

QUANTUM TUNNELLING AND MAGNETIZATION DYNAMICS IN LOW DIMENSIONAL SYSTEMS

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Quantum mechanics allows a system to overcome a classically-unsurmountable energy barrier through a mechanism called Quantum Tunnelling (QT). Although pertaining to the quantum domain, QT is the cause of important physical phenomena that can be detected at the macroscopic scale. Some of them have led to breakthrough applications in electronics (tunnel junctions) and imaging (scanning tunnelling microscope).

In solid state physics, a spectacular macroscopic manifestation of QT was discovered in the mid 1990s by studying the behavior of large magnetic molecules comprising several paramagnetic ions coupled by exchange forces [1,2]. Under favourable conditions, the molecules have a giant spin S (with an S quantum number as large as $83/2$) and exhibit an easy-axis magnetic anisotropy. This means that the giant spin has a strong preference to look along a specific molecular axis (say, the Z axis). For instance, in the tetrairon(III) complex with $S = 5$ shown in Fig. 1, this preferred direction is the normal to the molecular plane. Classically, the reversal of the magnetic moment is then subject to an energy barrier U , whose height typically ranges from 10 to 100 K (Fig. 1). Except that at extremely low temperatures (T), the barrier can be overcome by absorption and emission of phonons (i.e. oscillations of the crystal lattice) and the relaxation time, τ , follows the Arrhenius law $\tau = \tau_0 \exp(U/k_B T)$, which is typical of thermally-activated processes (k_B is Boltzmann constant). The exponential increase of τ with lowering temperature implies that at sufficiently low temperature each molecule exhibits a memory effect that can in principle be exploited to store magnetic information.

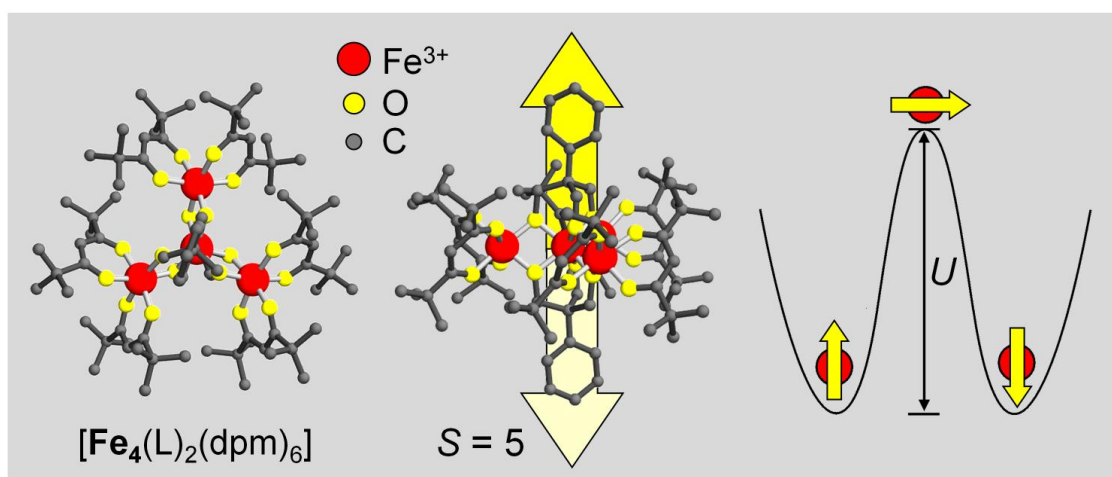


Fig. 1. Four iron(III) ions (each with $s = 5/2$) are exchange-coupled to give an $S = 5$ ground state in $[\text{Fe}_4(\text{L})_2(\text{dpm})_6]$. The easy axis anisotropy along the normal to the molecular plane (*center*) generates an energy barrier U that has to be overcome for the reversal of the magnetic moment (*right*).

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For this reason, these slowly-relaxing magnetic molecules are named Single Molecule Magnets (SMMs) and are investigated as the ultimate limit of high-density magnetic storage – one bit of information per molecule.

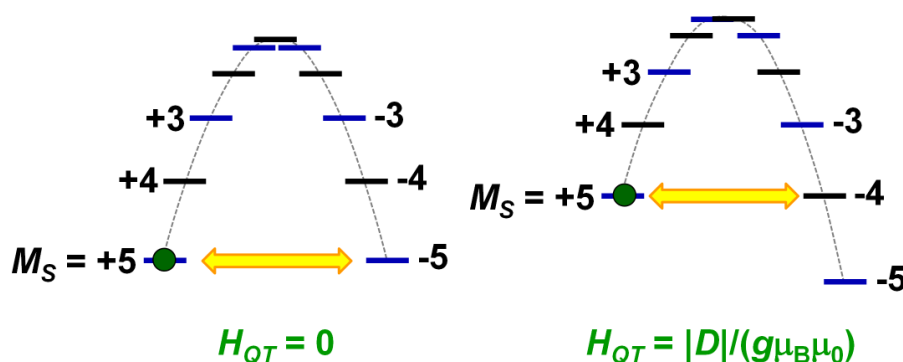


Fig. 2. Pictorial representation of the energy barrier in an SMM with $S = 5$ at two magnetic field values which enable QT. The left and right diagrams correspond to events a and b, respectively, in Fig. 3.

