Quantum Spin Dynamics in Molecular Nanomagnets

NSF NIRT Grant 0506926

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Introduction

This NIRT project focuses on molecule-based nanomagnets known as single-molecule magnets (SMMs)[1] and, specifically, on improving fundamental understanding of their quantum spin dynamics. SMMs represent a molecular or 'bottom-up' approach to nanomagnetism. Their key advantages include chemical control of molecular structure, spin, and magnetic anisotropy as well as intra- and intermolecular magnetic interactions. They display properties of much larger ferro- or ferrimagnetic particles prepared by conventional lithographic methods, but in a manner that enables fundamental physics studies. For example, quantum tunneling of the magnetization (QTM) and quantum phase interference[4] have clearly been demonstrated in these materials, leading to suggestions that SMMs could one day be utilized in quantum computational devices.[5-] Furthermore, it has recently become feasible to examine magnetic properties as the number of magnetic ions in a molecule is varied,[11] enabling experiments at the frontier between classical magnetization reversal and quantum tunneling.

Project Objectives

An important aim of this project is the exploration and control of magnetization dynamics. SMMs provide an ideal laboratory to explore magnetization dynamics, including coherent quantum dynamics that have been predicted theoretically. Further, SMMs enable the establishment of structure/property relationships. Specifically, supramolecular chemistry allows unprecedented control over the magnetic unit, and assembly of monodisperse SMMs into crystalline arrays enables very precise characterizations of single-molecule properties, *i.e.* SMMs may be systematically tailored to tackle particular scientific issues. To begin with, one can realize a wide variety of idealized quantum spin states through the choice of molecule, e.g. integer- versus half-integer-spin, uniaxial versus biaxial symmetry, etc. One can then control the magnetic couplings between the SMM and its environment, e.g. by controlling inter-molecular exchange and dipolar interactions through the variation of peripheral ligands or by varying electron-nuclear hyperfine couplings (a potentially important source of decoherence) through deuteration and other isotopic substitutions. Finally, as our collaboration has recently demonstrated, one can controllably engineer quantum couplings between SMMs (e.g. dimers, chains, etc.) as needed for viable multi-qubit devices. In fact, this NIRT team has access to the most extensive array of Mn, Fe, Ni and Co based SMMs of any team in the world.

The research by this NIRT team has contributed significantly to the understanding of the properties of SMMs, including a detailed understanding of the nature of the interactions that give rise to QTM[12-14]. However, many important questions concerning dynamics remain; indeed, essentially nothing is known concerning quantum coherence and QTM, i.e. how do environmental couplings affect the coherence of quantum states in SMMs. An important objective of this project is the development and application of time-domain techniques capable of probing quantum spin dynamics.

Specifically, this NIRT project will address: (1) quantum magnetization dynamics on short time scales; (2) the nature of energy and angular momentum relaxation; and (3) the nature of spin-excitations as SMM size and spin are increased.

Methods

We are developing experimental techniques with greater temporal resolution, to ultimately enable the measurement of coherence times, the characteristic time associated with dephasing of quantum mechanical superposition states. This includes (i) hole burning and two-photon EPR spectroscopy, and (ii) magnetometry combined with pulsed microwave excitation and NMR spectroscopies. We will first identify the main low-temperature sources of decoherence, and then reduce these as far as possible. The most likely sources of decoherence are: i) random (as opposed to controlled) inter-SMM dipolar and exchange interactions; and ii) electron-nuclear hyperfine couplings. The Christou and Hendrickson groups will systematically tackle these sources of decoherence by: i) isolating SMMs from each other through the attachment of bulky peripheral ligands, or by diluting SMMs into diamagnetic host crystals; and ii) working with magnetic ions with zero nuclear spin (e.g. Ni, Cr and ^{56}Fe), as well as labeling other constituent nuclei (e.g. ^{1}H → ^{2}H).

Our studies of QTM and EPR studies have thus far mainly probed incoherent tunneling and spin excitations. Specifically, efforts at UF have focused on continuous-wave (cw) EPR studies of a wide variety of SMMs, covering a broad range of frequencies (20−715 GHz), fields (up to 30 T), field orientations, anisotropies, temperatures, etc. High sensitivity magnetometry measurements at NYU (0.3 K, in a high field vector super-conducting magnet) probe dynamics that occur mainly on laboratory timescales (~1 s). It is only very recently that it has become possible to apply microwave fields and simultaneously monitor spin-state populations[15]. This work has resulted in several important discoveries, including: a resolution to the long standing question concerning the mechanism of QTM in the widely studied Mn_{12}-ac SMM[12-14]; direct observation of the energy splitting associated with the formation of a quantum superposition of high spin states in Ni_4 SMMs[15]; and the observation of coherently coupled (entangled) quantum states of $[Mn_4]_2$ dimers of SMMs[16]. We are presently extending these studies into the time domain to explore coherent QTM.

Educational and Outreach Activities

Many graduate, undergraduate students and postdoctoral fellows have received interdisciplinary research training as a direct consequence of this project. High school students have been involved as well. The PIs have also been actively involved in organizing national and international meetings on molecular magnetism as well as invited (2004-2006) and tutorial sessions (2005 and 2006) at the APS March Meeting. In addition, all the PI having participated in workshops and summer schools, including at Les Houches, France and at the ICTP in Italy.

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