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2002 J. Phys. A: Math. Gen. 35 3009

(http://iopscience.iop.org/0305-4470/35/12/320)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL
J. Phys. A: Math. Gen. **35** (2002) 3009–3014 PII: S0305-4470(02)29695-X

Non-Kramers degeneracy and oscillatory tunnel splittings in the biaxial spin system

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Received 5 October 2001, in final form 31 January 2002
Published 15 March 2002
Online at stacks.iop.org/JPhysA/35/3009

Abstract
We have investigated analytically quantum tunnelling of large spin in the biaxial spin system with the magnetic field applied along the hard and medium anisotropy axes by using Schrödinger's interpretation of quantum mechanics. When the magnetic field parallels the hard axis, the tunnel splittings of all the energy level pairs become oscillatory as a function of the magnetic field. The quenching points are completely determined by the coexistence of solutions of Ince's equation. When the magnetic field points to the medium axis, the tunnel splitting oscillations disappear due to the absence of coexistence of solutions. These results coincide with the recent experimental observations in the nanomagnet Fe_8.

PACS numbers: 75.10.Dg, 03.65.Ge, 03.65.Sq, 36.90.+f, 75.45.+j

In recent years much attention has been paid to quantum tunnelling of magnetization (large spin) in nanomagnets, both from experiment and theory [1]. Several magnetic particles have been identified as promising candidates for the observation of such macroscopic quantum phenomena, where the magnetization (or the Néel vector) tunnels from one potential minimum to another. Excellent examples that have widely been studied are the molecular nanomagnets Fe_8 [2–5] and Mn_{12} [6–8], which have well-defined structures and magnetic properties. On the one hand, these phenomena are very interesting from a fundamental point of view because they extend our understanding of the transition between quantum and classical behaviours. On the other hand, tunnelling of the magnetization changes the magnetic properties of the nanomagnets, which has potential application for data storage technology, e.g. for making qubits—the elements of quantum computers.

Recently, Wernsdorfer and Sessoli [9] observed a novel phenomenon, i.e. oscillations of tunnel splittings of the ground and excited states in the nanomagnet Fe_8 described well by the spin Hamiltonian [2–5]

$$\mathcal{H} = AS_x^2 - BS_y^2 - g\mu_B \boldsymbol{S}\cdot\boldsymbol{H} \tag{1}$$

where $\boldsymbol{S}$ is a spin operator, $\boldsymbol{H}$ is the magnetic field applied in the xz-plane, the spin quantum number $s = 10$, $A \approx 0.092$ K, $B \approx 0.229$ K, $g \approx 2$ is the g-factor, μ_B is the Bohr magneton. The zero-field Hamiltonian has a biaxial symmetry with hard, easy and medium axes along x, y and z, respectively. When $\boldsymbol{H}$ rotates from $\boldsymbol{x}$ to $\boldsymbol{z}$ direction, the oscillations of tunnel splittings of all the level pairs gradually disappear.

In fact, oscillation of the ground-state tunnel splitting ΔE_s of model (1) with the magnetic field H_x ($\boldsymbol{H}\|\boldsymbol{x}$) was predicted by using the instanton technique [10]. The tunnelling of spin is quenched when

$$h = h^*\left(1 - \frac{n}{s} - \frac{1}{2s}\right) \qquad n = 0, 1, \ldots, 2s-1. \tag{2}$$

