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Tunnel splitting for a high-spin molecule in an in-plane field

Jia-Lin Zhu

Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China
and
Centre for Advanced Study, Tsinghua University, Beijing 100084, People's Republic of China

E-mail: zjl-dmp@tsinghua.edu.cn

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Abstract. Direction and strength effects of a magnetic field on the ground-state tunnel splitting for a biaxial spin molecule with the model Hamiltonian $H = k_1 S_z^2 + k_2 S_y^2 - g\mu_B H_z S_z - g\mu_B H_y S_y$ have been investigated within a continuous-spin approach including the Wess–Zumino–Berry term. The topological oscillation and the non-Kramers freezing indicated in the approach are in agreement with those observed in a recent experiment on Fe_8 molecular nanomagnets. The behaviour of tunnel splitting with multiple orbits induced by strong fields has been revealed clearly.

Now that crystals formed by identical magnetic molecules, such as Mn_{12} acetate [1] and an octanuclear iron cluster Fe_8 [2], which have a well-defined structure with a well-characterized spin ground state and magnetic anisotropy, can be fabricated, it has become possible to study macroscopic quantum tunnelling and its topological effect for high-spin molecules; these have attracted considerable interest, from both theoreticians and experimentalists [3, 4]. An Fe_8 cluster in a magnetic field $\boldsymbol{H} = (0, H_y, H_z)$ can be described by the biaxial spin Hamiltonian

$$H = k_1 S_z^2 + k_2 S_y^2 - g\mu_B H_z S_z - g\mu_B H_y S_y \tag{1}$$

where μ_B is the Bohr magneton, and $g = 2$, $S = 10$, $k_1 \approx 0.321$ K and $k_2 \approx 0.229$ K, which have been confirmed by EPR [2] and neutron scattering [5] data and macroscopic magnetic measurements [6, 7].

The tunnel splitting Δ of the ground state for the model of equation (1) with $H_y = 0$ has been studied theoretically [8–10]. An interesting topological effect, i.e., oscillation of Δ as H_z changes, has been discovered for $H_z < H_G$ where $H_G = (1-\lambda)^{1/2} H_a$ with $\lambda = k_2/k_1$ and $H_a = 2k_1 S/g\mu_B$ [8]. The tunnelling is quenched at a certain H_z [6, 8], and the freezing need not be related to Kramers' degeneracy. Very recently, the disappearance of the oscillation and freezing in the region where $H_z > H_G$ has been demonstrated [11], and further clarified [12] in different approaches. What is the situation if $\boldsymbol{H}$ is away from the hard-magnetization z-axis? How are the oscillation and freezing related to the direction and strength of $\boldsymbol{H}$? What is the condition under which the oscillation disappears? To provide answers to these questions, the characteristic of the tunnel splitting for the biaxial spin molecule of equation (1) in a magnetic field with both $H_y \neq 0$ and $H_z \neq 0$ is investigated within a continuous-spin approach including the Wess–Zumino–Berry term in this article. The behaviour of the tunnel splitting with multiple orbits induced by strong fields in the region where $H_z^2 - H_y^2/\lambda > H_G^2$ has been clearly revealed.

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In the instanton method, the tunnel splitting Δ is given by

$$\Delta = \left| \sum_k \omega_k \mathrm{e}^{-S_k} \right| \tag{2}$$

where ω_k is a quantity with dimensions of frequency or energy, and $S_k = S_{kr} + \mathrm{i}S_{ki}$ is the classical action that can be obtained from the Euclidean action along a semiclassical path, or instanton, connecting the two states between which the tunnelling is occurring. The sum runs over all possible instantons. However, there is only one instanton needed for calculating Δ in the system with the biaxial spin Hamiltonian of equation (1) because of the symmetry. In general, the tunnel splitting Δ for a biaxial spin molecule can be written as

$$\Delta = p_1 \mathrm{e}^{-S_{1r}} |1 + p_{21} \mathrm{e}^{-2\mathrm{i}\Phi} \mathrm{e}^{-\Delta S_r}| = p_1 \mathrm{e}^{-S_{1r}} ((1 - p_{21} \mathrm{e}^{-\Delta S_r})^2 + 4 p_{21} \mathrm{e}^{-\Delta S_r} \cos^2 \Phi)^{1/2} \tag{3}$$

where $\Delta S_r = S_{2r} - S_{1r}$ and $2\Phi = S_{2i} - S_{1i}$. p_{21} is the ratio of the pre-exponential factor p_2 of one path to that of the other, p_1. p_{21} is the one for the symmetric case with $H_y = 0$.

