Quantum phase interference and parity effects at excited levels in biaxial spin models

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Tunnel splitting in excited states and resonant tunneling of biaxial spin models are investigated by spin-coherent-state path integral with a generalized instanton method. It is found that the interference phase between two symmetric tunneling paths is directly related to the quantization rule of excited states in consideration. Parity effects of both tunneling in excited states and resonant tunneling in biaxial spin models are successfully reproduced.

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Oscillatory tunnel splitting in nanospin systems has attracted considerable interest in recent years.[1–9] Of special interest is the molecular cluster $[(\mathrm{tacn})_6\mathrm{Fe}_8\mathrm{O}_2(\mathrm{OH})_{12}]^{8+}$(or shortly Fe_8) that shows very interesting parity effects in tunnel splitting.[2] Theoretically Fe_8 system was considered as a biaxial spin model with a spin $s=10$, and oscillations as a function of transverse fields applied along the hard axis in ground-state tunnel splitting was first predicted by Garg[3] and observed in the experiment.[2] This oscillation phenomena is understood as a result of the interference between two symmetric tunneling paths, namely, instanton and anti-instanton.[3] In fact, the interference phase comes from the well-known Wess-Zumino term in spin-coherent-state path integral, which also leads to parity effect in ground-state tunneling related to Kramers' degeneracy.[4,5] However, a direct application of the instanton method to tunnel splitting in excited states[6] did not reproduce the right parity effects.[2,7] Tunnel splitting in excited states has been investigated alternatively by a generalized spin-coherent-state path integral[8] and by a discrete WKB method.[9] In the present paper, both tunnel splitting in excited states and resonant tunneling in biaxial spin model are studied by spin-coherent-state path integral with a generalized instanton method. We found that the interference phase is directly related to the quantization rule of excited states in consideration, and parity effects are successfully reproduced by including the contribution of quantized classical orbits.

We first study the biaxial spin model with a field applied on the hard axis, the Hamiltonian is given by

$$\hat{H}=K_1\hat{S}_z^2+K_2\hat{S}_y^2-\alpha\hat{S}_z,\quad K_1>K_2, \tag{1}$$

where $\alpha=g\mu_B h<2K_1 s(1-\lambda)$, $\lambda=K_2/K_1$, and h is the applied field.[6] For a spin system, the Minkowski propagator from an initial state $|\hat{n}_i\rangle$ to a final state $|\hat{n}_f\rangle$ can be written as a spin-coherent-state path integral[3–6]

$$\mathcal{K}_M(\hat{n}_f,T/2;\hat{n}_i,-T/2)=\langle\hat{n}_f|e^{i\hat{H}T/\hbar}|\hat{n}_i\rangle=\int d\Omega\quad e^{iS[\hat{n}]/\hbar}, \tag{2}$$

where

$$S[\hat{n}]=\int_{-T/2}^{T/2}L[\hat{n}]dt,$$

$$L[\hat{n}]=-s\hbar(1-\cos\theta)\dot{\phi}-\langle\hat{n}|\hat{H}|\hat{n}\rangle, \tag{3}$$

and $\langle\hat{n}|\hat{H}|\hat{n}\rangle$ can be found by large spin approximation[3,10]

$$\begin{aligned}\langle\hat{n}|\hat{H}|\hat{n}\rangle&\simeq E(\theta,\phi)\\&=K_1s^2\cos^2\theta+K_2s^2\sin^2\theta\sin^2\phi-\alpha s\cos\theta.\end{aligned} \tag{4}$$

By employing the well-known mapping technique [i.e., by treating $(\phi,\hbar s\cos\theta)$ as canonical variables],[10] the propagator (2) is equivalent to

$$\mathcal{K}_M(\phi_f,T/2;\phi_i,-T/2)=\mathcal{N}_1\int d[\phi]e^{iS_{eff}/\hbar},$$

$$S_{eff}=\int_{-T/2}^{T/2}L_{eff}(\phi,\dot{\phi})dt, \tag{5}$$

where

$$\begin{aligned}L_{eff}(\phi,\dot{\phi})&=\frac{1}{2}m(\phi)\dot{\phi}^2-V(\phi)-\Theta(\phi)\dot{\phi},\\\Theta(\phi)&=s-\alpha m(\phi),\end{aligned} \tag{6}$$

and

$$\begin{aligned}V(\phi)&=K_2s^2\sin^2\phi-\frac{\alpha^2\lambda\sin^2\phi}{4K_1(1-\lambda\sin^2\phi)},\\m(\phi)&=\frac{1}{2K_1(1-\lambda\sin^2\phi)}.\end{aligned} \tag{7}$$

The propagator in Eq. (5) represents a particle with a position-dependent mass $m(\phi)$ moving in a double-well potential $V(\phi)$.