Here, $h = \frac{H_x}{H_c}$, $H_c = \frac{2s(A+B)}{g\mu_B}$, is the critical field at which the energy barrier vanishes, $-h^* < h < h^* = \sqrt{\frac{A}{A+B}}$, and s is an integer or half odd integer. This kind of topological quenching is the result of quantum interference of different instanton paths within the context of macroscopic quantum tunnelling [11, 12], and need not be related to Kramers' degeneracy. Up to the first order of the rate $\frac{B}{A+B}$, formula (2) was rederived by the quantum-mechanical perturbation theory [13]. Very recently, Garg extended his previous paper [10] to the excited states by using a discrete Wentzel–Kramers–Brillouin approach [14]. To order s^{-1}, the quenching points for the excited state pairs are the same as those for the ground-state pair. With increasing magnetic field, the quenching points gradually decrease and finally disappear. These results were also obtained by the potential field description of spin systems with exact spin-coordinate correspondence [15] and the instant technique [16, 17]. Because quantum tunnelling of spin in the nanomagnets was observed at very low temperatures, the quantization of spin levels becomes very important to explain the experiments well. In essence, the energy spectrum of the spin systems can help us to understand the mechanism of spin tunnelling thoroughly. In this paper, we have analytically diagonalized the Hamiltonian (1) in the framework of Schrödinger's interpretation of quantum mechanics. The energy spectrum of the spin model is obtained in the large-s limit. It is clearly shown that when $\boldsymbol{H}\|\boldsymbol{x}$, the tunnel splittings of the ground and excited state pairs are oscillatory as a function of H_x and the quenching points agree with the previous results and the numerical simulation of model (1). When $\boldsymbol{H}\|\boldsymbol{z}$, the tunnel splitting oscillations of all the energy level pairs disappear, which coincided with those obtained by the phase space path integral [18]. These phenomena have also been observed in the experiments [9, 19].

Let E and Φ_m be the eigenenergies and eigenstates of $\mathcal{H}$, respectively, then the eigenvalue equation in the basis $|s, m\rangle_z$ reads

$$\begin{aligned} u_{m-1}\Phi_{m-2} + u_{m+1}\Phi_{m+2} - t_{m-\frac{1}{2}}\Phi_{m-1} - t_{m+\frac{1}{2}}\Phi_{m+1} + \left\{-E + \tfrac{1}{2}(A-B)[s(s+1) - m^2]\right. \\ \left. - g\mu_B H_z m\right\}\Phi_m = 0 \end{aligned} \tag{3}$$

where

$$\begin{aligned} u_{m\pm1} &= \tfrac{1}{4}(A+B)\sqrt{[s(s+1) - (m\pm1)^2]^2 - (m\pm1)^2} \\ t_{m\pm\frac{1}{2}} &= \tfrac{1}{2}g\mu_B H_x\sqrt{s(s+1) - \left(m - \tfrac{1}{2}\right)^2 + \tfrac{1}{4}}. \end{aligned}$$

Obviously, it is very difficult to strictly solve equation (3) for arbitrary s. However, in the large-s limit, equation (3) becomes [20]

$$(1-x^2)\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} - 2x\frac{\mathrm{d}\Phi}{\mathrm{d}x} + \left[-\frac{E}{A+B} - \frac{1}{4} - \frac{1}{4}\frac{1}{1-x^2} + \frac{As(s+1)}{A+B}\left(1-x^2\right) - \frac{g\mu_B H_z\sqrt{s(s+1)}}{A+B}x - \frac{g\mu_B H_x\sqrt{s(s+1)}}{A+B}\sqrt{1-x^2}\right]\Phi = 0. \quad (4)$$

Here, $x = \frac{m}{\sqrt{s(s+1)}}$ and only the leading terms remain, i.e. $\mathrm{O}(s^{-1})$. In deriving equation (4), we used

$$\begin{aligned} u_{m\pm1}\Phi_{m\pm2} &= u_{m\pm1}\left[\Phi_{m\pm1} \pm \frac{\Phi'_{m\pm1}}{\sqrt{s(s+1)}} + \frac{\Phi''_{m\pm1}}{2s(s+1)} + \cdots\right] \\ &= u\Phi \pm \frac{1}{\sqrt{s(s+1)}}\frac{\mathrm{d}}{\mathrm{d}x}(u\Phi) + \frac{1}{2s(s+1)}\frac{\mathrm{d}^2}{\mathrm{d}x^2}(u\Phi) + \cdots \\ &\quad \pm \frac{1}{\sqrt{s(s+1)}}\left[u\frac{\mathrm{d}\Phi}{\mathrm{d}x} \pm \frac{1}{\sqrt{s(s+1)}}\frac{\mathrm{d}}{\mathrm{d}x}\left(u\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right) + \cdots\right] + \frac{u}{2s(s+1)}\frac{\mathrm{d}^2\Phi}{\mathrm{d}x^2} + \cdots \\ t_{m\pm\frac{1}{2}}\Phi_{m+1} &= t_{m\pm\frac{1}{2}}\left[\Phi_{m\pm\frac{1}{2}} \pm \frac{\Phi'_{m\pm\frac{1}{2}}}{2\sqrt{s(s+1)}} + \cdots\right] \\ &= t\Phi \pm \frac{1}{2\sqrt{s(s+1)}}\frac{\mathrm{d}}{\mathrm{d}x}(t\Phi) + \cdots \pm \frac{t}{2\sqrt{s(s+1)}}\frac{\mathrm{d}\Phi}{\mathrm{d}x} + \cdots \end{aligned}$$

