

Field-tuned quantum tunnelling of the magnetization in small magnetic particles

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Abstract. – We present staircase magnetization curves for single-spin models of uniaxial magnets as obtained from the numerically exact solution of the time-dependent Schrödinger equation. Steps are shown to correspond to field-tuned tunnelling between different pairs of nearly degenerate energy levels. The role played by second-order and fourth-order transverse anisotropy, the transverse field and the orientation and sweep speed of the applied field are studied. Magnetization curves for excited and non-saturated initial states are also presented. These results are discussed in relation to recent experiments on high-spin compounds.

The study of quantum tunnelling of the magnetization (QTM) [1] in small magnetic systems addresses the intriguing problem of how quantum mechanics underlies classical physics. Magnetization tunnelling in mesoscopic systems has been semiclassically studied by several authors [2]-[4]. More recently, quantum-dynamical calculations for models of nano-magnets such as the Heisenberg model [5] and the single-spin quantum model [6] have shown the occurrence of resonant coherent QTM at zero temperature. Also theoretically, several authors have studied the problem of spin tunnelling in a swept magnetic field [7]-[9].

Recent experiments in magnetic macromolecules arrayed in a crystal [10] have shown steps in the magnetic hysteresis at values of the magnetic field where the energy levels cross. At these values, the magnetization changes at a much shorter time scale than at other values of the field. The experimental observations have been attributed to thermally assisted resonant tunnelling between quantum states in magnetic macromolecules [10]. This interpretation is based on a single-spin $S = 10$ model with strong uniaxial anisotropy, $\mathcal{H} = -DS_z^2 - g\mu_B\mathbf{S}\mathbf{H}$, where D is the uniaxial anisotropy energy. The energy levels of this model ($|Sm\rangle$ for $\mathbf{H}||\hat{z}$, where $S_z|Sm\rangle = m|Sm\rangle$) coincide at regularly spaced magnetic field values, $g\mu_B H_n = nD$, and the separation between the steps observed in experiments leads to reasonable values of D . For QTM to occur this model has to be extended to include symmetry breaking terms such as those

originated from dipolar interaction, interaction with nuclear spins or phonons, etc. [11]-[13].

In this letter we present quantum-mechanical calculations for a single-spin quantum model with uniaxial anisotropy for $S = 10$. We have analysed the effect of a second-order and fourth-order transverse anisotropy, a transverse field (which might have a hyperfine or dipolar origin) and the orientation and sweep speed of the applied magnetic field. The most general Hamiltonian for a single quantum spin including all these interactions is

$$\mathcal{H} = -K_x S_x^2 - K_y S_y^2 - K_z S_z^2 - C_x S_x^4 - C_y S_y^4 - C_z S_z^4 - \Gamma S_x - \mathbf{H}(t)\mathbf{S}, \quad (1)$$

where K_z , K_x and K_y are the anisotropy constants along the easy, medium and hard axes, respectively, $\mathbf{S} = (S_x, S_y, S_z)$ is the vector representing the magnetization, C_x , C_y , C_z are the fourth-order anisotropy constants, Γ is the transverse field and $\mathbf{H}(t) = H(t)(\sin \theta, 0, \cos \theta)$ denotes the time-dependent applied magnetic field.