Quantization of excited states in a spin system can be done in the same way used for a double-well system.[11] Classical orbits[12] of the Hamiltonian (1) are the intersections of the energy surface $K_1S_z^2+K_2S_y^2-\alpha S_z=E_n$ and the sphere

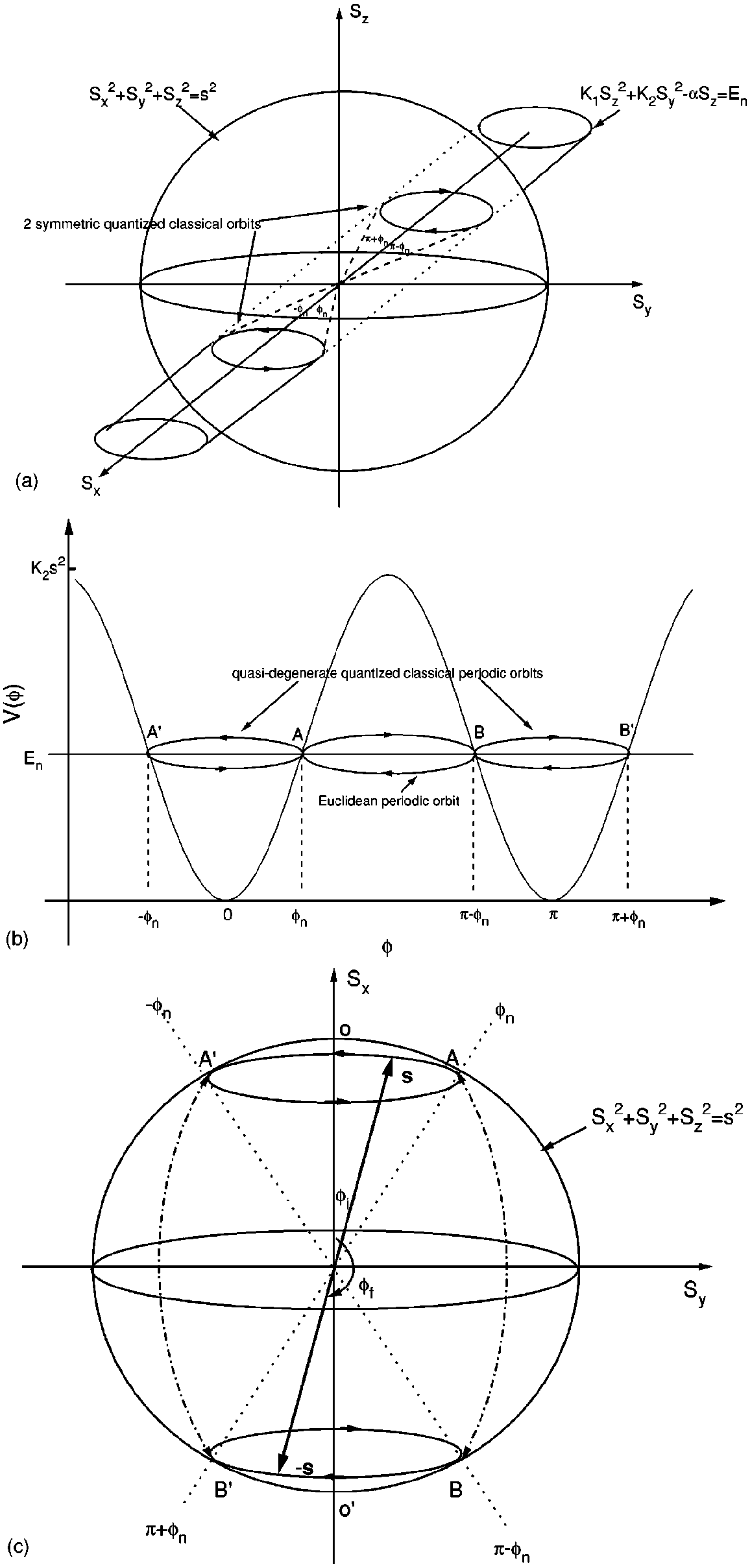

FIG. 1. (a) Illustration of classical orbits as the intersections of energy surface $K_1^2S_z^2+K_2S_y^2-\alpha S_z=E_n$ and the sphere $S_x^2+S_y^2+S_z^2=s^2$. The field angles of symmetric ellipses in XY plane are shown in the figure, these field angles are corresponding to the turning points of the classical periodic orbits shown in (b). (b) Illustration of the mapped double-well potential and classical periodic orbits in zero-field condition. (c) Illustration of a complete tunneling for a spin from one quantized classical orbit to another quasidegenerate orbit. There are two symmetric tunneling paths, path$_1$: $-\mathbf{s}\rightarrow B'\rightarrow A'\rightarrow A\rightarrow \mathbf{s}$; path$_2$: $-\mathbf{s}\rightarrow B'\rightarrow B\rightarrow A\rightarrow \mathbf{s}$. For ground-state tunneling, two quasidegenerate orbits shrink into two points o and o', then two symmetric tunneling paths reduce to instanton and anti-instanton.

$S_x^2+S_y^2+S_z^2=s^2$, which show as symmetric ellipses in Fig. 1(a). In the mapped double-well system, such classical orbits represents classical periodic orbits inside the well[11] as shown in Fig. 1(b). Quantization of classical orbits can be done by introducing the Bohr-Sommerfeld quantization rule,[12] i.e., $\oint p\,dx=n2\pi\hbar$, or $\oint s\cos\theta d\phi=n2\pi$. In general, p(or $s\cos\theta$) can be expressed as a function of E_n and ϕ by the relation $E(\theta,\phi)=E_n$, then the quantization condition reads as

$$2\int_{-\phi_n}^{\phi_n} d\phi p(E_n,\phi) = 2\int_{\pi-\phi_n}^{\pi+\phi_n} d\phi p(E_n,\phi) = n2\pi\hbar, \quad n=0,1,2,\ldots, \quad n<s \tag{8}$$

where ϕ_n is determined by $V(\phi_n)=E_n$. In the present case, we have

$$p(E_n,\phi)/\hbar=\{2m(\phi)[E_n-V(\phi)]\}^{1/2}+\frac{u_0}{(1-\lambda\sin^2\phi)},$$