where

$$\begin{aligned} u &= \frac{1}{4}(A+B)\sqrt{s^2(s+1)^2(1-x^2)^2 - s(s+1)x^2} \\ &\approx \frac{1}{4}(A+B)\{s(s+1)(1-x^2) - x^2/[2(1-x^2)]\} \end{aligned}$$

and $t \approx \frac{1}{2}g\mu_B H_x\sqrt{s(s+1)}\sqrt{1-x^2}$ for large s.

Taking the transformations $\Phi = (1-x^2)^{-\frac{1}{4}}y(x)$ and $x = \sin(2t)$, and substituting them into equation (4), we finally obtain Hill's equation [21]

$$\frac{\mathrm{d}^2y}{\mathrm{d}t^2} + \left[\Lambda + (a-b)\cos(2t) + (c-b)\sin(2t) + \frac{b^2}{8}\cos(4t)\right]y = 0 \quad (5)$$

where

$$\begin{aligned} \Lambda &= \frac{-4E + 2As(s+1)}{A+B} \qquad & a &= b - \frac{4g\mu_B H_x\sqrt{s(s+1)}}{A+B} \\ b &= \pm 4\sqrt{\frac{As(s+1)}{A+B}} \qquad & c &= b - \frac{4g\mu_B H_z\sqrt{s(s+1)}}{A+B}. \end{aligned} \quad (6)$$

Up to now, we have mapped the spin problem (1) onto a particle problem (5). The energy spectrum of $\mathcal{H}$ is completely determined by the characteristic levels of Hill's equation. We note that when $A = 0$ and $\boldsymbol{H} = 0$, $\Lambda = m^2$. So $E = -B\left(\frac{m}{2}\right)^2$ which are the eigenvalues of the Hamiltonian (1) with integer s for even m or with half odd integer s for odd m.

For equation (5), there exist two monotonically increasing sequences of real numbers $a_0, a_{2i}, b_{2i}, a'_{2i-1}$ and b'_{2i-1} $(i = 1, 2, \ldots)$ such that equation (5) has a solution with period π if and only if $\Lambda = a_0, a_{2i}$ or b_{2i}, and a solution with period 2π if and only if $\Lambda = a'_{2i-1}$ or b'_{2i-1}. The $a_0, a_{2i}, b_{2i}, a'_{2i-1}$ and b'_{2i-1} satisfy inequalities

$$a_0 < b'_1 \leqslant a'_1 < b_2 \leqslant a_2 < b'_3 \leqslant a'_3 < b_4 \leqslant a_4 < \cdots. \quad (7)$$

According to the relation between E and Λ in equation (6), it is easy to see that the ground state of $\mathcal{H}$ corresponds to the highest characteristic level of Hill's equation with period π or 2π

allowed, depending on integer or half odd integer spin s. The lower the characteristic level of equation (5), the higher the associated eigenstate of the Hamiltonian (1). The tunnel splitting of the characteristic level pair of equation (5) with period π is

$$\Delta\Lambda_{2i} = a_{2i} - b_{2i} \tag{8}$$

and the tunnel splitting of the characteristic level pair of equation (5) with period 2π is

$$\Delta\Lambda'_{2i-1} = a'_{2i-1} - b'_{2i-1}. \tag{9}$$

The tunnel splitting of the energy level pair of the Hamiltonian (1) can be evaluated by the tunnel splitting of its associated characteristic level pair using equation (6). We note that when two of the three parameters A, H_x and H_z vanish, Hill's equation (5) becomes the well-known Mathieu equation [22]. So the tunnel splittings of all the energy level pairs of the Hamiltonian (1) are monotonically increasing rather than oscillatory in the three cases [20]. For arbitrary parameters A, B, H_x and H_z, it is difficult to analytically solve equation (5). Here we only consider the following two special cases.

