Vol 13 No 7, July 2004
1009-1963/2004/13(07)/1124-05

Chinese Physics

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Comparison of calculation methods for the tunnel splitting at excited states of biaxial spin models

Cui Xiao-Bo(崔晓波)[a)†] and Chen Zhi-De(陈芝得)[b)]

[a)] *Department of Physics and Institute of Modern Condensed Matter Physics, Guangzhou University, Guangzhou* 510405, *China*

[b)] *Department of Physics, Jinan University, Guangzhou* 510632, *China*

(Received 15 January 2003; revised manuscript received 9 December 2003)

We present the calculation and comparison of tunnel splitting at excited levels of biaxial spin models by various methods, including the generalized instanton method, the generalized path integral method for coherent spin states, the perturbation method, and the exact method by numerical diagonalization of the Hamiltonian. It is found that, for integer spin with spin number around 10, tunnel splitting predicted by the generalized path integral for coherent spin states is about 10^{-n} times of the exact numerical result for the nth excited level, while the ratio of the results of the perturbation method and the exact numerical method diverges in the large spin limit. We thus conclude that the generalized instanton method is the best approximate way for calculating tunnel splitting in spin models.

Keywords: tunnel splitting, biaxial spin models, single molecular magnet
PACC: 7500, 0365S, 7530G

1. Introduction

Macroscopic quantum tunnelling in nano-scale magnetic molecular clusters or so-called single molecular magnets (SMMs) has been an interesting subject in recent years.[1−5] Research on this subject can help us to bridge between the macroscopic classical mechanics and the microscopic quantum mechanics.[2,3] Early theoretical study was concentrated on the ground state tunnelling which makes the dominant contribution at low temperatures.[6−9] However, when we consider tunnelling at higher temperature, as for the quantum–classical cross-over,[10,11] the excited state tunnelling becomes important. Interestingly, the calculation of tunnel splitting at excited levels is shown to be much more complicated than the ground state tunnelling. Application of the periodic instanton method [12] or a direct generalization of the instanton method [13] to the tunnel splitting at excited levels did not re-produce the right quantum interference phase.[5,14] In order to recover the right quantum interference phase, a generalized path integral for coherent spin states was introduced for spin models with m-fold rotation symmetry [15] and a generalized instanton method was proposed for biaxial spin models.[16] Both methods are based on the large spin approximation,[7] and are able to re-produce the right quantum interference phase. From a practical viewpoint, however, the real SMMs usually have a spin number around 10, and it is necessary to know if these methods still work well for such spin numbers. This is the main purpose of the present paper. By adopting the parameters of the well studied SMM Fe_8,[5], tunnel splitting at the excited states is found by the methods mentioned above. As a comparison, we also present the result by the perturbation method [8] which is considered as another important way to calculate tunnel splitting in spin systems.[17] The organization of the paper is as follows: in Sec.2, we present a description of the models and the methods to calculate tunnel splitting at the excited state. The comparison and analysis are provided in Sec.3 and the conclusion is given in the last section.

2. Models and methods

In the present paper, our main interest is in the biaxial spin model, for which the Hamiltonian is given by [5,11,14]

$$\widehat{H} = K_1\widehat{S}_z^2 + K_2\widehat{S}_x^2 - g\mu_B\widehat{S}_z h, \qquad (1)$$

†E-mail: xiaobo.cui@163.com

where $K_1 > K_2 > 0$ are the anisotropic parameters and h is the magnetic field applied along the hard axis. A customary way to evaluate tunnel splitting is to use the spin-coherent-state (SCS) path integral method [7,18]

$$\mathcal{K} = \langle \boldsymbol{n}_2 | \mathrm{e}^{-\widehat{H}T/\hbar} | \boldsymbol{n}_1 \rangle = \int [\mathrm{d}\boldsymbol{n}] \mathrm{e}^{-\frac{1}{\hbar} S_\mathrm{e}[\boldsymbol{n}]}, \quad (2)$$