$$u_0=\frac{\alpha}{2K_1 s}. \tag{9}$$

Since $p(E_n,\phi+\pi)=p(E_n,\phi)$, the quantized levels found in this way are pairs of quasidegenerate levels. By taking the anisotropic parameters suitable for Fe_8 ($s=10$),[2] it is found that the first four pairs of quasidegenerate excited levels determined by the above scheme are in good agreement with the diagonalization of the Hamiltonian (the error is within 1%).

Now we consider tunneling between two quantized quasidegenerate excited spin states with energy E_n. As shown in Fig. 1(c), the situation is different from the ground state where both the initial and final state are points in the sphere surface, in the case of excited state, however, tunneling happens between two quantized classical orbits. Can such a tunneling be described by an imaginary time tunneling $A\rightarrow B$ (or $A'\rightarrow B'$) as in the case of ground state? The answer is **no**. It is because that the Hamiltonian (1) has two fold rotation symmetry around z axis [i.e., $H(\theta,\phi+\pi)=H(\theta,\phi)$], the two quasidegenerate excited spin states should have the same symmetry. Consequently, tunneling should be described by a propagator $\mathcal{K}_M^{E_n}(\phi_f,T/2;\phi_i,-T/2)$ with $\phi_f-\phi_i=\pi$, where ϕ_i and ϕ_f are two symmetric points in two quasidegenerate quantized orbits as shown in Fig. 1(c). Hence a complete description for tunneling in excited states should include both imaginary and real-time propagator.[13] Such a kind of propagator was first evaluated by McLaughlin[14] by choosing a contour in the lower half complex t plane joining $-$T/2 to T/2 in such a way that Im(t) decreases. The contour suitable for the present case is shown in Fig. 2, then by McLaughlin's result,[14] we have

$$\lim_{\hbar\to 0}\mathcal{K}_M^{E_n}(\phi_f,T/2;\phi_i,-T/2) = \lim_{\hbar\to 0}\int\int d\phi_1 d\phi_2 \mathcal{K}_M^{E_n}(\phi_1,t_1;\phi_i,-T/2) \times\mathcal{K}_E^{E_n}(\phi_2,t_1-iT_1;\phi_1,t_1) \times\mathcal{K}_M^{E_n}(\phi_f,T/2-iT_1;\phi_2,t_1-iT_1), \tag{10}$$