In the continuous approach, the classical actions of a spin system can be computed by using the coherent-spin-state path integrals [8]. The imaginary-time propagator for spin S is given by

$$\langle \hat{n_2} | \exp[-HT] | \hat{n_1} \rangle = \int [\mathrm{d}\hat{n}] \exp[-S_E[\hat{n}]] \tag{4}$$

where the $|\hat{n}\rangle$ denote coherent states. The path integral is over paths satisfying $|n(-\hat{T}/2)\rangle = |\hat{n_1}\rangle$ and $|n(\hat{T}/2)\rangle = |\hat{n_2}\rangle$. S_E is the Euclidean action which is given by

$$S_E = \int_{-T/2}^{T/2} \mathrm{i}S(1 - \cos\theta)\dot{\phi}(\tau)\, \mathrm{d}\tau + \int_{-T/2}^{T/2} E(\theta, \phi)\, \mathrm{d}\tau \tag{5}$$

where (θ, ϕ) are the polar coordinates of $\hat{n}$, and $E(\theta, \phi) = \langle \hat{n} | H | \hat{n} \rangle$. For large spin, and large time T, the path integral of equation (4) can be evaluated using instanton or steepest-descent methods [8, 13].

For the model of equation (1), $E(\theta, \phi)$ can be obtained easily as shown below:

$$E(\theta, \phi) = K_1(\cos\theta - \cos\theta_0)^2 + K_2(\sin\theta \sin\phi - \sin\theta_0 \sin\phi_0)^2 + E_0 \tag{6}$$

where E_0 is a constant that makes $E(\theta, \phi)$ zero in the initial state, and $\cos\theta_0 = H_z/H_a$, $\sin\theta_0 \sin\phi_0 = H_y/\lambda H_a$, and $K_{1,2} = k_{1,2}S^2$. The critical field at which the energy barrier disappears is as follows:

$$H_c = \frac{\lambda H_a}{(\sin^2\theta_H + \lambda^2 \cos^2\theta_H)^{1/2}} \tag{7}$$

where $\theta_H = \tan^{-1}(H_y/H_z)$. For the special cases where $\theta_H = 0$ and $\pi/2$, we have $H_c = H_a$ and λH_a, respectively. There are two energy minima, at $(\theta, \phi) = (\theta_0, \phi_0)$ and at $(\theta, \phi) = (\theta_0, \pi - \phi_0)$, which are degenerate, so this corresponds to the ground-state tunnel splitting which appears below H_c.

Along an instanton, $E(\theta, \phi)$ is conserved, so the orbit, without regard to its time dependence, can be found purely by using energy conservation, and it can be expressed as a complex function of real ϕ. This point is of great utility in calculating the classical actions. However, we should note that the orbits are essentially different in the two cases $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$ and $(h^2 + h^{*2})/2 > 1 - \lambda$, where

$$h = h_z + \mathrm{i}h_y = H_z/H_a + \mathrm{i}H_y/\sqrt{\lambda}H_a.$$

For $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$, the orbit which corresponds to an instanton solution is found as

$$\cos\theta(\phi) = \frac{h^* + \mathrm{i}\lambda^{1/2} \sin\phi V(\phi)}{1 - \lambda \sin^2\phi} \tag{8}$$

where $V(\phi) = v_+(\phi) + \mathrm{i}v_-(\phi)$. $v_\pm(\phi) = ((v_a(\phi)^2 + v_b^2)^{1/2} \pm v_a(\phi))^{1/2}/\sqrt{2}$ with $v_a(\phi) = 1 - \lambda\sin^2\phi - (h^2 + h^{*2})/2$ and $v_b = \mathrm{i}(h^{*2} - h^2)/2$. $v_a(\phi)$ is larger than zero in all of the real-ϕ regions. The single orbit becomes multiple orbits as the condition $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$ changes into the condition $(h^2 + h^{*2})/2 > 1 - \lambda$ under which $v_a(\phi)$ is not always larger than zero. $v_a(\phi)$ is less than zero in the regions where $\phi_c \leqslant \phi \leqslant \pi - \phi_c$ and $-\pi + \phi_c \leqslant \phi \leqslant -\phi_c$ and still larger than zero in the other regions, where ϕ is between $-\pi$ and π. The condition for ϕ_c is

