

Quantum Information Processing Using Molecular Nanomagnets As Qubits

Richard E. P. Winpenny*

EPR spectroscopy · molecular magnetism ·
polyoxometalates · quantum chemistry

The idea that the superposition of quantum states could be utilized as a way of performing computation seems, at least on the surface, almost self-contradictory. However in 1994 Shor^[1] proposed an algorithm that would allow a quantum computer to factorize numbers much faster than a classical computer, and, shortly afterwards, Grover^[2] proposed an algorithm that would lead to much faster database searching with a quantum computer. As a result of these proposals much effort has been expended on finding physical systems that could be used in quantum information processing (QIP). One of the most promising systems—and one where chemists can make a very significant contribution through the synthesis of appropriate molecules—involves using molecular nanomagnets.

The initial proposal was made in 2001 by Leuenberger and Loss,^[3] when they showed that the Grover algorithm could be implemented using a single molecule of the dodecanuclear manganese cluster $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_4]$.^[4] The physical implementation of the experiment proposed looks extremely challenging. However, this proposal has inspired further schemes^[5–7] to implement QIP with molecular nanomagnets.

The majority of these proposals look to implement the Shor algorithm, which is in itself probably more valuable than the Grover algorithm as factorizing large numbers is the method used to encode much data in the modern world using, in general, the RSA code (so named after its inventors Rivest, Shamir, and Adleman).^[8] The first proposal to use a molecular system to implement the Shor algorithm came from the Loss group,^[5,6] with further schemes proposed by Troiani et al.^[7] The core idea is, at one level, remarkably simple to understand. If a cage complex can be made which has an $S = 1/2$ ground state, that spin ground state can be regarded as a two-level system, which is the first criterion for a “qubit”; a “qubit” plays the same role in QIP that a “bit” plays in a classical computer. The two-level system arises from regarding the spin as “up” in one level and “down” in the other. An $S = 1/2$ system is a qubit because of superposition of the spin-up/spin-down states. Controlled interaction of the

qubits then allows QIP.^[5–7] For QIP to be possible there are several further criteria that have to be met by individual qubits.

Firstly, the ground state has to be a “pure” $S = 1/2$ state. If there are significant admixtures of higher spin states, then the two-level system is lost, which brings in the second consideration; that the energy gap to the first excited state must be reasonably large. If the gap is too small, other values of S would have to be considered in describing the system. Thirdly, it must be possible to populate one state in preference to the other without inducing significant loss of population to the higher S states. For an $S = 1/2$ state this is simply achieved by introducing a magnetic field; Zeeman splitting will lead to this separation and a population increase in the lower energy state. The major advantage electron spin has over nuclear spin is that the electron Zeeman splitting is much larger and hence offers a greater possibility of making usable devices.

In principle, many molecules can satisfy these criteria. In practice, studies have thus far been restricted by concerns about the next challenge—described by Stamp as the “most formidable”^[9]—which is the problem of decoherence, that is, loss of information stored before it is processed. For QIP to work, the “two-level” system has to encode the information without losing that information to the surroundings. Two major potential sources of decoherence can be foreseen for any molecular system. Interaction between molecules could induce decoherence due to dipolar coupling—essentially one $S = 1/2$ qubit interacting in an uncontrolled way with another. Secondly, interaction of the electron spin with nuclear spins within the molecule—the hyperfine interaction—could also induce decoherence. The more atoms (and hence nuclei) a molecule contains, the greater the possibility of hyperfine coupling and hence the faster the decoherence. The rate of decoherence is best quantified by a coherence time, which is essentially equivalent to the spin–spin relaxation time as measured in EPR or NMR spectroscopy.

Yet for some time there has been some evidence that decoherence in complex molecules, such as molecular nanomagnets, might not be such a severe problem. Firstly, pulsed electron paramagnetic resonance (EPR) spectroscopy^[10] is increasingly used to characterize the active sites of metalloenzymes and other proteins. For this method to work at all, relaxation times must be reasonably long. Secondly, theoretical work from Katsnelson and co-workers^[11] suggested that coherence times in a $\{\text{V}_{15}\}$ polyoxometallate (POM)^[12] could

[*] Prof. R. E. P. Winpenny
The Lewis Magnetism Laboratory, The School of Chemistry
The University of Manchester
Oxford Road, Manchester, M13 9PL (UK)
Fax: (+44) 161-275-4616
E-mail: richard.winpenny@manchester.ac.uk

be long, despite the hyperfine interaction with the ^{51}V nuclei present ($I=7/2$, 99.8% natural abundance). More than fifty papers have appeared containing physical studies of this $\{\text{V}_{15}\}$ POM, but until recently the theoretical proposal^[11] concerning coherence had not been tested.

Most importantly, pulsed EPR spectroscopic studies on the *endo*-fullerene N@C_{60} performed by Morton et al.,^[13] showed coherence times of approximately 200 μs at 190 K. This species also exhibited beautiful “Rabi oscillations” (Figure 1), where the molecule absorbs and then re-emits energy as it cycles between the two states of the system. These

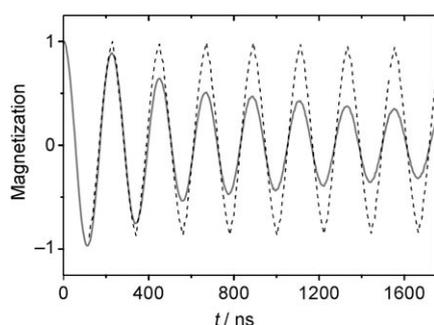


Figure 1. Rabi oscillations for N@C_{60} in CS_2 solution at 190 K (solid curve). The dashed curve shows BB1–Rabi oscillations, exploiting BB1 composite pulses to remove the decay caused by pulsed field inhomogeneity. Taken from reference [13] with permission.

oscillations are regarded as perhaps the strongest evidence for coherence in a two-state system. Using a corrective pulse sequence, known as BB1,^[13] it was even possible to prevent the Rabi oscillations decaying quickly (Figure 1).