where $S_\mathrm{e}[\boldsymbol{n}] = \int_{-T/2}^{T/2} L_\mathrm{e}[\boldsymbol{n}] \mathrm{d}\tau$, $|\boldsymbol{n}\rangle$ denotes the SCS defined by $\widehat{S} \cdot \boldsymbol{n} | \boldsymbol{n} \rangle = s | \boldsymbol{n} \rangle$; $\boldsymbol{n}$=$(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ is a unit vector. L_e is the Euclidean Lagrangian given by

$$L_\mathrm{e}[\boldsymbol{n}] = \mathrm{i}\hbar(1-\cos\theta)\dot{\phi}(\tau) + \langle \boldsymbol{n} | \widehat{H} | \boldsymbol{n} \rangle. \quad (3)$$

In large spin approximation, $\langle \boldsymbol{n} | \widehat{H} | \boldsymbol{n} \rangle$ can be found by replacing the spin operator in the Hamiltonian with the vector $s\boldsymbol{n}$, i.e. $\langle \boldsymbol{n} | \widehat{H} | \boldsymbol{n} \rangle = \widehat{H}(s\sin\theta\cos\phi, s\sin\theta\sin\phi, s\cos\theta)$. The ground state tunnel splitting of this model has been evaluated by the instanton method and the result is found to be in good agreement with the exact numerical result for spin number around 10.[14]

2.1. Generalized path integral for SCS

The key point of this method is to use the fact that the SCSs are over-complete. To find out tunnel splitting at the nth excited state, one can construct the coherent spin state $|\Omega, m\rangle$ in the Hilbert space with the basis $\{|s_z = m\rangle\}$, where $-s+n \le m \le s-n$: namely, the spin states $|s_z\rangle$ with $|s_z| > |s-n|$ are dropped. It can be shown that the coherent spin state constructed in this way is still complete, and thus a path integral of the defined coherent spin states can be found.[15] The corresponding propagator can be expressed as [15]

$$\langle \tilde{\Omega}, m | \mathrm{e}^{-\widehat{H}T/\hbar} | \Omega, m \rangle = \int \mathrm{d}\Omega \mathrm{e}^{-\mathrm{i}\,\Phi(m) - S_\mathrm{dyn}}, \quad (4)$$

where

$$\Phi(m) = m \int_0^\pi \mathrm{d}\phi(1-\cos\phi)$$

is the Berry phase and

$$S_\mathrm{dyn} = \frac{1}{\hbar} \int_{-T/2}^{T/2} \langle \Omega, m | \widehat{H} | \Omega, m \rangle \mathrm{d}\tau$$

is the dynamical action. In the large spin approximation, we have $\langle \Omega, m | \widehat{H} | \Omega, m \rangle = \widehat{H}(m\sin\theta\cos\phi, m\sin\theta\sin\phi, m\cos\theta)$. In other words, using the defined path integral for SCS, tunnelling at the nth excited state is in fact equivalent to the ground state tunnelling of a spin system with a spin number $s_1 = m = s-n$. Consequently, tunnel splitting of the nth excited state can be found by using the instanton method and the result is [19]

$$\Delta_m = Q_m \mathrm{e}^{-S_m} \left| \cos\left(m\pi - \frac{g\mu_B h\pi}{2K_1\sqrt{1-\lambda}} \right) \right|, \quad (5)$$

where

$$S_m = 2m\,\mathrm{arctanh}\sqrt{\frac{\lambda}{1-u_m^2}} - 2m\sqrt{\frac{u_m^2}{1-\lambda}}\,\mathrm{arctanh}\sqrt{\frac{u_m^2\lambda}{(1-u_m^2)(1-\lambda)}}, \quad (6)$$

$u_m = g\mu_B h/(2K_1 m)$, $\lambda = K_2/K_1$. Q_m is the prefactor

$$Q_m = 16 \left(\frac{\sqrt{1-u_m^2} - \sqrt{\lambda}}{\sqrt{1-u_m^2} + \sqrt{\lambda}} \right)^d m^{3/2} \lambda^{1/4} (1-u_m^2)^{5/4} \times \left(\frac{2K_1K_2}{1-u_m^2-\lambda} \right)^{1/2}, \quad (7)$$

where $d = \frac{1}{2}\sqrt{\lambda(1-u_m^2)}$.