$$\sin\phi_c = \lambda^{-1/2}\sqrt{1 - (h^2 + h^{*2})/2}. \tag{9}$$

This is the point at which $\arg v_\pm(\phi)$ changes from 0, for regions where ϕ is between $-\pi$ and π, to $\pi/2$ in regions where $\phi_c \leqslant \phi \leqslant \pi - \phi_c$ and to $3\pi/2$ in regions where $-\pi + \phi_c \leqslant \phi \leqslant -\phi_c$.

The two classical actions are

$$S_1 = \mathrm{i}S\int_{C_1(\phi_0 \to \pi - \phi_0)} (1 - \cos\theta(\phi))\,\mathrm{d}\phi \qquad S_2 = \mathrm{i}S\int_{C_2(\phi_0 \to -\pi - \phi_0)} (1 - \cos\theta(\phi))\,\mathrm{d}\phi.$$

In both of the integrals, it is no longer necessary to regard ϕ as running over the original instanton contour given by $\phi(\tau)$. The classical actions of the single orbit can be obtained by integration just along the real axis since there are no singularities of the orbit on the real ϕ-axis.

Noting that $\cos\theta(\phi)$ and $\sin\phi V(\phi)$ are respectively periodic and odd functions of ϕ, we find the action difference $\Delta S = S_2 - S_1 = \Delta S_r + \mathrm{i}\,2\Phi$ between the two paths to be

$$\Delta S = -\mathrm{i}S\int_{-\pi}^{\pi}\left(1 - \frac{h^* + \mathrm{i}\lambda^{1/2}\sin\phi V(\phi)}{1 - \lambda\sin^2\phi}\right)\mathrm{d}\phi = -\mathrm{i}\,2\pi S\left(1 - \frac{h^*}{\sqrt{1-\lambda}}\right) \tag{10}$$

with

$$S_{1r} = 2S\left(\frac{h_y}{\sqrt{1-\lambda}}\left(-\frac{\pi}{2} + \tan^{-1}(\sqrt{1-\lambda}\tan\phi_0)\right) + \int_{\phi_0}^{\pi/2}\frac{\lambda^{1/2}\sin\phi v_+(\phi)\,\mathrm{d}\phi}{1 - \lambda\sin^2\phi}\right). \tag{11}$$

In the strong-field case of $(h^2 + h^{*2})/2 > 1 - \lambda$ with $\phi_c > \phi_0$, the integral paths $C_1(\phi_0 \to \pi - \phi_0)$ and $C_2(\phi_0 \to -\pi - \phi_0)$ of the single orbit become the integral paths $C_1(\phi_0 \to \phi_c \to \pi - \phi_c \to \pi - \phi_0)$ and $C_2(\phi_0 \to -\phi_c \to -\pi + \phi_c \to -\pi - \phi_0)$ of the multiple orbits, in which the arguments of $v_\pm(\phi)$ are changed at $\phi = \pm\phi_c$ and $\phi = \pm(\pi - \phi_c)$, respectively. For $\phi_0 > \phi_c$, only $C_2(\phi_0 \to -\pi - \phi_0)$ is changed to $C_2(\phi_0 \to \phi_c \to -\phi_c \to -\pi + \phi_c \to -\pi - \phi_c \to -\pi - \phi_0)$. Here $C_1(\phi_0 \to \pi - \phi_0)$ is not changed; however, the multiple orbits should be used instead of the single orbit to calculate ΔS. It is as follows:

$$\begin{aligned}\Delta S = -\mathrm{i}S\int_{-\pi}^{\pi}\left(1 - \frac{h^*}{1 - \lambda\sin^2\phi}\right)\mathrm{d}\phi + S\int_{-\phi_c}^{-\pi+\phi_c}\frac{\lambda^{1/2}\sin\phi V(\phi)}{1 - \lambda\sin^2\phi}\,\mathrm{d}\phi \\ - S\int_{\phi_c}^{\pi-\phi_c}\frac{\lambda^{1/2}\sin\phi V(\phi)}{1 - \lambda\sin^2\phi}\,\mathrm{d}\phi.\end{aligned} \tag{12}$$