The time-evolution of the magnetization at $T = 0$ is obtained from the exact numerical solution of the time-dependent Schrödinger equation (TDSE), $i\hbar\partial|\Psi(t)\rangle/\partial t = \mathcal{H}|\Psi(t)\rangle$, where $|\Psi(t)\rangle$ denotes the wave function of the spin system at time t . We study the following situation: First we set the applied magnetic field to its minimum value $H(t = 0) = -H_0$ and put the system in the corresponding ground state, *i.e.* $|\Psi(0)\rangle = |\Phi_0(0)\rangle$, where $\mathcal{H}(-H_0)|\Phi_0(0)\rangle = E_0(-H_0)|\Phi_0(0)\rangle$. The time-evolution of the wave function is then calculated by means of $|\Psi(t + \tau)\rangle = \exp[(-i\tau\mathcal{H})|\Psi(t)\rangle]$, where τ is the time-step used to integrate the TDSE. During the integration of the TDSE, the applied field changes from $-H_0$ to H_0 with a given speed, which is defined by the field step ΔH between two consecutive field values and the amount of time τ_H the system feels each constant field. The temporal evolution of the α -th ($\alpha = x, y, z$) component of the spin can be calculated from $\langle S_\alpha(t) \rangle = \langle \Psi(t) | S_\alpha | \Psi(t) \rangle$. For each constant field value we compute the expectation value of S_α averaged over time, $\bar{S}_\alpha = 1/\tau_H \int_0^{\tau_H} dt \langle S_\alpha(t) \rangle$. In the following we will refer to $M = \bar{S}_z/S$ as the magnetization. The energy of the system is given by $E(H(t)) = \langle \Psi(t) | \mathcal{H} | \Psi(t) \rangle$.

Figure 1 shows an example of staircase magnetization curves for model (1) in the case of second-order transverse anisotropy, a transverse field and for an external applied magnetic field with a misalignment of 1 degree. Curves (i) correspond to sweeping the field from $-H_0$ to H_0 and curves (ii) to the opposite case. In both cases the system starts from its ground state. For equidistant field values and only when the field is increasing in absolute value, several steps in the magnetization curve can be clearly observed. In this case $H_n = \pm n0.6K_z$, where $n = 0, 1, 2, 3$ and 4. In order to understand this result it is necessary to look at the spectrum. In fig. 2 we present the energy levels scheme corresponding to fig. 1 exhibiting level crossings at regularly spaced values of the field. Steps can only occur at values of the field where the energy levels are nearly degenerate. The probability for QTM to occur or equivalently, the size of the step, depends on the energy-level splitting of the participating levels, the weight of the corresponding eigenstates in the current state of the system, the field sweep speed and the value of the magnetization itself. If the system is in an eigenstate (Φ_i) that approaches another one (Φ_{i+1}) without crossing it, as in the inset of fig. 2, there are three possibilities: 1) The field changes slowly enough and the energy splitting is not too small. Then the adiabatic theorem applies and the system will stay in the eigenstate it started from. In this case the probability for QTM is one and a maximum step results. 2) The energy splitting is very small or the field sweep speed is too high. Then the probability of staying in the same eigenstate, p_i , becomes negligible. The system is scattered into the other eigenstate and there is no step in the magnetization curve. 3) The intermediate situation in which the system tunnels from Φ_i to Φ_{i+1} . The final state is a linear combination of both eigenstates with weights p_i and $1 - p_i$. In this case, the step of the magnetization is given by $\Delta M = M^{\text{final}} - M^{\text{initial}} = p_i M_i^{\text{final}} + (1 - p_i) M_{i+1}^{\text{final}} - M_i^{\text{initial}}$, where the superscripts *initial*