At subKelvin temperatures, however, Arrhenius-like behavior breaks down in most systems and the relaxation time becomes temperature independent. This residual ability of the spin to relax even when no thermal energy is available reflects the intimate quantum character of the molecular spin, which can bypass the barrier via QT. In quantum mechanics, a spin \mathbf{S} can adopt a finite number $(2S+1)$ of different orientations with respect to a given axis (Z). Each orientation corresponds to a different projection of \mathbf{S} along Z and is labelled with the quantum number M_S ($-S \leq M_S \leq S$). The energy barrier is thus constituted by $2S+1$ discrete spin levels, rather than being continuous, as shown in Fig. 2. In order to occur, the QT phenomenon requires two states on opposite sides of the barrier to be degenerate (“in resonance”) and quantum-mechanically admixed. It is straightforward to prove that the former condition is met at evenly-spaced field values given by $H_{QT} = n|D|/(g\mu_B\mu_0)$ where $D < 0$ is the axial zero-field splitting (ZFS) parameter that measures the magnetic anisotropy, μ_B is Bohr magneton, g is Landè factor and n is an integer number (see Figs. 2, 3a and Box 1).

Box 1. The essence of SMM behavior is captured by spin-Hamiltonian

$$\hat{\mathcal{H}}_{\text{ZFS}} = D[\hat{S}_Z^2 - S(S+1)/3] + \mu_B\mu_0g\hat{\mathbf{S}}\cdot\hat{\mathbf{H}} \quad (1)$$

which describes the magnetic anisotropy (first term) and the interaction of the spin \mathbf{S} with the applied field \mathbf{H} (second term). Supposing that \mathbf{H} is applied along the anisotropy axis Z , the energy is a linear function of H (see Fig. 3a):

$$E_{\text{ZFS}}(M_S) = D[M_S^2 - S(S+1)/3] + \mu_B\mu_0gM_SH \quad -S \leq M_S \leq S \quad (2)$$

Since $D < 0$, Eq. (2) predicts that the two states with $M_S = \pm S$ will be found at the lowest energy in zero field and that the other values of M_S correspond to excited states, in accordance with the preference of the spin to lie along Z . The energy difference

$$U = E_{\text{ZFS}}(0 \text{ or } \pm 1/2) - E_{\text{ZFS}}(\pm M_S) \quad (3)$$

gives the energy barrier to spin reversal in zero field (notice that the highest energy state can have $M_S = 0$ or $\pm 1/2$ depending on S being integer or half integer). If the system is now prepared in the $M_S = +S$ state, it is straightforward to show that the level-crossing condition $E_{\text{ZFS}}(S) = E_{\text{ZFS}}(-S+n)$ is satisfied at the field values:

$$H_{QT} = n|D|/(g\mu_B\mu_0) \quad (4)$$

At these evenly-spaced fields, couples of levels are degenerate and QT is possible, provided that quantum mechanical admixture takes place. This implies that Hamiltonian (1) must be complemented with terms that do not commute with \hat{S}_Z , such as those associated with transverse anisotropies and transverse fields.

The resonant character of QT is manifest in the hysteresis loops recorded by cyclically sweeping the applied field at subKelvin temperatures (Fig. 3b). While traditional magnetic materials exhibit smoothly-shaped hysteresis loops, SMMs show spectacular steps in magnetization vs field curves due to QT amplified to a macroscopic level. The plateaus correspond to nonresonant conditions, while the abrupt, stepwise variations of the magnetization indicate sudden accelerations of relaxation due to field-induced degeneracy between spin levels. Notice that, contrary to a commonsense interpretation, relaxation *slows down* by applying a weak magnetic field against the magnetization of a saturated sample! Magnetization steps are most clearly detected by applying the external magnetic field exactly along the anisotropy axis. This is the reason why SMMs have represented a breakthrough in nanomagnetism: they assemble into molecular crystals comprising regularly-spaced and iso-oriented identical magnets, as opposed to the distribution of sizes, shapes and orientations found in a sample of magnetic nanoparticles.