2.2. The generalized instanton method

This method is based on the SCS path integral given in Eq.(2). The starting point [16] is to define the excited states by using the Bohr–Sommerfeld quantization rule with the help of the mapping technique:[7] that is, $s \oint \cos\theta \mathrm{d}\phi = n2\pi$. The defined excited states are quantized classical orbits around the easy axis, hence tunnelling between the excited states is the tunnelling between quasi-degenerate classical orbits. The total tunnelling amplitude from one quantized orbit $\mathcal{L}$ to another quasi-degenerate orbit $\mathcal{L}'$ should be expressed as

$$\mathcal{K}_{\mathcal{L}\mathcal{L}'} = \int_{\mathcal{L}\mathcal{L}'} \mathrm{d}\boldsymbol{s}_i \mathrm{d}\boldsymbol{s}_f \mathcal{K}(\boldsymbol{s}_f, T/2; \boldsymbol{s}_i, -T/2), \quad (8)$$

where $\mathcal{K}(\boldsymbol{s}_f, T/2; \boldsymbol{s}_i, -T/2)$ is the tunnelling amplitude of the tunnelling trajectory starting from an arbitrary point $\boldsymbol{s}_i$ at $\mathcal{L}$ and ending at $\boldsymbol{s}_f$ at $\mathcal{L}'$ and the integration is done over the quasi-degenerate classical orbits. The propagator in Eq.(8) can be found in the way proposed by McLaughlin [20] and the tunnel splitting of the nth excited state is found [16] to be

$$\Delta E_n = 4c^2 \mathrm{e}^{-S_\mathrm{c}/\hbar} \left| \cos\left[(s-n)\pi - \frac{g\mu_B h\pi}{2K_1\sqrt{1-\lambda}} \right] \right|, \quad (9)$$

where S_c is the real part of the classical action

$$S_\mathrm{c} = \int_{\phi_n}^{\pi-\phi_n} \mathrm{d}\phi \sqrt{2m(\phi)[V(\phi) - E_n]}, \quad (10)$$

E_n is the quantization energy of the nth excited state, $m(\phi) = 1/[2K_1(1-\lambda\sin^2\phi)]$ and $V(\phi) = K_2 s^2\sin^2\phi - (g\mu_B h)^2\lambda\sin^2\phi/[4K_1(1-\lambda\sin^2\phi)]$ are the mapped particle mass and the potential, respectively. ϕ_n can be found by $V(\phi_n) = E_n$ and c is given by

$$c^{-2} = \int_{-\phi_n}^{\phi_n} \mathrm{d}\phi \left\{\frac{1}{2}m(\phi)/[E_n - V(\phi)]\right\}^{1/2}. \quad (11)$$

It can be seen from Eqs.(5) and (9) that the interference factor is the same for both methods, the difference is the amplitude of the tunnel splitting.

2.3. The perturbation method and exact method

The perturbation method is not based on the large spin approximation, but on the perturbation theory in quantum mechanics.[8] In the limit $(K_1-K_2) \ll K_2$, tunnel splitting between $|s_z = \pm m\rangle$ can be expressed as

$$\Delta_m^{\mathrm{p}} = \frac{8K_2}{[(m-1)!]^2}\frac{(s+m)!}{(s-m)!}\left(\frac{K_1-K_2}{16K_2}\right)^m. \quad (12)$$

For the ground state tunnel splitting (i.e. $m = \pm s$), in the limit $s \gg 1$, the above result reduces to [8]

$$\Delta_s^{\mathrm{p}} = \frac{8K_2 s^{3/2}}{\pi^{1/2}}\left(\frac{K_1-K_2}{4K_2}\right)^s. \quad (13)$$