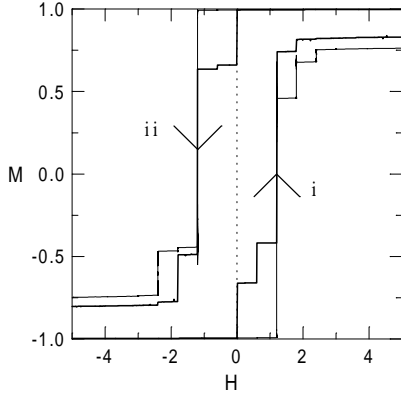


Fig. 1

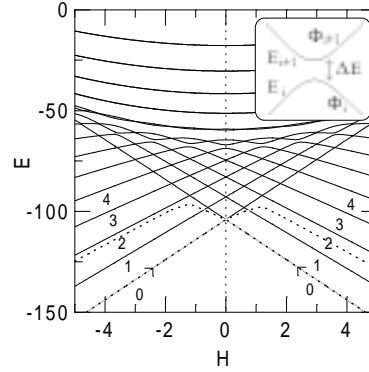


Fig. 2

Fig. 1. – M vs. H for model (1) with $S = 10$, $K_x = 0.6$, $K_y = 0.1$, $K_z = 1.0$, $C_x = C_y = C_z = 0$, $\Gamma = 0.02$ and $\theta = 1^\circ$ when the field goes i) from $-H_0$ to H_0 and ii) from H_0 to $-H_0$ for $H_0 = 9.6$, starting from $\Phi_0(\mp H_0)$, respectively. Field sweep parameters: thick lines, $\Delta H = 0.0012$, $\tau_H = 10^5$; thin lines, $\Delta H = 2.86 \times 10^{-7}$, $\tau_H = 24$.

Fig. 2. – Energy levels (E_i) scheme corresponding to the case of fig. 1. Dashed lines represent the system energy. The inset shows a schematic picture of the “crossing” of two energy levels.

and *final* refer to before and after the crossing. If the field step is small enough, this process can be viewed as a Landau-Zener (LZ) transition [14], [15], the staircase magnetization curves resulting from the succession of these events [9]. In this case the probability of staying in the same eigenstate is well estimated by $p_i = 1 - \exp[-\pi\Delta E^2\tau_H/4M_i^{\text{final}}\Delta H]$. However, if ΔH is too large, LZ theory does not apply and the size of the steps depends in a non-trivial way on ΔH , τ_H and ΔE . Thin lines in fig. 1 ($\Delta H = 2.9 \times 10^{-7}$) agree with LZ predictions while the thick ones ($\Delta H = 0.0012$) do not.

In fig. 1 (thick lines), field-tuned tunnelling occurs between low-energy levels: The first step (at $H = 0$) corresponds to tunnelling between the ground state and the first excited level, the second to tunnelling between the first and second excited levels, and so on. Since the system is initially in the ground state Φ_0 and the energy levels scheme as a function of the magnetic field is such that E_0 only crosses another level at zero field, it is obvious that no step can appear when $|\mathbf{H}|$ decreases. After the first crossing and if a step takes place as in fig. 1, the system state has components in both the ground (E_0) and first excited (E_1) states. The weight of Φ_0 is then fixed. As the field changes a new step can result when E_1 becomes almost degenerate with the second excited level (E_2), after which the weight of Φ_1 is also fixed. This process continues until the probability of a new step becomes negligible. In the calculations, M cannot reach the saturation value even for $H \rightarrow \infty$ since the system can only gain or lose energy through the time-dependent field but not through interaction with the environment. There is an exception and that is when the system stays in the ground state when crossing $H = 0$. Then the maximum step from $M = -1$ to $M = +1$ is found.

In fig. 3 we present results for the Hamiltonian $\mathcal{H} = -K_z S_z^2 - \mathbf{H}(t)\mathbf{S}$, with $\mathbf{H} \parallel \hat{z}$ and $S = 10$, *i.e.* the model used to explain the recent experimental data [10], supplemented by terms that allow for tunnelling processes, *i.e.* model (1). All these cases have in common that for some specific fields H_n , pairs of energy levels become almost degenerate. If $\Phi_0(-H_0)$ is the initial state, the levels involved in the crossing at H_n are E_n and E_{n+1} . As shown in fig. 3(a), the