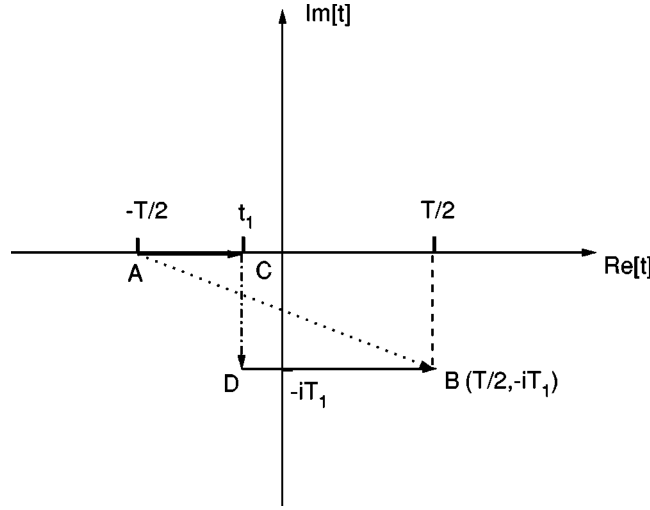

FIG. 2. Illustration for the contour of path integration to ensure that each propagator in Eq. (10) can be evaluated by saddle-point approximation.

where T_1 is the time interval for Euclidean propagator, $T_1=\int_{\phi_n}^{\pi-\phi_n}d\phi m(\phi)/|p(E_n,\phi)|$, while ϕ_1 and ϕ_2 are turning points. By symmetry, there are two symmetric tunneling paths from ϕ_i to ϕ_f, namely,

$$\text{path}_1:\phi_i\rightarrow\phi_n\rightarrow\pi-\phi_n\rightarrow\phi_f;$$
$$\text{path}_2:\phi_i\rightarrow-\phi_n\rightarrow\pi+\phi_n\rightarrow\phi_f, \tag{11}$$

which play similar roles as instanton and anti-instanton in ground-state tunneling.[3,15,16] The propagator of path_1 and path_2 can be found by using Eqs. (6) and (10), and the contour shown in Fig. 2. Up to one loop approximation, we have

$$\mathcal{K}_{1,2}^{E_n}(\phi_f,T/2-iT_1;\phi_i,-T/2) = I(0,T/2-iT_1;0,-T/2)e^{(i/\hbar)S^{1,2}}, \tag{12}$$

where $I(0,T/2-iT_1;0,-T/2)$ is the well-known fluctuation functional integral that can be found by the shifting method,[11,15] while

$$S^1=-\Theta\hbar+iS_c-E_n(T-iT_1) +\left(\int_{\phi_i}^{\phi_n}+\int_{\pi-\phi_n}^{\phi_f}\right)d\phi p(E_n,\phi), \tag{13}$$

$$S^2=\Theta\hbar+iS_c-E_n(T-iT_1) +\left(\int_{\phi_i}^{-\phi_n}+\int_{\pi+\phi_n}^{\phi_f}\right)d\phi p(E_n,\phi), \tag{14}$$

and

$$\Theta=s\pi-\theta_s, \quad \theta_s=s\int_0^{\pi}\alpha m(\phi)d\phi,$$

$$S_c=\int_{\phi_n}^{\pi-\phi_n}d\phi\sqrt{2m(\phi)[V(\phi)-E_n]}. \tag{15}$$

The total transition amplitude from one quantized orbit to another orbit can be found by an integration over ϕ_i (and thus ϕ_f),[17] i.e.,

$$A_{+-}^{E_n}=\langle E_{n+}|\exp[-i\hat{H}(T-iT_1)/\hbar]|E_{n-}\rangle$$
$$=\int\int d\phi_i d\phi_f \Psi^*_{E_{n+}}(\phi_f)\Psi_{E_{n-}}$$
$$\times(\phi_i)\mathcal{K}_M^{E_n}(\phi_f,T/2-iT_1;\phi_i,-T/2), \qquad (16)$$

where $\Psi_{E_{n\pm}}(\phi_{i,f})=\langle\phi_{i,f}|E_{n\pm}\rangle$ represent quasidegenerate excited states in consideration. By employing the expansion

$$\mathcal{K}_M^{E_n}(\phi_f,T/2-iT_1;\phi_i,-T/2)$$
$$=\hat{P}_{E_n}\sum_j \Psi_j^*(\phi_i)\Psi_j(\phi_f)\exp[-iE_j(T-iT_1)/\hbar], \qquad (17)$$