The exact method is based on numerical diagonalization of the following Hamiltonian:[5,14]

$$\widehat{H}_1 = -\frac{1}{2}(K_1+K_2)\widehat{S}_z^2 + \frac{1}{2}(K_1-K_2)(\widehat{S}_x^2 - \widehat{S}_y^2) - g\mu_B h\widehat{S}_x, \quad (14)$$

which is equivalent to the Hamiltonian in Eq.(1). In the representation of $|s_z\rangle$, the above Hamiltonian can be expressed as a $(2s+1)\times(2s+1)$ matrix which can be diagonalized by a standard Fortran program.[14] The resulting $(2s+1)$ eigen values have been listed in order and they are in pairs. The difference between the lowest pair is the ground state tunnel splitting, the difference between the next upper pair is the first excited state tunnel splitting, and so on.

3. Comparison of various methods

Our main interest focuses on the Fe_8 molecular magnet with a spin number $s = 10$. Up to second order approximation, the anisotropy parameters for Fe_8 system [5] are $-(K_1+K_2)/2 = 0.275$K and $-(K_1-K_2)/2 = 0.0462$K which implies $\lambda \simeq 0.713$. In the following calculation, we take $g = 2$. The oscillation of the tunnel splitting at excited state can be found from Eqs.(5) and (9). The results for the first excited state are shown in Fig.1 with the exact numerical result for comparison. As one can see from the figure, both approximation methods predict right oscillation period as the exact method. Tunnel splitting found by the generalized instanton method is very close to the exact result, while tunnel splitting predicted by the generalized path integral method is about an order lower than the exact result. The discrepancy between the results of generalized path integral of SCS and the exact result becomes larger as higher excited states are considered. In Fig.2, we present the results of the first four excited states for $h = 0.0$, $\lambda = 0.713$ with s ranging from $s = 6$ to $s = 12$. The results shown in Fig.2 show that the prediction of the generalized instanton method of Eq.(9) is always close to the exact result for all spin numbers. However, for s around 10, the prediction by the generalized path integral of SCS in Eq.(5) is about 10^{-n} times lower than the exact result for the nth excited state. This conclusion is also true for $s = 10$ but with different values of λ. The results are shown in Fig.3.

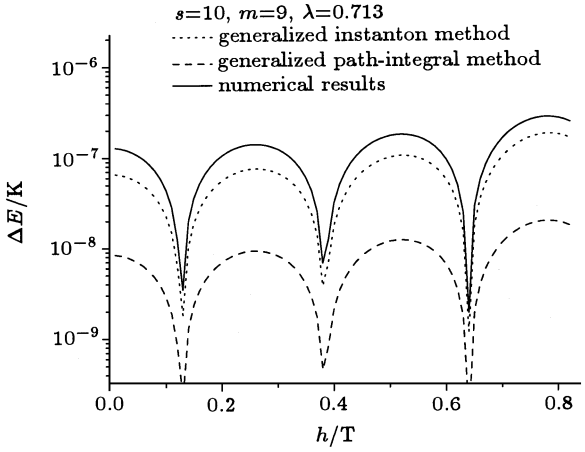


Fig.1. Illustration of the oscillation of the tunnel splitting at the first excited state (s=10, m=9) in semi-log plot. It can be seen from the figure that tunnel splitting by generalized path integral of SCS (dashed line) is about an order lower than the exact numerical result (solid line).

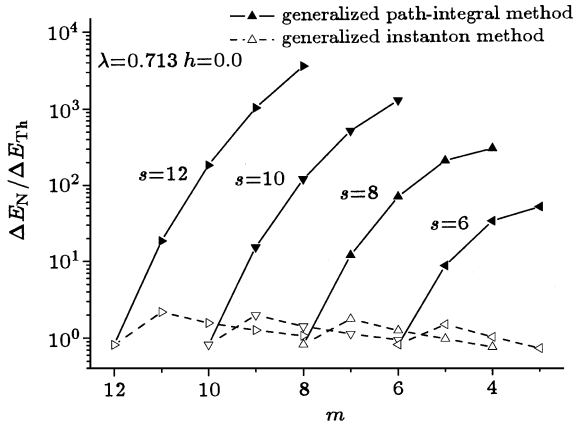


Fig.2. Illustration of the ratio of the exact result $\Delta E_{\rm N}$ to the theoretical prediction $\Delta E_{\rm Th}$ of Eqs.(5) and (9) in semi-log plot.