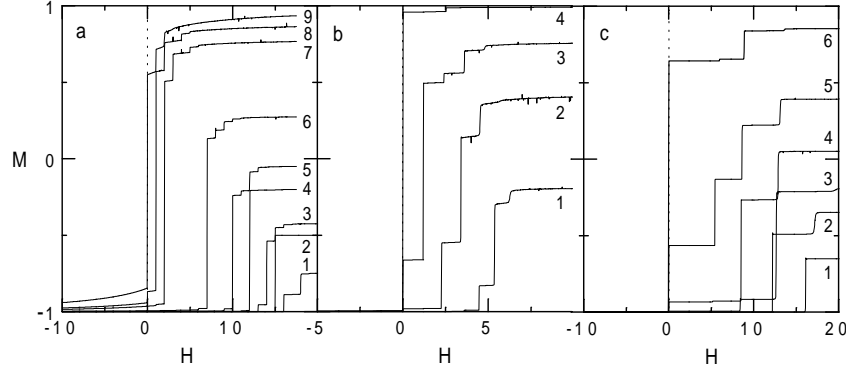


Fig. 3. – M vs. H for model 1) with $S = 10$, $K_z = 1$, $\theta = 0^\circ$ and a) a transverse field term for Γ equal to 1) 0.046, 2) 0.1, 3) 0.25, 4) 0.5, 5) 1, 6) 2, 7) 5, 8) 6.35 and 9) 10; b) second-order anisotropy terms with $K_x = 0.6$ and K_y equal to 1) 0.5, 2) 0.2, 3) 0.1, and 4) 0.0; and c) fourth-order anisotropy terms with $C = C_x = C_y = C_z$ equal to 1) 0.0001, 2) 0.001, 3) 0.003, 4) 0.004, 5) 0.005, 6) 0.007. Field sweep parameters: a) $\Delta H = 0.005$, $\tau_H = 2 \times 10^5$; b) $\Delta H = 0.0025$, $\tau_H = 10^5$; c) $\Delta H = 0.005$, $\tau_H = 1.5 \times 10^5$.

transverse field Γ breaks the rotational symmetry about the z -axis, leading to the occurrence of field-tuned QTM and the corresponding steps in the magnetization. Γ allows all transitions $\Delta m = \pm 1$. At resonance $H_n = nK_z = n$, and the values of n for which steps appear depend on Γ . Thus, for $\Gamma = 0.046K_z = 0.046$ we find $n = 16, 17$; for $\Gamma = 0.25$, $n = 13, \dots, 16$; for $\Gamma = 2$, $n = 6, \dots, 11$; and for $\Gamma = 6.35$, $n = 0, \dots, 5$. The presence of second-order transverse anisotropy terms can also induce QTM. In fig. 3(b) results are shown for $K_z = 1$, $K_x = 0.6$ and several values of K_y . For $K_y = K_x$, the energy and S_z commute and no tunnelling occurs. These transverse anisotropy terms change the spacing between resonant fields although they remain regularly spaced as in case a). These terms allow transitions that obey the selection rule $\Delta m = \pm 2$. For $K_y = 0.5$, $n = 8, 10, 12$ and 14 ; for $K_y = 0.2$, $n = 0, 4, 6$ and 8 ; and for $K_y = 0.1$, $n = 0, 2, 4, 6$ and 8 . Fourth-order anisotropy terms allow the occurrence of field-tuned tunnelling between levels satisfying $\Delta m = \pm 4$. In this case, the fields at which pairs of energy levels cross are not equally spaced. Figure 3(c) shows results for different values of $C_x = C_y = C_z = C$. For instance, for $C = 0.0001K_z = 0.0001$, $n = 16$; for $C = 0.001$, $n = 12$ and 16 ; and for $C = 0.005$, $n = 0, 4, 8$ and 12 . Another parameter in this problem is the field orientation. Calculations for several values of θ show that the time-dependent transverse component H_x can also induce tunnelling. The component that must be tuned to match the level crossings is H_z . The field sweep rate is another important parameter as the probability of QTM depends on it. The lower the sweep rate, the larger the size of the step.