Noting the changes of $\arg v_\pm(\phi)$ in the different regions mentioned above, we have

$$\Delta S_r = 2\pi S\left(\frac{h_y}{\sqrt{1-\lambda}}\right) - 4S\int_{\phi_c}^{\pi/2}\frac{\lambda^{1/2}\sin\phi v_{m-}(\phi)}{1 - \lambda\sin^2\phi}\,\mathrm{d}\phi \tag{13}$$

and

$$2\Phi = -2\pi S\left(1 - \frac{h_z}{\sqrt{1-\lambda}}\right) - 4S\int_{\phi_c}^{\pi/2}\frac{\lambda^{1/2}\sin\phi v_{m+}(\phi)}{1 - \lambda\sin^2\phi}\,\mathrm{d}\phi \tag{14}$$

where $v_{m\pm}(\phi) = ((v_{ma}(\phi)^2 + v_b^2)^{1/2} \pm v_{ma}(\phi))^{1/2}/\sqrt{2}$ with $v_{ma}(\phi) = -v_a(\phi) > 0$ ($\arg v_{ma}(\phi) = 0$) in the region where $\phi_c \leqslant |\phi| \leqslant \pi - \phi_c$.

S_{1r} is as follows:

$$S_{1r} = 2S\left(\frac{h_y}{\sqrt{1-\lambda}}\left(-\frac{\pi}{2} + \tan^{-1}(\sqrt{1-\lambda}\tan\phi_0)\right)\right) + R_{mr} \tag{15}$$

with

$$R_{mr} = \theta(\phi_c - \phi_0)\,2S\int_{\phi_0}^{\phi_c}\frac{\lambda^{1/2}\sin\phi v_+(\phi)\,\mathrm{d}\phi}{1-\lambda\sin^2\phi} + 2S\int_{\phi_m}^{\pi/2}\frac{\lambda^{1/2}\sin\phi v_{m-}(\phi)}{1-\lambda\sin^2\phi}\,\mathrm{d}\phi \tag{16}$$

where $\theta(\phi_c - \phi_0) = 1$ and $\phi_m = \phi_c$ if $\phi_c > \phi_0$, and $\theta(\phi_c - \phi_0) = 0$ and $\phi_m = \phi_0$ if $\phi_c \leqslant \phi_0$. The integral in equation (14) represents the effect of the strong field on the quantum phase difference while the integral in equation (13) and R_{mr} in equation (15) represent that of the strong field on the tunnelling rate. It is interesting to note that equations (12) and (15) become equations (10) and (11) at $(h^2 + h^{*2})/2 = 1 - \lambda$ ($\phi_c = \pi/2$).

For $h_z \neq 0$ with and without $h_y = 0$, the topological tunnelling oscillation exists under the condition $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$. It is easy to see the topological oscillation as h_z changes, with $h_y = 0$ [8], where two instanton paths ($\theta = \theta_0, \phi = \phi_0 \to \theta, \phi = \pi/2 \to \theta = \theta_0, \phi = \pi - \phi_0$ and $\theta = \theta_0, \phi = \phi_0 \to \theta, \phi = -\pi/2 \to \theta = \theta_0, \phi = -\pi - \phi_0$) are equivalent for the tunnelling rate due to the symmetry ($\phi_0 = 0$). As shown in equation (10), the tunnelling is completely frozen out whenever $h_z = (1-\lambda)^{1/2}(S - n - 1/2)/S$ where $n = 0, 1, 2, \ldots$. The oscillation and freezing are due to the spin quantization and the level crossings [8, 14]. The two instanton paths are not equivalent for the rate due to applying H_y, which makes the symmetry broken and $\phi_0(h_y)$ non-zero. h becomes complex, and ΔS_r is not equal to zero. Then the other type of topological oscillation appears, and the non-Kramers freezing is partial. It is clearly seen from equation (3) with equation (10) that the position and degree of the freezing are determined by h. The degree of the freezing can be defined as a ratio σ of the oscillation part $4p_{21}\mathrm{e}^{-\Delta S_r}$ to the non-oscillation part $(1 - p_{21}\mathrm{e}^{-\Delta S_r})^2$ in equation (3). σ is changed from ∞ (the completely freezing region) to a small value (the unfreezing region)—for example, 0.1—as h_y varies from zero to $h_{yc} \approx 0.06(1-\lambda)^{1/2}$. It is easily seen that the degree of freezing is very sensitive to h_y, i.e., the orientation θ_H of the magnetic field. The larger h_y is, the less freezing there is. For a spin molecule with medium anisotropy, partial freezing can be observed in a slightly larger region of $h_y(\theta_H)$. This is why partial freezing can be observed in Fe_8 molecular nanomagnets with $\lambda = 0.71$ [6].