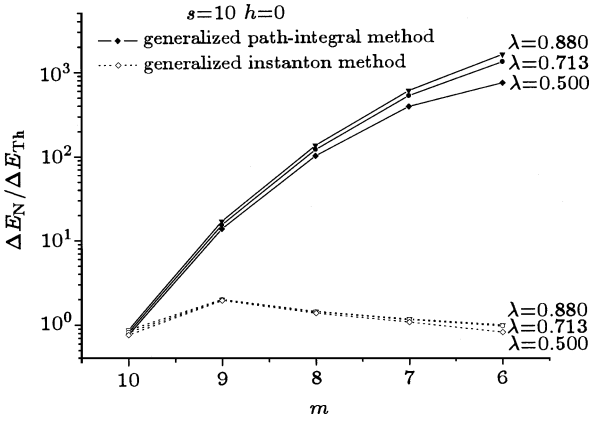


Fig.3. Illustration of the ratio of the exact result $\Delta E_{\rm N}$ to the theoretical prediction $\Delta E_{\rm Th}$ of Eqs.(5) and (9) in semi-log plot. Here s=10, h=0, λ=0.5, 0.713, and 0.880.

The above results clearly indicate that the generalized path integral of SCS does predict right quantum interference phase, but does not predict credible tunnel splitting at excited states for spin number around 10. On the other hand, both quantum interference phase and tunnel splitting predicted by the generalized instanton method are in good agreement with the exact numerical results. Now let us examine why the generalized path integral of SCS predicts tunnel splitting lower than the exact result. For simplicity, we shall consider the case of $h = 0$. Using the mapping technique,[7] namely $(\phi, s\hbar\cos\theta)$ are regarded as a pair of conjugate canonical variables, the spin tunnelling problem can be mapped into a tunnelling problem in a double well potential. Then the real part of the classical action is determined by the integration over the potential barrier to penetrate. If we start from the path integral in Eq.(2), the mapped potential in the case of h=0 is given by $V(\phi) = K_2 s^2 \sin^2\phi$, and then the barrier is determined by the turning points of $V(\phi_n) = E_n$. Illustration of the first excited state is shown in Fig.4 by solid line. If we start from the generalized path integral in Eq.(4), the effective potential is given by $V_{\rm e}(\phi) = K_2 m^2 \sin^2\phi$ and the barrier to penetrate is from 0 to π. Such a barrier for s=10 and m=9 is shown in Fig.4 by dotted line. As one can see from the figure, the barrier is exaggerated by the generalized path integral, thus the resulting real part of the classical action will be larger than the true one, which leads to lower tunnel splitting. For a quantitative comparison, the real part of the classical action by both methods is shown in Table 1.

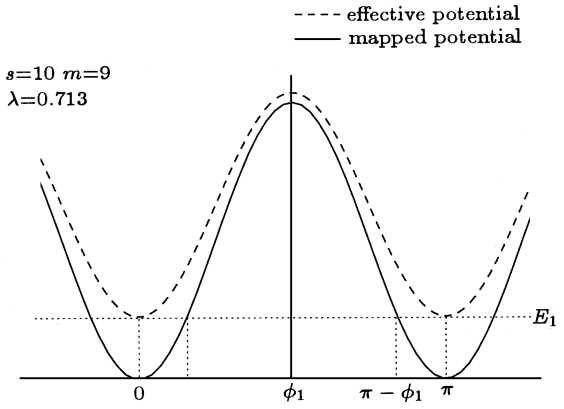


Fig.4. Illustration of the energy barrier to penetrate for the first excited state. The solid line represents the mapped potential starting from Eq.(2) and the dotted line represents the effective potential starting from Eq.(4).