Anomalously, the first proposal for use of molecular nanomagnets in QIP was made in 2001 and coherence times had been measured in *endo*-fullerenes,^[13] yet the first measurements of coherence times in molecular nanomagnets were only reported in 2007 by Ardavan and co-workers.^[14] The measurements were made using standard pulsed EPR spectroscopic techniques.^[10] Dipolar effects were largely eliminated by using a very dilute solution of a $\{\text{Cr}_7\text{Ni}\}$ cage^[15] in toluene. The results were extremely promising, with coherence times of 3 μs achieved at low temperature. It was also possible to examine the influence of nuclear spin on decoherence by preparing deuterated versions of the $\{\text{Cr}_7\text{Ni}\}$ cages.^[14] The coherence time increased by a factor of six on deuteration, which is exactly the ratio of nuclear magnetic moment for ^1H versus ^2D nuclei. Clearly, the hyperfine interaction is important, but also chemically controllable.

The first report of Rabi oscillations in a molecular nanomagnet has now been made by Bertaina et al.,^[16] from studies of an anionic $\{\text{V}_{15}\}$ POM (Figure 2). These results are largely in agreement with the proposal made by Katsnelson and colleagues in 2000.^[11] The dipolar contributions to decoherence are suppressed by a beautifully simple piece of chemistry: a cationic surfactant, $[\text{NMe}_2(\text{C}_{18}\text{H}_{37})_2]^+$, is added to the anionic POM, leading to a hybrid material where the $\{\text{V}_{15}\}$ anions are widely separated by the surfactant cations. The cage has two low-lying $S=1/2$ states with an $S=3/2$ excited

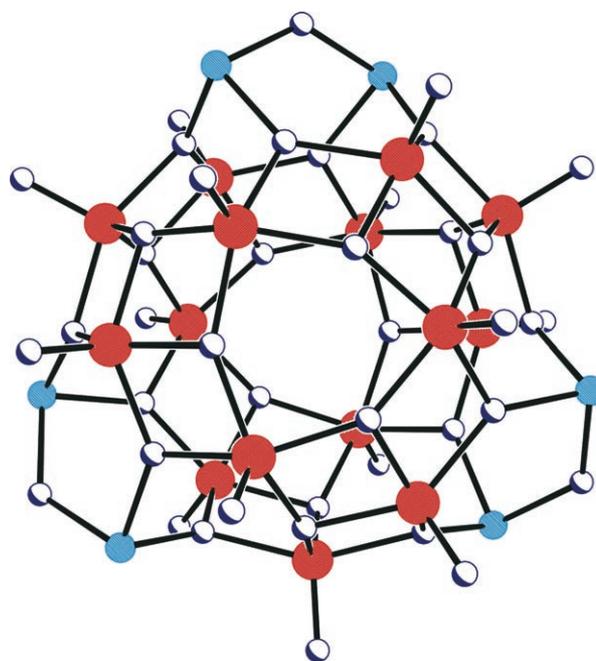


Figure 2. The structure of $[\text{V}_{15}\text{As}_6\text{O}_{42}]$ in the crystal. V red; O white; As blue.^[12]

state at about 3.7 K above this pair of levels. The results show Rabi oscillations occur for both the $S=1/2$ states and the low-lying $S=3/2$ state at low temperature.^[16]

Within the $\{\text{V}_{15}\}$ cage the major source of decoherence is coupling to nuclear spins. The obvious source of hyperfine interactions is ^{51}V , but protons on the surfactant molecules could also be important. Deuteration of the surfactant would be the next step forward. The coherence times measured on $\{\text{V}_{15}\}$ are hundreds of nanoseconds. Given the complexity of the molecule and the presence of a metal center with a significant nuclear spin, it is unsurprising that coherence times are shorter than in $\{\text{Cr}_7\text{Ni}\}$ and much shorter than those obtained for *endo*-fullerenes.^[13] However the most important observation is that, even in $\{\text{V}_{15}\}$, where hyperfine coupling is important, pulsed EPR spectroscopy experiments show that the coherence times in molecular nanomagnets are sufficient to be able to manipulate the spins of the system and hence, at least in principle, to perform QIP.

The next step for chemists is to make “scalable” structures, which is very challenging as it requires controlled entanglement of spins on neighboring qubits, without causing decoherence of individual qubits through dipolar exchange. To a chemist, the obvious means of entangling spins on qubits is to bring the qubits into close proximity with a switchable link between them, however the strange rules of quantum mechanics do not actually require a chemical bond between the qubits. Theorists have already given us the blueprints as to how this might work,^[6,7,17] presenting an unusual challenge to our creativity—can we design and then synthesize components for computational devices? Initial attempts^[18] have provided the chemical link, but not the electronic entanglement. Given the huge advances in supramolecular chemistry it seems likely chemists can construct the sophisticated

architectures required. The major bottleneck may lie in constructing the apparatus needed to perform appropriate experiments to study such linked qubits. However the opportunity for chemists to contribute, by design and synthesis of linked molecules with $S = 1/2$ states, is considerable, especially as the obstacle of decoherence through nuclear hyperfine interactions seems less great than had previously been thought.

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