Let us now consider the case of an initial state which is not the ground state but a linear combination of several eigenstates. Unlike the ground state, the excited levels can become nearly degenerate with other levels for $\mathbf{H} \neq 0$, and therefore there is a non-zero probability of finding steps when $|\mathbf{H}|$ decreases, as illustrated in fig. 4(a). Moreover, if the field is reversed after one sweep from $-H_0$ to H_0 (fig. 4(b)), the system restarts from a linear combination of several eigenstates (corresponding to a non-saturated state in an experiment) and the situation is similar to that of fig. 4(a). As shown in fig. 4(b), there is some probability of finding steps when $|\mathbf{H}|$ decreases and of getting both negative and positive steps. The same reasoning applies to QTM from thermally populated excited levels. Although the tunnelling probability increases with the excitation level, and smaller off-diagonal terms are required to induce field-tuned

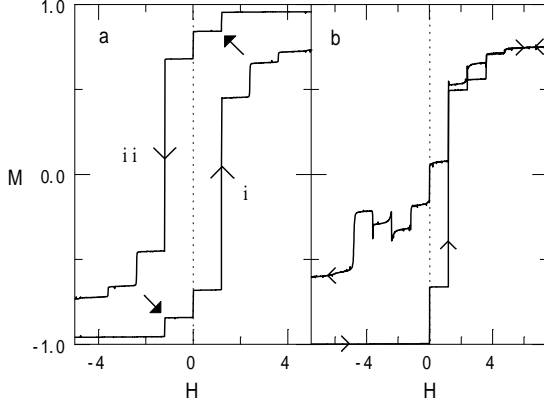


Fig. 4

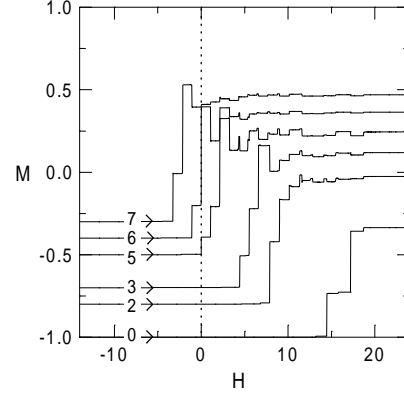


Fig. 5

Fig. 4. – a) M vs. H for model (1) with $S = 10$, $K_x = 0.6$, $K_y = 0.1$, $K_z = 1.0$, $C = \Gamma = 0$ and $\theta = 0^\circ$ when the field goes i) from $-H_0$ to H_0 and ii) from H_0 to $-H_0$ for $H_0 = 10.0$, starting from the initial states: $\Psi_i^{(i)}(0) = c_0\Phi_0(\mp H_0) + c_1\Phi_1(\mp H_0) + c_2\Phi_2(\mp H_0)$, respectively, where $c_0 = 0.7$, $c_1 = 0.22$ and $c_2 = 0.08$. Field sweep parameters: $\Delta H = 0.0025$, $\tau_H = 10^5$. Arrows point at steps for decreasing $|\mathbf{H}|$. b) Same as a) for an initial state in the ground state $\Phi_0(-H_0)$ and when the field goes from $-H_0$ to H_0 and then, before reaching saturation, back to $-H_0$, for $H_0 = 10.0$. At $H = H_0$, where the field is reversed, $\Psi(H_0) = \sum_n c_{2n}\Phi_{2n}(H_0)$, where $c_0 = 0.168$, $c_2 = 0.653$, $c_4 = 0.038$, $c_6 = 0.111$, $c_8 = 0.027$ and $c_{10} = 0.002$.

Fig. 5. – M vs. H for model $\mathcal{H} = -K_z S_z^2 - C_z S_z^4 - C_\pm(S_+^4 + S_-^4) - \Gamma S_x - H_z(t)S_z$ with $S = 10$, $K_z = 1$, $C_z = 0.00198$, $C_\pm = -0.000626$ and $\Gamma = 0.1$ when the initial state is $\Phi_i(-H_0)$, $i = 0, 2, 3, 5, 6, 7$, for $H_0 = -15$. Field sweep parameters: $\Delta H = 0.0015$, $\tau_H = 3.6 \times 10^3$.

QTM, the fact that the tunnelling processes involve excited levels implies that some probability of finding steps when $|\mathbf{H}|$ decreases exists, at variance with the experimental results. Moreover, preliminary experimental results in which the field is reversed before saturation is reached show that steps can appear when $|\mathbf{H}|$ decreases [16], in qualitative agreement with our findings.

