

# Crossover temperature for quantum tunnelling in spin systems

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**Abstract.** We derive an analytical expression for the crossover temperature corresponding to the transition from classical activation mechanism to temperature assisted quantum tunnelling in spin systems. The crossover temperature depends on the magnetic configuration and Hessian at the first order saddle point on the energy surface of the system. The theory is applied to several single spin models, including a system with four-fold anisotropy. Good agreement is obtained with experimental results for a molecular magnet containing Mn<sub>4</sub>.

## 1. Introduction

Investigations of the quantum tunnelling in spin systems have been the topic of theoretical and experimental studies over the past few decades. From the theoretical point of view, these problems are of great interest for fundamental basis of quantum theory. They are also practical, because small magnetic particles are good candidates for memory devices and the knowledge of their quantum behaviour helps us evaluate the lower limit of the size of a potential memory unit [1].

In case of spin systems, transitions between stable states separated by a potential barrier can occur via classical thermal activation over the barrier or by quantum tunnelling through the barrier. At sufficiently high temperature the transitions are governed by thermal activation and the rate,  $\Gamma$ , obeys the Arrhenius law,  $\Gamma = \Gamma_0 e^{-U/k_B T}$ , with  $U$  being the height of the energy barrier between the states. As the temperature is lowered, quantum tunnelling becomes the dominant mechanism and the rate eventually becomes temperature independent if the final state is equal or lower in energy than the initial state. The crossover temperature,  $T_c$ , indicates at what temperature the transition mechanism changes from thermal activation to thermally activated quantum tunnelling [2].

We propose a general approach for calculating the crossover temperature and give an analytical formula for  $T_c$  derived for a wide range of spin systems with arbitrary anisotropy in an external magnetic field. The formula reduces to known analytical solutions for simple spin systems [3,4], but also works for complex systems, for which only numerical results have been available so far.



## 2. Derivation of the formula

The thermally averaged escape rate is given by

$$\Gamma(T) = \frac{1}{Z_0} \sum_n \Gamma_n e^{\frac{-E_n}{k_B T}}, \quad (1)$$

where  $Z_0$  is the partition function of the initial state,  $\Gamma_n$  are quantum transition probabilities from energy levels  $E_n$ , and  $T$  is the temperature of the bath. The transition probabilities can be estimated from the Euclidean (imaginary-time) action as functional integral from the  $\exp(-S_E)$ . Within the semi-classical approximation, the dominant contribution to the escape rate is given by the saddle point of the action and the escape rate can be estimated with an exponential accuracy as

$$\Gamma(T) \propto \exp[-S(\mathbf{q}_{inst})], \quad (2)$$

where  $\mathbf{q}_{inst}$  is the classical path that corresponds to a saddle point to the action  $S$  surface. Hereafter we use atomic units ( $\hbar = 1, e = 1, m_e = 1$ ).

We consider a system with a quantum spin number,  $s$ , energy specified as a function of the angles  $\theta$  and  $\varphi$  giving the direction of the magnetic vector. The Euclidean action is

$$S(\theta, \varphi) = \int_{-\beta/2}^{\beta/2} d\tau [-is(1 - \cos \theta)\dot{\varphi} + E(\theta, \varphi)]. \quad (3)$$

where  $\beta=1/k_B T$ .

Our method is based on a quadratic expansion of the action around the saddle point of the potential energy surface. In order to find the saddle point, we write the first variation of the action (3):

$$\delta S = \int_{-\beta/2}^{\beta/2} d\tau \left[ \left( -is \sin \theta \dot{\varphi} + \frac{\partial E(\theta, \varphi)}{\partial \theta} \right) \delta \theta + \left( is \sin \theta \dot{\theta} + \frac{\partial E(\theta, \varphi)}{\partial \varphi} \right) \delta \varphi \right], \quad (4)$$

and by setting it to zero, we obtain the equations of motion:

$$\dot{\varphi} = \frac{-i}{s \sin \theta} \frac{\partial E(\theta, \varphi)}{\partial \theta}, \quad (5)$$

$$\dot{\theta} = \frac{i}{s \sin \theta} \frac{\partial E(\theta, \varphi)}{\partial \varphi}. \quad (6)$$