(i) $H_z = 0$ (i.e. $c = b$). In this case, equation (5) reduces to Ince's equation, which has been studied in a set of literature due to its physically basic importance [21]. To observe the oscillations of tunnel splittings of model (1), we must find some vanishing points at which its eigenstates are degenerate, i.e. $a_{2i} = b_{2i}$ or $a'_{2i-1} = b'_{2i-1}$. This is equivalent to finding the coexistence of solutions of Ince's equation, which means that two linearly independent solutions (one even and one odd) with period π or 2π exists. Fortunately, due to the positive coefficient of the last term $\cos(4t)$, Ince's equation has the coexistence of solutions [21] with period π when

$$a = -2nb \tag{10}$$

and with period 2π when

$$a = -(2n-1)b \tag{11}$$

where $n = 0, \pm1, \pm2, \ldots$. Obviously, the quenching points of tunnel splittings of the characteristic level pairs with period π are exactly shifted by half a period relative to those with period 2π. Under conditions (10) and (11), Ince's equation becomes the Whittaker equation [21]

$$\frac{\mathrm{d}^2 y}{\mathrm{d}t^2} + \left[\Lambda - pb\cos(2t) + \frac{b^2}{8}\cos(4t)\right] y = 0. \tag{12}$$

Here, $p = 2n+1$ or $2n$ for equation (10) or (11), respectively. For equation (12), when $b \to 0$, then $a_0 \to 0$, a_{2i} and $b_{2i} \to (2i)^2$, and a'_{2i-1} and $b'_{2i-1} \to (2i-1)^2$ [23].

Integer spin s. Due to equation (6), the eigenstates of the Hamiltonian (1) correspond to the characteristic levels of Ince's equation with period π, i.e. $E_0^a = -\frac{1}{4}(A+B)a_0 + E_0$, $E_i^a = -\frac{1}{4}(A+B)a_{2i} + E_0$ and $E_i^b = -\frac{1}{4}(A+B)b_{2i} + E_0$, $E_0 = \frac{1}{2}As(s+1)$, $i = 1, 2, \ldots, s$. So the tunnel splitting of the energy level pair $\left(E_i^a, E_i^b\right)$ is

$$\Delta E_i = E_i^b - E_i^a = \tfrac{1}{4}(A+B)\Delta\Lambda_{2i}. \tag{13}$$

From equation (10), we have $\Delta E_i = 0$ when

$$H_x = \frac{(2n+1)\sqrt{A(A+B)}}{g\mu_B}. \tag{14}$$

The existence of the quenching fields (14) clearly shows that the tunnel splittings of all the energy levels of $\mathcal{H}$ are oscillatory as a function of H_x and the period of oscillations $\Delta H = \frac{2\sqrt{A(A+B)}}{g\mu_B}$. This coincides with Garg's result (2) [10, 14]. For equation (12), when

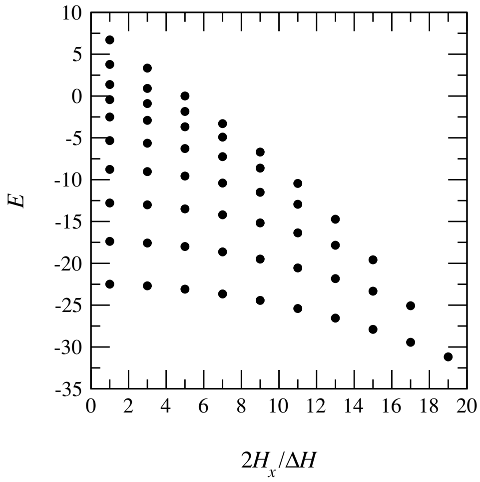

Figure 1. The exact quenching points of all the level pairs of the Hamiltonian (1) with $s = 10$, $A = 0.092K$, $B = 0.229K$ and $H_z = 0$.

$|p| = 2l + 1$, then the even intervals of instability on the Λ axis disappear with at most $l + 1$ exceptions [21]. In other words, the characteristic values a_0, a_{2i} and b_{2i} satisfy

$$a_0 < b_2 < a_2 < \cdots < b_{2l} < a_{2l} < b_{2(l+1)} = a_{2(l+1)} < \cdots < b_{2s} = a_{2s}. \quad (15)$$

This means that the tunnel splittings of the l highest excited state pairs of the Hamiltonian (1) do not vanish while those of the other $s - l$ energy level pairs vanish. With increasing magnetic field H_x (i.e. $|p|$), the quenching points gradually decrease and finally disappear when $l \geqslant s$. The configuration of the quenching points agrees with that from the numerical simulation of the Hamiltonian (1) (see figure 1).