Table 1. Real part of the classical action of the generalized path integral (the first line) and the generalized instanton method (s=10, h=0).

m	9	8	7	6
generalized path integral	22.268	19.794	17.320	14.845
generalized instanton method	18.359	13.535	9.437	5.921

Now we turn to the result predicted by the perturbation method. The results for λ=0.713 and h=0 are shown in Fig.5. In contrast to the generalized path integral, the perturbation method predicts tunnel splitting larger than the exact numerical results. The ground state tunnel splitting found by the pertur-

bation method is about five times larger than the exact numerical result for s=10. For a given s, the higher the excited state, the closer the predicted tunnel splitting to the exact numerical result. It can be seen from Figs.2 and 5 that the discrepancy between the perturbation method and the exact method is lower than the generalized path integral, but larger than the generalized instanton method. The results in Fig.5 also indicate that the discrepancy increases as the spin number increases, especially for the ground state tunnel splitting. In fact, the contribution of the classical action of the ground state in the case of h=0 can be known from Eq.(6), namely

$$\mathrm{e}^{-S_{\mathrm{ci}}} = \left(\frac{q}{1+\sqrt{1-q^2}}\right)^s, \tag{15}$$

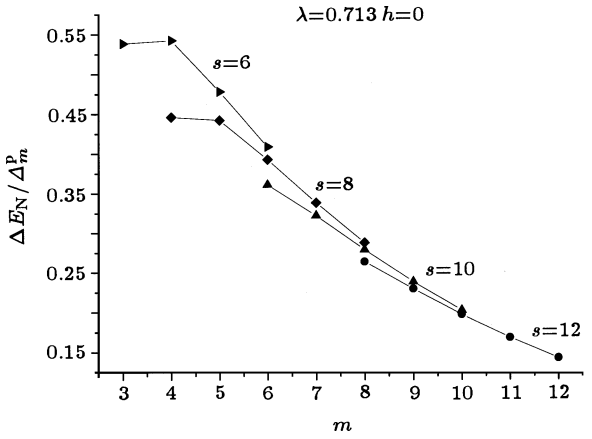


Fig.5. Illustration of the ratio of the exact result ΔE_{N} to the theoretical prediction Δ_m^{P} of Eq.(12) in semi-log plot

where $q = (K_1 - K_2)/(K_1 + K_2)$, while from Eq.(13), the corresponding term by the perturbation method is $\mathrm{e}^{-S_{\mathrm{cp}}} = [q/2/(1-q)]^s$. In the limit $q \ll 1$, one can find that

$$\mathrm{e}^{-S_{\mathrm{cp}}}/\mathrm{e}^{-S_{\mathrm{ci}}} \simeq \left[\frac{1+q}{1+q^2/4}\right]^s \simeq 1.$$

However, since $(1+q)/(1+q^2/4) > 1$, we have

$$\lim_{s\to\infty}(\mathrm{e}^{-S_{\mathrm{cp}}}/\mathrm{e}^{-S_{\mathrm{ci}}}) \to \infty, \tag{16}$$

that is, the discrepancy between the perturbation theory and the path integral diverges in the limit $s \to \infty$. Since the path integral of SCS is exact in the limit $s \to \infty$, this result shows that the discrepancy between the perturbation method and the exact result tends to infinity as the spin number becomes very large. The results shown in Fig.5 confirm the above analysis: i.e., the discrepancy increases with the spin number s.

4. Conclusion

We have presented the calculation of tunnel splitting at the excited states using various methods. Our results show that, for spin number around 10, tunnel splitting of the nth excited state predicted by the generalized path integral of SCS is about 10^{-n} times of the exact result. The discrepancy between the perturbation method and the exact result increases with the spin number and tends to infinity in the limit $s \to \infty$. We conclude that the generalized instanton method is the best approximate way to calculate the tunnel splitting in the excited states.

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