These equations have two types of the solutions: The first is the trivial one,  $\theta = \theta_0$  and  $\varphi = \varphi_0$ , corresponding to a point on the energy surface  $E(\theta, \varphi)$ . The second one is the instanton – a closed trajectory, for which the energy is conserved. When the temperature is close to the crossover temperature, the amplitude of the instanton is small and the trajectory involves only small oscillations in the vicinity of the saddle point,  $\theta = \theta^\dagger$  and  $\varphi = \varphi^\dagger$ , on the potential surface

$$\theta = \theta^\dagger + \delta\theta, \quad \varphi = \varphi^\dagger + \delta\varphi \quad (7)$$

We expand the action (3) in a Taylor series around the saddle point in order to get the second variation

$$S(\theta, \varphi) = S(\theta^\dagger, \varphi^\dagger) + \delta S + \frac{1}{2} \delta^2 S, \quad (8)$$

where

$$\delta^2 S = \int_{-\beta/2}^{\beta/2} d\tau [-2is \sin \theta \delta\dot{\varphi} \delta\theta + (a\delta^2\theta + 2b\delta\theta\delta\varphi + c\delta^2\varphi)], \quad (9)$$

with

$$a = \frac{\partial^2 E}{\partial \theta^2}, \quad b = \frac{\partial^2 E}{\partial \theta \partial \varphi}, \quad c = \frac{\partial^2 E}{\partial \varphi^2} \quad (10)$$

Since the  $\delta\theta$  and  $\delta\varphi$  in (7) correspond to closed trajectories, they can be expanded in Fourier series:

$$\delta\theta = \sum_{n=-\infty}^{\infty} \theta_n e^{\frac{2\pi i n \tau}{\beta}}, \quad (11)$$

$$\delta\varphi = \sum_{n=-\infty}^{\infty} \varphi_n e^{\frac{2\pi i n \tau}{\beta}}, \quad (12)$$

and the second variation of the action in (9) written in terms of the Fourier coefficients  $\theta_n$  and  $\varphi_n$ :

$$\frac{1}{2} \delta^2 S = \beta \sum_{n=0}^{\infty} \left[ \frac{2\pi s \sin \theta^\dagger}{\beta} n (\varphi_n \theta_n^* - \theta_n \varphi_n^*) + a \theta_n \theta_n^* + b (\varphi_n \theta_n^* + \theta_n \varphi_n^*) + c \varphi_n \varphi_n^* \right]. \quad (13)$$

At sufficiently high temperature,  $\delta^2 S$  has only one negative eigenvalue, giving correspondence between  $\delta^2 S$  and the Hessian at the saddle point. However, as the temperature is lowered, a second negative eigenvalue appears, signifying the crossover from the classical regime to a quantum tunnelling regime. Thus, the crossover temperature is the highest temperature at which the  $\delta^2 S$  has two negative eigenvalues. The expression for the crossover temperature can be written as:

$$T_c = \frac{\sqrt{b^2 - ac}}{2\pi k_B s \sin \theta^\dagger}. \quad (14)$$

### 3. Applications

#### 3.1. Uniaxial spin system with a two-fold anisotropy

In order to test our approach, we choose the simple and well-studied spin system with axial symmetry and transverse applied magnetic field:

$$\hat{H} = -DS_z^2 - H_x S_x, \quad (15)$$

here  $D$  is an anisotropy and  $H_x$  is an applied field. The corresponding classical energy surface is:

$$E(\theta, \varphi) = -Ds^2 \cos^2 \theta - H_x s \sin \theta \cos \varphi, \quad (16)$$

with a saddle point at  $(\theta^\dagger, \varphi^\dagger) = (\frac{\pi}{2}, 0)$ . The crossover temperature obtained from eq. (14) is

$$T_c = \frac{\sqrt{H_x(2Ds - H_x)}}{2\pi k_B}. \quad (17)$$

This solution is equivalent to previously published results for this special case (see eq. 13 in ref. [3]).