Half odd integer spin s. The eigenstates of the Hamiltonian (1) correspond to the characteristic levels of equation (12) with period 2π, i.e. $E^{a'}_{i-\frac{1}{2}} = -\frac{1}{4}(A+B)a'_{2i-1} + E_0$ and $E^{b'}_{i-\frac{1}{2}} = -\frac{1}{4}(A+B)b'_{2i-1} + E_0$, $i = 1, 2, \ldots, s + \frac{1}{2}$. The tunnel splitting of the energy level pair $\left(E^{a'}_{i-\frac{1}{2}}, E^{b'}_{i-\frac{1}{2}}\right)$ reads

$$\Delta E'_{i-\frac{1}{2}} = E^{b'}_{i-\frac{1}{2}} - E^{a'}_{i-\frac{1}{2}} = \tfrac{1}{4}(A+B)\Delta\Lambda'_{2i-1}. \quad (16)$$

According to equation (11), we obtain $\Delta E'_{i-\frac{1}{2}} = 0$ when

$$H'_x = \frac{2n\sqrt{A(A+B)}}{g\mu_B}. \quad (17)$$

Obviously, the period of oscillations of tunnel splittings for all the energy level pairs $\left(E^{a'}_{i-\frac{1}{2}}, E^{b'}_{i-\frac{1}{2}}\right)$ is $\Delta H' = \frac{2\sqrt{A(A+B)}}{g\mu_B}$, which is the same for the energy level pairs $\left(E^a_i, E^b_i\right)$. However, the quenching points for half odd integer spin s are shifted half a period (i.e. $\frac{\sqrt{A(A+B)}}{g\mu_B}$) relative to those for integer spin s. For equation (12), if $|p| = 2l$, then at most $l + 1$ odd intervals of instability on the Λ axis remain, i.e.

$$b'_1 < a'_1 < b'_3 < a'_3 < \cdots < b'_{2l-1} < a'_{2l-1} < b'_{2l+1} = a'_{2l+1} < \cdots < b'_{2s} = a'_{2s}. \quad (18)$$

It is easy to see that the tunnel splittings of the $s - l + \frac{1}{2}$ lowest energy level pairs vanish, but the tunnel splittings of the other l highest energy level pairs do not. When $l > s - \frac{1}{2}$, quenching points do not exist. These results also coincide with those obtained by the discrete WKB approach [14].

(ii) $H_x = 0$ (i.e. $a = b$). Let $t \to t + \frac{\pi}{4}$, then equation (5) becomes Ince's equation

$$\frac{\mathrm{d}^2 y}{\mathrm{d}t^2} + \left[\Lambda + (c - b)\cos(2t) - \frac{b^2}{8}\cos(4t)\right] y = 0. \tag{19}$$

Because the coefficient of the last term $\cos(4t)$ is negative, equation (19) does not possess the coexistence of solutions, i.e. two linearly independent solutions [21]. This means that the sign of equality in inequalities (7) cannot hold and each energy level of $\mathcal{H}$ is singlet in the parameter space. So the tunnel splittings of all the level pairs are not oscillatory with H_z, which coincides with the experiments [9, 19].

In conclusion, we studied quantum tunnelling of large spin in the biaxial spin systems using quantum mechanics. The energy spectrum of spin model (1) is obtained by solving Hill's equation (5), which is derived directly from the eigenvalue equation of the spin problem in the large-s limit. It is surprising that when $\boldsymbol{H} \| \boldsymbol{x}$, the vanishing points of the tunnel splittings of all the energy level pairs obtained here by the coexistence of solutions of Ince's equation coincide with those given by the WKB method [10, 14] and other approaches [15–17]. However, our approach is a natural way of explaining the oscillations of tunnel splitting in the biaxial spin system, which is also applied in other spin Hamiltonians.

Acknowledgments

This work was supported in part by grants from the Hong Kong Research Grants Council (RGC), the Hong Kong Baptist University Faculty Research Grant (FRG), the Sichuan Youth Science and Technology Foundation and the NSF of the Sichuan Educational Commission.

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