To better understand the main picture mentioned above and compare the theoretical approach with the experimental measurement, the pre-exponential factors in tunnel splitting are evaluated for small fields, and then $\Delta_0 = p_1\mathrm{e}^{-S_{1r}}$ is found to be

$$\Delta_0 = c(\lambda^{1/2}\cos\phi_0)^{3/2}\frac{8\sin^{5/2}\theta_0}{(\sin^2\theta_0 - \lambda)^{1/2}}\left(\frac{K_1}{\pi S}\right)^{1/2}\left(\frac{\sin^2\theta_0}{\sin^2\theta_0 + \lambda\cos^2\theta_0\sin^2\phi_0}\right)^{1/2}\mathrm{e}^{-S_{1r}} \tag{17}$$

where the dimensionless prefactor c can often be of the order of 1 or so. We have plotted Δ for the Fe_8 spin molecule as a function of the field strength H_S $(=(H_y^2 + H_z^2)^{1/2})$ for $\theta_H = 0^\circ, 3^\circ, 5^\circ, 7^\circ, 20^\circ, 50^\circ$, and 90° in figure 1. It is interesting to note that the result obtained from the theoretical approach is in good agreement with the numerical diagonalization of the Hamiltonian and that both of them reproduce the main picture of the experiment [6]. In figure 1, furthermore, the smallest Δ is at $H_S = 0.128$, 0.126, 0.109, and 0 T for $\theta_H = 0^\circ, 7^\circ, 20^\circ$, and 90°, respectively. This is due to the combination of the oscillation part with the non-oscillation part and its dissociation, and can be used to explain what was observed for Fe_8 molecular nanomagnets, as shown in the figure in reference [6]. However, a fourth-order term $C(S_+^4 + S_-^4)$ should be taken into account in order to recover quantitatively the experimental values of the splitting Δ [6]. It would be interesting to solve the problem in the continuous-spin approach.

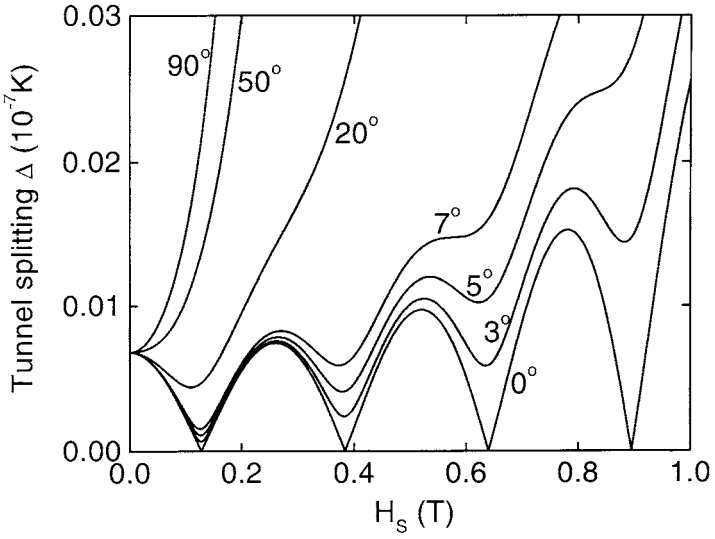

Figure 1. Δ versus H_S for $\theta_H = 0^\circ, 3^\circ, 5^\circ, 7^\circ, 20^\circ, 50^\circ$, and 90°.