As shown in this paper, $T = 0$ field-tuned QTM leads to staircase magnetization curves. When comparing to experiments on Mn-12 the following points deserve attention: a) A transverse field Γ allows $\Delta m = \pm 1$ transitions and yields equally spaced steps, in agreement with experiments [17]. However, the theoretical magnetization curves (with Γ as the only off-diagonal term and $\Phi_0(-H_0)$ as the initial state) look similar to the experimental ones (steps at the first energy level crossings $g\mu_B H_n = nD$, n small) for much larger values ($\Gamma \sim 1-5D \equiv 0.44-2.2$ T) than those estimated for dipolar (~ 0.01 T) or hyperfine (~ 0.05 T) interactions [13]. b) Second-order transverse anisotropy terms are often discarded due to Mn-12 tetragonal symmetry, although local symmetries could affect the structure of the spectrum. These terms are relevant for other systems as “Fe₈” [18]. c) Fourth-order anisotropy terms cannot account for all observed steps and lead to non-equally spaced steps. They can be responsible for small deviations from $\Delta m = \pm 1$ transitions and equally spaced steps. The magnitude of these contributions have recently been estimated from experimental data yielding the following zero-field splitting terms: $\mathcal{H} = \alpha S_z^2 + \beta S_z^4 + \gamma(S_+^4 + S_-^4) + \text{constant terms}$, where $\alpha = -0.39(3)$ cm⁻¹, $\beta = -7.7(7) \times 10^{-4}$ cm⁻¹, and $\gamma = \pm 2.0(5) \times 10^{-5}$ cm⁻¹ [19]. The corresponding energy level scheme shows crossings at fields comparable to the experimental ones. Thus, for instance, levels E_n and E_{n+1} cross at $H = 0$ for $n = 0, 2, 4, \dots$; at $H =$

1.36, 1.17, $1.08\alpha \equiv 0.57, 0.49, 0.45$ T for $n = 1, 7, 11$, respectively; or at $H = 2.65, 2.29, 2.13\alpha \equiv 1.11, 0.96, 0.90$ T for $n = 2, 8, 12$, respectively. The crossings occur at smaller fields for higher levels. Figure 5 shows simulation results using such model in a transverse field $\Gamma = 0.1\alpha \equiv 0.04$ T, for different initial states. The first observable positive steps for some initial states (in brackets the pair of levels involved in the crossing) are: for $\Phi_0(-H_0)$, $H = 14.46$ (12,13), $H = 15.80$ (13,14), $H = 17.21$ (14,15), etcetera; for $\Phi_3(-H_0)$, $H = 4.46$ (10,11), $H = 5.52$ (11,12), and $H = 6.59$ (12,13); for $\Phi_5(-H_0)$, $H = 0$ (10,11), $H = 1.08$ (11,12), and $H = 2.13$ (12,13); and for $\Phi_6(-H_0)$, $H = -1.08$ (11,12), and $H = 0$ (12,13). Larger than estimated symmetry-breaking contributions when starting from the ground state or tunnelling from higher levels (thermal assistance) are necessary to obtain steps at the first energy crossings as in experiments. The latter possibility allows steps for decreasing $|\mathbf{H}|$ (as for Φ_6, Φ_7) and negative (opposite to the field) steps (as for $\Phi_i, i \geq 1$) which had not been previously reported. Further experimental work investigating the possibility of obtaining these types of steps could clarify the effect of thermal activation. Recent experiments [17] have shown that resonant tunnelling from the ground state can also occur. According to our calculations and in agreement with their conclusions, this suggests larger off-diagonal matrix elements. d) Our results and some experimental findings [17] could indicate that the single-spin model proposed for the Mn-12 molecule is too simple to mimic the actual energy spectrum: The single-spin $S = 10$ system is described by 21 eigenstates whereas a proper description of the magnetic state of Mn-12 molecule requires 10^8 states.

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