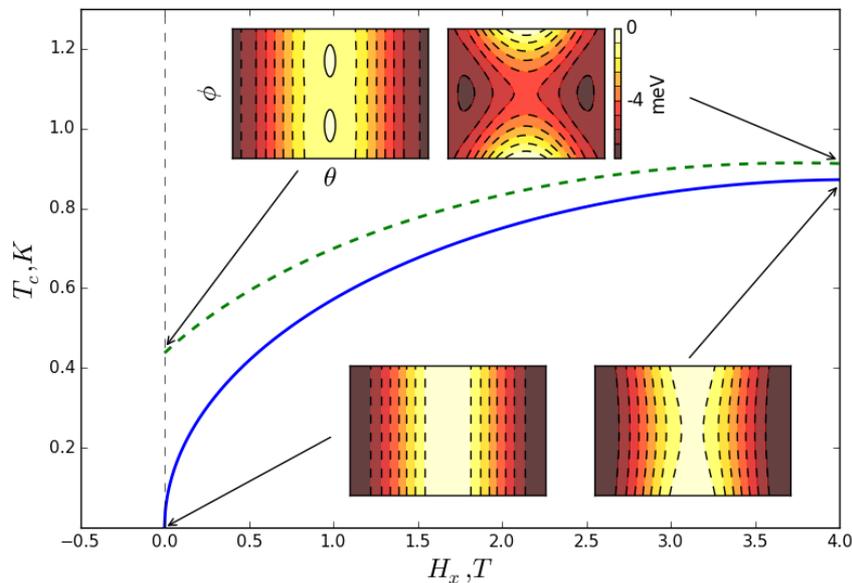
#### 3.2. Uniaxial spin system with a four-fold anisotropy

When eq. (14) is applied to a system with four-fold transverse anisotropy, described by the Hamiltonian:

$$\hat{H} = -DS_z^2 - BS_z^4 - C(S_+^2 + S_-^2) - H_x S_x, \quad (18)$$

the higher-order anisotropy terms are found to play a crucial role. Even for a small value of the parameter  $C$  (usually it is four orders of magnitude smaller than  $D$ ), the crossover temperature becomes non-zero even in the absence of a field, as can be seen from figure 1. The crossover temperature in this case is

$$T_c = \frac{\sqrt{(H_x + 32Cs^3)(2Ds - 8Cs^3 - H_x)}}{2\pi k_B}. \quad (19)$$



**Figure 1.** Dependence of  $T_c$  on applied magnetic field,  $H_x$ , for a systems with two-fold and four-fold anisotropy. Solid line shows results for a system with two-fold anisotropy, eq. (15). The dashed line shows results for a system with four-fold anisotropy, eq. (18). All parameters are taken from ref. [6]. By adding higher-order anisotropy, the crossover temperature becomes finite even in the absence of a magnetic field. The insets show contour graphs of the energy surfaces (two-fold anisotropy below, fourfold above) at zero field and a field of 4 T.

This example shows how the method works for more complex systems for which only numerical results have been reported previously.

### 3.3. Crossover temperature of $Mn_4$ complex

The molecular magnet  $Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3$  ( $Mn_4$  for short) is a trigonal pyramidal complex with a spin ground state corresponding to  $s = 9/2$ . The Kramers degeneracy prohibits a molecule with a half-integer spin to tunnel. A transverse component in the Hamiltonian is needed to break the symmetry so as to allow for tunnelling [5]. The system is described by the Hamiltonian:

$$\hat{H} = D \left[ S_z^2 - \frac{1}{3} s(s+1) \right] + B_4^0 O_4^0 + B_4^4 O_4^4, \quad (20)$$

where  $O_4^0 = 35S_z^4 - 30s(s+1)S_z^2 + 25S_z^2 + 6s(s+1)$  and  $O_4^4 = \frac{1}{2}(S_+^4 + S_-^4)$ . The application of our formula to estimate the crossover temperature gives  $T_c = 0.6$  K, which is in excellent agreement with experimental measurements [5].

## 4. Conclusions

We have derived an analytical expression for the crossover temperature in spin systems characterized by a single magnetic vector. The crossover temperature corresponds to the transition from classical activation mechanism to temperature assisted quantum tunnelling. Using our formula,  $T_c$ , can be estimated given the magnetic configuration and Hessian at the first order saddle point on the energy surface characterizing the system. The formula has been applied to several single spin models, including a system with four-fold anisotropy. It is in agreement with previously obtained analytical results for simple axial spin system. It was also applied to a system with four-fold symmetry for which

only numerical simulations had been reported previously. Good agreement with experimental results were obtained for a molecular magnet containing  $Mn_4$ .

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