In rare cases, hysteresis loops present additional steps that cannot be explained by a one-body QT mechanism. Again with reference to Fig. 3b, the extra steps labelled with d and d' are associated to pairs of molecules, which undergo a simultaneous spin state change with energy conservation but a net change of magnetization (see Fig. 3a).

As shown by the staircase structure of hysteresis loops, an *externally*-applied magnetic field is a powerful tool to tune the relaxation rate of SMMs. Magnetic fields may however be of *internal* origin as well, as a consequence of intermolecular interactions. In this case, the magnetic field felt by each molecule (H_{tot}) is the sum of the external field H plus the internal field H' . For instance, pairs of exchange-coupled SMMs relax differently than separate individuals because of an internal exchange-bias. More generally, dipolar interactions afford weak communication channels between molecules in a crystal over long distances. The effect of dipolar coupling is most directly revealed by studying the behavior of magnetically-diluted samples. For instance, an Fe^{3+} -based SMM can be embedded in crystals of its diamagnetic Ga^{3+} analogue. Recent work on the Fe_4 complex of Fig. 1 has shown that the zero-field step in the lower branch of the hysteresis loops occurs at $\mu_0 H = 8$ mT in the pure phase but at $H = 0$ in the diluted phase. It follows that each molecule in a saturated sample of the pure phase experiences an internal field H' that is parallel to the magnetization and needs to be externally compensated to achieve resonance ($H_{tot} = 0$). Furthermore, the diluted sample does not show two-body QT resonances (Fig. 3b) due to suppression of intermolecular couplings.

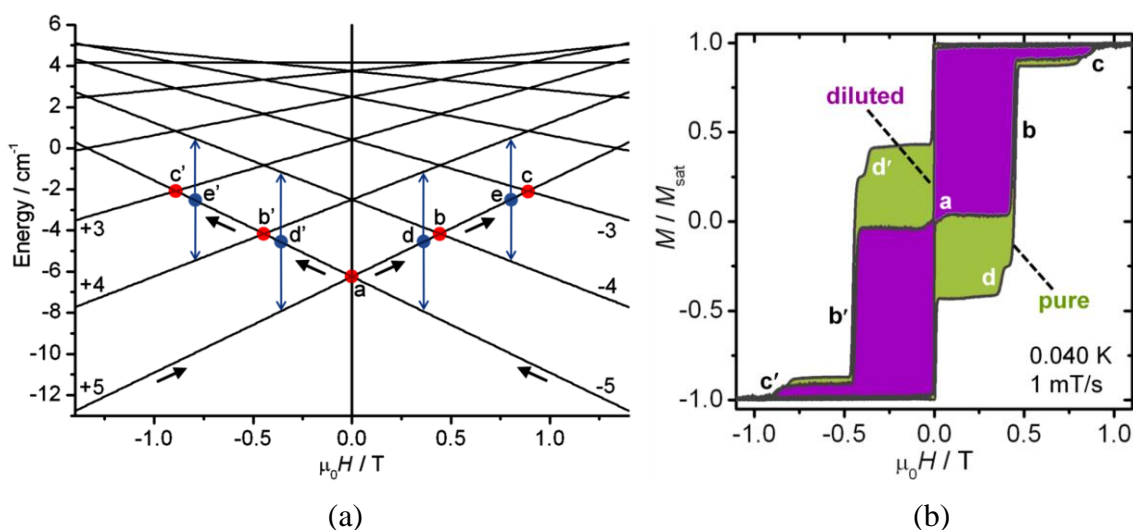


Fig. 3. (a) Zeeman diagram calculated from Eq. (2) with $S = 5$, $D = -0.416 \text{ cm}^{-1}$ and $g = 2.00$. The lowest levels are labelled with the M_S quantum number. One-body QT events are possible at a, b, b', c and c', while two-body QT is expected at d, d', e and e'. (b) Hysteresis cycles recorded by applying the magnetic field along the easy axis (Z) of the tetrairon(III) complex in Fig. 1, in pure and diluted crystalline form (M_{sat} is saturation magnetization).

Resonant QT effects are now regarded as the most distinctive feature of SMMs. Their efficiency and exact position are however very sensitive to minor changes in the molecular structure and in the coupling with the environment. For this reason, the recent observation of QT steps in the magnetization of SMMs supported on a metal surface has provided an important proof-of-concept for the development of SMM-based applications [3].

One of the big research challenges now is to find SMM types that function at higher temperature (above, say, liquid helium temperature). Owing to their large anisotropies, lanthanide-containing complexes are giving very promising results, with anisotropy barriers up to several hundreds of Kelvin in systems based on Dy³⁺ and Tb³⁺ ions [4].

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