$\hat{P}_{E_n}$ means that we take only terms with energy closest to E_n, then in the same way as that of instanton method,[15,16] we can find

$$A_{+-}^{E_n}\simeq\exp[-iE_n(T-iT_1)/\hbar]\sinh\left[\frac{1}{2}\Delta E_n i(T-iT_1)/\hbar\right], \qquad (18)$$

where ΔE_n represents the tunnel splitting.

In the following, we use the WKB approximation

$$\Psi_{E_n}(\phi_i)=\frac{c}{\sqrt{\dot{\phi}_i}}\exp\left[\frac{i}{\hbar}\int_{-\phi_n}^{\phi_i}d\phi p(E_n,\phi)\right],$$

$$\Psi_{E_n}(\phi_f)=\frac{c}{\sqrt{\dot{\phi}_f}}\exp\left[\frac{i}{\hbar}\int_{\pi-\phi_n}^{\phi_f}d\phi p(E_n,\phi)\right], \qquad (19)$$

where

$$c^{-2}=T/2=\int_{-\phi_n}^{\phi_n}d\phi\left\{\frac{1}{2}m(\phi)/[E_n-V(\phi)]\right\}^{1/2}. \qquad (20)$$

Substituting Eqs. (12) and (19) into Eq. (16), and evaluating the integration over ϕ_i (or ϕ_f) by the method of steepest descent,[15,17] we can find

$$A_{1,2}^{E_n}\simeq c^2\exp[iE_n(T-iT_1)/\hbar]e^{iS_c^{1,2}/\hbar}\ \ i(T-iT_1),$$
$$S_c^{1,2}=-\Theta\hbar+iS_c+\Delta_{1,2}, \qquad (21)$$

where

$$\Delta_1=\int_{-\phi_n}^{\phi_n}d\phi p(E_n,\phi)=n\pi\hbar,$$

$$\Delta_2=-\int_{\pi-\phi_n}^{\pi+\phi_n}d\phi p(E_n,\phi)=-n\pi\hbar, \qquad (22)$$

then the total transition amplitude can be found by[4,15,16]

$$A_{+-}^{E_n}=\exp[-iE_n(T-iT_1)/\hbar]$$
$$\times\sum_{m_1m_2}^{m_1+m_2:\text{odd}}\frac{[c^2\ \ i(T-iT_1)]^{m_1+m_2}}{m_1!m_2!}$$
$$\times\exp[im_1S_c^1/\hbar+im_2S_c^2/\hbar]$$
$$=\exp[iE_n(T-iT_1)/\hbar]\sinh$$
$$\times[c^2(e^{iS_c^1/\hbar}+e^{iS_c^2/\hbar})i(T-iT_1)/\hbar]. \qquad (23)$$

Comparing with Eq. (18), one can read off

$$\Delta E_n=2|c^2(e^{iS_c^1/\hbar}+e^{iS_c^2/\hbar})|$$
$$=4c^2e^{-S_c/\hbar}|\cos[(s-n)\pi-\theta_s]|, \quad n<s. \qquad (24)$$

This result shows that tunnel splitting of the nth quantized excited level will oscillate with the transverse field in exactly the same way as the ground state (i.e., when $n=0$), and thus reproduces analytically what has been found by numerical diagonalization of the Hamiltonian.[2,7] As a matter of fact, the interference phase $[(s-n)\pi-\theta_s]$ has been found by Garg using a discrete WKB method,[9] but here there is no constraint $n\ll s$. Furthermore, the above derivation clearly shows that the extra factor $-n\pi$ comes from the quantization rule of excited states [i.e., Eq. (8)], our result thus indicates that the interference between spin trajectories of quasidegenerate excited states is directly related to the quantization rule of excited states.