The behaviour of the tunnel splitting Δ with $(h^2 + h^{*2})/2 > 1 - \lambda$ is quite different from that with $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$ due to the multiple orbits induced by the strong field. This is the case of references [11] and [12], as $h_y = 0$ and thus $\Delta S_r = 0$, because $h_y = 0$ and $v_{m-}(\phi) = 0$ in equation (13). The integral in equation (14) can be calculated as follows:

$$\int_{\phi_c}^{\pi/2} \frac{\lambda^{1/2} \sin\phi v_{m+}(\phi)}{1 - \lambda \sin^2\phi}\, \mathrm{d}\phi = \int_{\phi_c}^{\pi/2} \frac{\lambda^{1/2} \sin\phi \sqrt{\lambda \sin^2\phi - \sin^2\theta_0}}{1 - \lambda \sin^2\phi}\, \mathrm{d}\phi = \frac{\pi}{2}\left(\frac{h_z}{\sqrt{1-\lambda}} - 1\right). \tag{18}$$

2Φ is also exactly equal to zero because the real part $v_+(\phi)$ of $V(\phi)$ ($V(\phi) = v_+(\phi) + \mathrm{i}v_-(\phi)$ with $\arg v_a(\phi) = 0$) in the single orbit becomes the imaginary parts $v_{m+}(\phi)$ and $-v_{m+}(\phi)$ of $V(\phi)$ ($V(\phi) = \mathrm{i}(v_{m+}(\phi) + \mathrm{i}v_{m-}(\phi))$ with $\arg v_{ma}(\phi) = 0$ and $V(\phi) = -\mathrm{i}(v_{m+}(\phi) + \mathrm{i}v_{m-}(\phi))$ with $\arg v_{ma}(\phi) = 0$) in the multiple orbits in the regions where $\phi_c \leqslant \phi \leqslant \pi - \phi_c$ and $-\pi + \phi_c \leqslant \phi \leqslant -\phi_c$, respectively. In other words, the imaginary-time motion becomes the real-time motion in the regions between $\pm\phi_c$ and $\pm(\pi - \phi_c)$, and then the phase contribution of the imaginary-time motion is cancelled exactly by that of the real-time motion [11]. From a physical point of view, this occurs because there is no more level crossing when $h_z > \sqrt{1-\lambda}$ [8, 12]. It is easily seen that for the case of $h_y = 0$ ($\phi_0 = 0$), $S_{1r} = R_{mr}$ with $\theta(\phi_c - \phi_0) = 1$ and $v_{m-}(\phi) = 0$, and $S_{1r}(\phi_c)$ decreases and then Δ increases monotonically with increasing h_z.

However, ΔS_r and 2Φ are not exactly equal to zero when $(h^2 + h^{*2})/2 > 1 - \lambda$ with $h_y \neq 0$. There is no purely real-time motion in the case of a complex h which makes both of $v_{m+}(\phi)$ and $v_{m-}(\phi)$ non-zero. For $(h^2 + h^{*2})/2 > 1 - \lambda$ with a fixed $\arg h$, both 2Φ and ΔS_r approach their limits as $|h|$ increases. The limit values decrease and approach zero as $\arg h$ changes from some values allowed by the multiple orbits to zero. We can conclude, therefore, that under the condition of $(h^2 + h^{*2})/2 > 1 - \lambda$ with a fixed $\arg h$, the oscillation of Δ disappears and then Δ increases monotonically with $|h|$ and that Δ is sensitive to $\arg h$, i.e., the field direction in all of the tunnel regions.

In summary, the direction and strength effects of a magnetic field on the ground-state tunnel splitting for a biaxial spin molecule have been investigated. It is found that for $(h^2 + h^{*2})/2 \leqslant 1 - \lambda$, 2Φ and ΔS_r are respectively dependent on h_z and h_y only, and that

oscillation and freezing of Δ can occur. The degree of freezing is sensitive to the field direction and the molecular anisotropy. This is in good agreement with the main picture observed in the recent experiment on Fe_8 molecular nanomagnets. For $(h^2 + h^{*2})/2 > 1 - \lambda$, the single orbit becomes the corresponding multiple orbits. On the basis of the multiple orbits obtained exactly, the direction and strength effects are clearly revealed, and are in agreement with those obtained in the special case of $h_y = 0$ in references [11] and [12]. Finally, it is worth pointing out that the multiple orbits exist not only in the biaxial spin molecule but also in the other systems, and that the concept is useful for studying the tunnel problem. The prediction as regards the behaviour of Δ in the strong field can be tested for Fe_8 molecular nanomagnets with $H_G = (1 - \lambda)^{1/2} H_a = 0.54 H_a$.

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