Quantum Nanomagnets and Nuclear Spins: An Overview

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Abstract This mini-review presents a simple and accessible summary on the fascinating physics of quantum nanomagnets coupled to a nuclear spin bath. These chemically synthesized systems are an ideal test ground for the theories of decoherence in mesoscopic quantum degrees of freedom, when the coupling to the environment is local and not small. We shall focus here on the most striking quantum phenomenon that occurs in such nanomagnets, namely the tunneling of their giant spin through a high anisotropy barrier. It will be shown that perturbative treatments must be discarded, and replaced by a more sophisticated formalism where the dynamics of the nanomagnet and the nuclei that couple to it are treated together from the beginning. After a critical review of the theoretical predictions and their experimental verification, we continue with a set of experimental results that challenge our present understanding, and outline the importance of filling also this last gap in the theory.

1 Introduction

In the vast and diverse field of quantum magnetism, the quantum properties of large magnetic molecules have enjoyed a strong and motivated research activity for more than a decade. Physicists and chemists, theoreticians and experimentalists, engineers and philosophers, all would find at least one good reason to be interested in these systems. We shall refer here to “quantum nanomagnets” as the broad family of molecules containing a core of magnetic transition-metal ions, which interact by
strong superexchange and which possess magnetic anisotropy due to crystal field effects [13]. At sufficiently low temperatures (typically \( \sim 10 \) K), i.e. much lower than the typical intramolecular exchange interaction energy, the whole molecule effectively behaves as a nanometer-sized magnet. The total ground state spin value can be rather large, \( S \sim 10 \), and is often called “giant spin”. The best studied examples are Mn\(_{12}\) [22], Fe\(_8\) [50] and Mn\(_4\) [3]. The magnetic core of each molecule is stabilized by organic ligands, and the molecules are typically bound to each other by van der Waals forces to form electrically insulating crystals (Fig. 1). With just a few exceptions [49, 16], the magnetic interaction between different molecules is only of dipolar origin, thus orders of magnitude weaker than the intramolecular exchange. Single-ion anisotropies, exchange interactions, point symmetry and crystal structure all contribute in a complicated way to the total magnetic anisotropy of the giant spin. The first great success of molecular magnets consisted in the demonstration of magnetic bistability and hysteresis at the molecular level [35], i.e. not arising from long-range interactions but only from local ones. Molecules possessing this sort of bistability were named “Single Molecule Magnets” (SMMs). One could then think of 2D arrays of such molecules [30] as the ultimate magnetic recording medium [18], with information density \( \sim 10^{12} \) bit/cm\(^2\). For this purpose, the main research goal is to achieve the highest possible single-molecule anisotropy, to allow magnetic bistability up to–ideally!–room temperature.

However, a proper description of bistability in nanomagnets would be incomplete without quantum mechanics. Since the anisotropy barrier for reorientation of the giant spin is large but not infinite, there is in principle a non-vanishing probability for the spin to invert its direction by quantum-mechanical tunneling through the barrier [7]. That is, the magnetic memory would delete itself because of quantum mechanics! The tunneling probability can be estimated with the knowledge of the anisotropy parameters of the giant spin, obtained e.g. by electron paramagnetic resonance or neutron scattering. The resulting tunneling rate turns out to be extremely sensitive to the external magnetic fields applied to the molecule. In Mn\(_{12}\) for instance, one would naively expect the tunneling rate to become astronomically long if a stray field of just \( 10^{-9} \) T is applied along the anisotropy axis. The experimental observation of quantum tunneling of magnetization in Mn\(_{12}\) [41, 10, 15, 12] represented a major breakthrough, but in some sense a puzzling one.

The puzzle was solved by carefully considering the role played by the coupling between giant spin and surrounding nuclei, which are always present in the ligands (\(^1\)H, \(^{13}\)C, \(^{35}\)Cl, \( \ldots \)) or in the magnetic ions themselves (\(^{55}\)Mn, \(^{57}\)Fe, \(^{53}\)Cr, \( \ldots \)). The dynamics of the nuclear spins generates a fluctuating magnetic field on the giant spin, thereby sweeping its energy levels through the tunneling resonance and yielding a finite tunneling probability [32]. Once the giant spin is allowed to have (quantum) fluctuations of its own, it exerts a back-action on the nuclei and essentially determines their dynamics. Thus, the system of giant spin + nuclei must be analyzed as a whole, and the resulting theoretical description is now known as “theory of the spin bath” [34]. It predicts, among other things, a square-root law for the relaxation of magnetization at very low-\( T \) [33], and a dependence of the tunneling rate on the isotopic composition of the sample. These predictions have...