The above analysis can be directly generalized to resonant tunneling when the Hamiltonian is given by (h_1 is the field along the easy axis)

$$\hat{H}=K_1\hat{S}_z^2+K_2\hat{S}_y^2-\alpha_1\hat{S}_x, \quad \alpha_1=g\mu_Bh_1. \qquad (25)$$

To follow both mapping technique and quantization scheme given above, we can use the approximation $\sin\theta=\sqrt{1-\cos^2\theta}\simeq 1-\frac{1}{2}\cos^2\theta$, owing to the fact that the spin vector lies almost in XY plane. The position-dependent mass and potential are now given by

$$m_1(\phi)=\frac{1}{2K_1(1-\lambda\sin^2\phi)+(\alpha_1/s)\cos\phi},$$

$$V_1(\phi)=K_2s^2\sin^2\phi-\alpha_2 s\cos\phi, \qquad (26)$$

since $V_1(\phi+\pi)\neq V_1(\phi)$, quantization condition (8) will produce two sets of quantized levels $\{E_m^1\}$ and $\{E_n^2\}$, which represent excited levels belong to two unsymmetric wells. By tuning h_1 to some appropriate values, classical resonance[12] happens between the mth quantized excited state of one well and the nth level in the other well, namely, $E_m^1=E_n^2$, $(m-n)=N$. Since h_1 does not affect the rotation symmetry around the easy axis, there will still be two symmetric tunneling paths: path$_1$: $\phi_i\rightarrow\phi_m\rightarrow\pi-\phi_n\rightarrow\phi_f$ and path$_2$: $\phi_i\rightarrow-\phi_m\rightarrow\pi+\phi_n\rightarrow\phi_f$. The situation is the same as we have done for the symmetric wells except that two degenerate orbits are unsymmetric, which leads to modification, $\Delta_1 = m\pi\hbar$, $\Delta_2 = -n\pi\hbar$. The tunnel splitting is now given by

$$\Delta E = 2c_1^2 e^{-S_{c1}/\hbar}|e^{-i(s-n)\pi} + e^{i(s-n)\pi}e^{-i(m-n)\pi}|$$
$$= \begin{cases} 4c_1^2 e^{-S_{c1}/\hbar}|\cos[(s-n)\pi]|, & m-n=N=2k, \\ 4c_1^2 e^{-S_{c1}/\hbar}|\sin[(s-n)\pi]|, & m-n=N=2k+1, \end{cases} \tag{27}$$

where $k=0,1,2,\ldots$, and

$$S_{c1} = \int_{\phi_m}^{\pi-\phi_n} d\phi \sqrt{2m(\phi)[V_1(\phi)-E_m^1]},$$

$$c_1^{-2} = \int_{-\phi_m}^{\phi_m} d\phi \{\tfrac{1}{2} m_1(\phi)/[E_m^1 - V_1(\phi)]\}^{1/2}. \tag{28}$$

The above result provides a complete description for parity effects in tunneling of biaxial spin model. When $N=0$ (i.e., $h_1=0$), the result reduces to that of Eq. (24) with $\theta_s=0$. In resonance case ($N\neq 0$), parity effect depends on both the spin s and N. For integer spin, tunneling will be suppressed when N is odd, while for half-integer spin, tunneling will be suppressed when N is even. Taking the experimental setup for Fe_8 ($s=10$) system as an example,[2] resonance happens between the ground state ($n=0$) of the well centered at $\phi=\pi$ and the Nth excited state in the other well, the above result tells that tunneling will be suppressed when $N=1,3,5,\ldots$, in analogy with the ground-state tunneling for half-integer spin as found in the experiment.[2] In fact, the predicted parity effects have been found by numerical diagonalization of the Hamiltonian.[2,7]

As we knew, a complete description for the Fe_8 system needs to include the higher-order term such as $C(S_-^4 + S_+^4)$,[2] we can show that the conclusion on parity effects will not be modified by the higher-order term by following the way we have done. In both resonate tunneling and zero-field condition, one can find that $s\cos\theta$ can be expressed as a purely real function of E_n and ϕ in the classical allowed region, but purely imaginary in classical forbidden region. This implies the interference phase of tunneling path is given by $s\pi + \int_{ca} s\cos\theta d\phi$, the integration is bounded in the classical allowed regions that can be determined by the quantization rule (8), hence the interference phase is exactly the same as we have found. The present work can be considered as a generalized instanton method suitable for tunneling in excited states and resonant tunneling, and applications to other spin systems will be presented elsewhere.

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