Tale 5
Tunneling of Magnetization

In this Tale about the tunneling of magnetization in molecular clusters, we use the results of Tale 75.

Imagine a large molecule - a cluster hosted by a rigid matrix and containing atoms of transition elements. The exchange interaction between the spins of these atoms leads to magnetic ordering which we assume to be ferromagnetic, so that the molecule has a total magnetization $\mathbf{M}$. Let s be the spin associated with this magnetization and let the magnetization be directed along the unit vector $\mathbf{n}$ characterized by spherical angles θ and ϕ. We assume that the energy of magnetic anisotropy E_A is of the "easy-plane" type and it dependence on spherical angles has the form :

$$E_A(\theta,\phi) = K_z \cos^2\theta + K_y \sin^2\theta \sin^2\phi, \quad K_z > K_y > 0, \tag{1}$$

where $K_{y,z}$ are the constants of anisotropy.
The lines of equal energy E_A, as it is given by Eq (1), are shown in Fig 1. One can see that the energy E_A has two maxima at M_+ $(\theta = 0)$ and M'_+ $(\theta = \pi)$, two minima at M_- $(\theta = \pi/2,\ \phi = 0)$ and M'_- $(\theta = \pi/2,\ \phi = \pi)$ and

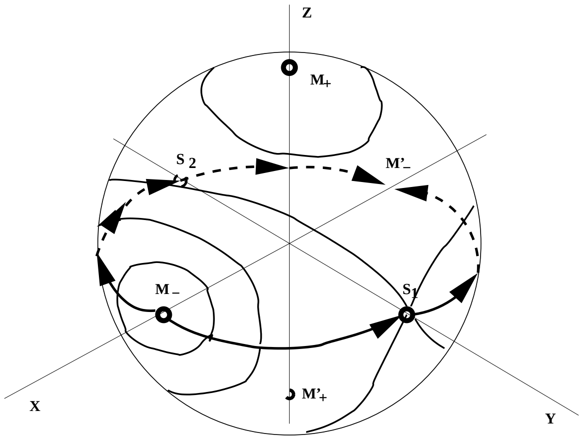

Figure 1: The lines of equal energy of magnetic anisotropy E_A in a molecular cluster. M_+ and M'_+ denote maxima, M_- and M'_- - minima and $S_{1,2}$ - saddle points of E_A. Solid lines $M_-S_1M'_-$ and $M_-S_2M'_-$ show optimal trajectories for tunneling between the minima.

two saddle points at S_1 $(\theta = \pi/2,\ \phi = \pi/2)$ and S_2 $(\theta = \pi/2,\ \phi = 3\pi/2)$. For $s \to \infty$, the magnetization is at one of the mimima and is directed either along or opposite to the x-axis. Since the spin components do not commute at finite values of s, the magnetization is involved in a zero-point motion which results in its tunneling between the minima and a possible splitting of the energy of the ground state. as in the case of a quantum particle in the two-well potential. The difference between this well-known case and that the magnetization may tunnel along different trajectories on the sphere. In particular, the action A corresponding to the motion along the trajectories $M_-S_1M'_-$ and $M_-S_2M'_-$ is the same, which makes these trajectories equivalent.
In order to find the energy splitting, one must calculate the

mixing amplitude

$$G_t = \langle M'_- | e^{-\mathcal{H}t} | M_- \rangle = \int \mathcal{D}\theta(t)\ \mathcal{D}\phi(t)\ e^{-\int \mathcal{L}dt'}, \qquad (2)$$

where the Hamiltonian of the cluster $\mathcal{H}$ and the Lagrangian $\mathcal{L}$ contain the energy of magnetic anisotropy E_A as a potential energy. The kinetic energy contribution to the Lagrangian of moving spin is the same as for a charged particle moving around a magnetic monopole as discussed in Tale 75. Therefore, the Lagrangian has the form

$$\mathcal{L} = is\left(\dot{\phi} - \dot{\phi}\cos\theta\right) + E_A(\theta, \phi) \qquad (3)$$

The equation of motion for the Lagrangian (3) is the the well-known Bloch equation : the first term in (3) generates the time derivative, while the second term - the term with a torque. For $s \gg 1$, probability of tunneling is small and the mixing amplitude (2) can be estimated using the method of steepest descend for Feynman's path integral. Two optimal trajectories for the tunneling are shown by the solid lines in Fig 1. Therefore,

$$G_t \propto e^{-E_0 t} \sum_{m,l\geq 1}^{\langle m+l \rangle} \frac{(Dt)^{m+l}}{m!l!} e^{is\pi(m-l)} e^{-A_0(m+l)}, \qquad (4)$$

where the sum is taken over the numbers m and l of passing along different optimal trajectories respectively. Here D is the determinant related to the integration over Gaussian fluctuations in the method of steepest descend, A_0 is the action corresponding to a single optimal path:

$$e^{-A_0} = \left(\frac{1-\sqrt{\lambda}}{1+\sqrt{\lambda}}\right)^s, \quad \lambda = \frac{K_y}{K_z}. \qquad (5)$$

and $\langle k \rangle$ means that k is an odd integer.
Evaluating the sum in the right-hand side of Eq (5), obtain the following expression for G_t

$$G_t \propto e^{-E_0 t} \ \sinh \left[2Dt \cos \pi s \ e^{-A_0} \right], \tag{6}$$

which shows that, due to the tunneling, the twofold degenerate level of energy E_0 splits into two levels of energies $E_0 \pm \Delta/2$, where

$$\Delta = 4D |\cos \pi s| \tag{7}$$

Note that for a half-integer s splitting vanishes and degeneracy remains unbroken. This is a general phenomenon (*Kramers degeneracy*), related to the symmetry with respect to time inversion. In our calculations, this phenomenon reveals itself in the cancellation for half-integer s of the contributions of two optimal trajectories.
If a magnetic field H is applied along the "hard" (z) axis, the symmetry with respect to time inversion is broken resulting in the energy splitting. Indeed, the extra contribution to the Lagrangian could be written in the form

$$\delta \mathcal{L} = \frac{H}{\pi} \ \dot{\phi} \ \sin \theta \tag{8}$$

which gives for the splitting Δ

$$\Delta = 4D |\cos(\pi s + H)| \tag{9}$$

Figure 2 presents the data of an experiment in which the oscillations of *Delta* as a function of magnetic field H have been observed.