. 96, 206801 (2006).
8. J. J. Henderson, C. M. Ramsey, E. del Barco, A. Mishra, and G. Christou, J. Appl. Phys. 101, 09E102 (2007).
9. S. Voss, M. Fonin, U. Rudiger, M. Burgert, and U. Groth, Phys. Rev. B 78, 155403 (2008).
10. A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton University Press, Princeton, New Jersey, 1957).
11. J. H. Van Vleck, Rev. Mod. Phys. 23, 213 (1951).
12. E. M. Chudnovsky, Phys. Rev. Lett. 72, 3433 (1994).
13. J.R. Friedman, V. Patel, W. Chen, S.K. Tolpygo, and J.E. Lukens, Nature - London 406, 43 (2000).
14. C.H. van der Wal, A.C.J. ter Haar, F.K. Wilhelm, R.N. Schouten, C.J.P.M. Harmans, T.P. Orlando, S. Lloyd, and J.E. Mooij, Science 290, 773 (2000).
15. J. Clarke and F. K. Wilhelm, Nature - London 453, 1031 (2008).
16. E. M. Chudnovsky and D. A. Garanin, Phys. Rev. B 81, 214423 (2010).
17. E. M. Chudnovsky, Sov. Phys. JETP 50, 1035 (1979) [JETP 50, 1035 (1979)].
18. E. M. Chudnovsky and L. Gunther, Phys. Rev. Lett. 60, 661 (1988).
19. E. M. Chudnovsky and J. Tejada, Macroscopic Quantum Tunneling of the Magnetic Moment (Cambridge University Press, Cambridge, UK, 1998).
20. R. Jaafar and E. M. Chudnovsky, Phys. Rev. Lett. 102, 227202 (2009).
21. R. Jaafar, E. M. Chudnovsky, and D. A. Garanin, Europhys. Lett. 89, 27001 (2009).
22. A. A. Kovalev, L. X. Hayden, G . E. W. Bauer, and Y. Tserkovnyak, Phys. Rev. Lett. 106, 147203 (2011).
23. D. A. Garanin and E. M. Chudnovsky, Phys. Rev. X 1, 011005 (2011).
24 O. Klein, Z. Physik 58, 530 (1929).
25 D. A. Garanin, J. Phys. A 24, L61-L62 (1991).
26 M. F. O’Keeffe and E. M. Chudnovsky, Phys. Rev. B 83, 092402 (2011).