Magnetism on a Mesoscopic Scale: Molecular Nanomagnets Bridging Quantum and Classical Physics

Nikolaos P Konstantinidis, Alexander Sundt, Joscha Nehrkorn, Anna Machens and Oliver Waldmann
Physikalisches Institut, Universität Freiburg, 79104 Freiburg, Germany
E-mail: oliver.waldmann@physik.uni-freiburg.de

Abstract.
In recent years polynuclear transition metal molecules have been synthesized and proposed for example as magnetic storage units or qubits in quantum computers. They are known as molecular nanomagnets and belong in the class of mesoscopic systems, which are large enough to display many-body effects but small enough to be away from the finite-size scaling regime. It is a challenge for physicists to understand their magnetic properties, and for synthetic chemists to efficiently tailor them by assembling fundamental units. They are complementary to artificially engineered spin systems for surface deposition, as they support a wider variety of complex states in their low energy spectrum. Here a few characteristic examples of molecular nanomagnets showcasing unusual many-body effects are presented. Antiferromagnetic wheels and chains can be described in classical terms for small sizes and large spins to a great extent, even though their wavefunctions do not significantly overlap with semiclassical configurations. Hence, surprisingly, for them the transition from the classical to the quantum regime is blurred. A specific example is the Fe$_{18}$ wheel, which displays quantum phase interference by allowing Néel vector tunneling in a magnetic field. Finally, the Co$_5$Cl single-molecule magnet is shown to have an unusual anisotropic response to a magnetic field.

1. Introduction
During the last fifteen years or so high-nuclearity molecules with magnetic exchange couplings between their transition metal ions have attracted enormous interest due to their novel magnetic properties. They are known as molecular nanomagnets (MNMs) and apart from their structural beauty, they present a challenge for physicists to interpret and understand their quantum magnetism. They have a relatively small size ranging from 2 to 80 metal centers, and belong in the class of mesoscopic quantum systems, which are large enough to show many-body effects, but small enough to be away from the finite-size scaling regime. With their small size they provide an ideal testing ground for studying basic questions of quantum mechanics in mesoscopic systems, such as which metal centers and topologies might be more efficient towards a desired magnetic property or the transition from the quantum to the classical regime when the ion spins are large. From the synthesis point of view they are a challenge for chemists to assemble molecules with a large number of magnetic subunits connected by bridging groups (ligands), which mediate the magnetic interactions between the metal centers. It is therefore necessary for the two disciplines
to be in close collaboration to achieve MNMs with the desired properties. Importantly, inter-molecular interactions for MNMs are very weak, consequently experiments probe directly the properties of individual molecules.

A very prominent representative of the MNM class are the so-called single-molecule magnets (SMMs) [1]. Their singular properties are slow relaxation and quantum tunneling of the magnetization (QTM), which make SMMs promising candidates for technical applications involving magnetic data storage [2, 3] and quantum computing on a molecular scale [4]. These appealing properties were observed only below a blocking temperature $T_B$ less than $\sim 4.5$ K, which is indeed too low for applications. Thus the search for molecules showing SMM behavior at higher temperature is the subject of ongoing research. It is widely accepted that a high-spin ground state and large magnetic anisotropy are necessary for a SMM [5], with the latter being of higher importance to enhance in order to improve SMM behavior [6, 7].

Besides SMMs, the large class of MNMs are of special interest for basic sciences, as several striking magnetic quantum phenomena occur due to their mesoscopic size. For instance, in the Keplerate Fe$_{30}$ strong magnetic frustration effects were observed [8, 9, 10, 11], in antiferromagnetic (AFM) molecular wheels rotations of the Néel vector and quantized AFM spin waves could be studied [12, 13, 14, 15, 16], and heteronuclear 'doped' AFM wheels have been in the focus for a number of phenomena such as coherent magnetic oscillations or thermal entanglement [17, 18, 19]. Two examples of molecules are shown in figure 1. Apart from the practical point of view, the understanding of the magnetism resulting from magnetic interactions between a dozen or so metal ions has often proved to be a challenge, as many-body quantum effects may play a crucial role in determining the properties [20]. Therefore, the MNMs can often support quite complex quantum states, and may show a drastically different behavior compared to extended systems (the finite-sized MNMs are practically 'zero-dimensional' systems).

The field of 'molecular nanomagnetism' appears hence as a very promising research area. This review focuses on three different topics that showcase the novel many-body effects and associated complex quantum many-body states that can be observed in MNMs despite their small size. Firstly, even AFM wheels and even and odd AFM chains are considered in a more

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Molecular cores of (a) the AFM wheel Fe$_{18}$, and (b) the AFM chain Cr$_7$. Blue: nitrogen, red: oxygen, yellow: flour, green: iron, dark blue: chromium. Carbons and hydrogens are omitted for clarity.}
\end{figure}
general fashion. It has been found that for even wheels the physics can be understood by the concepts of Néel vector and spin waves that were characteristically put forward for infinite systems [12], and may be considered as classical in nature. These concepts can be carried over to the case of short AFM chains. However, even though the low-energy spectrum and operator expectation values can accurately be described by a semiclassical two-sublattice Hamiltonian, its overlap with the exact wavefunction is not approaching unity as would be expected. This motivated us to study the overlap of the exact wavefunctions with valence-bond states, which may be considered as quantum mechanical in nature. Surprisingly, both sets of wavefunctions, the ‘classical’ sublattice states and the ‘quantum mechanical’ valence-bond states work equally well in the small $N$ and large $S_i$ regime (where $N$ is the number of ions in the wheel or chain, and $S_i$ their spin lengths), revealing that for even AFM wheels and short AFM chain the line between classical and quantum physics is blurred.

Secondly, following the general discussion about even AFM wheels a particularly interesting example, the Fe$_{18}$ wheel is considered, where quantum phase interference effects related to the dynamics of the Néel vector were observed [21, 22, 23]. Quantum interference was first found for the SMM Fe$_8$ [24], where it leads to zero tunneling between states in the same symmetry sector. In Fe$_{18}$ it is related to quantum tunneling of the Néel vector, and this generalizes the standard QTM typically observed in a SMM. This appealing effect and the advantages and disadvantages of its descriptions in a semiclassical, a quantum mechanical and a two-sublattice model will be discussed.

The search for molecules with enhanced SMM behavior was recently extended to molecular clusters incorporating metal ions with unquenched orbital angular momentum such as Co$^{2+}$, as they can have large magnetic anisotropy [25]. Even though the obtained molecules show none or only weak SMM behavior, the description of the magnetism in them turned out to be an interesting challenge, leading to new insights. As the third example the molecule Co$_5$Cl will be discussed, which behaves as a SMM at temperatures less than 1.8 K. In apparent contradiction to the measured susceptibility, which would usually be interpreted as evidencing dominant AFM couplings, a ferromagnetic anisotropic interaction was found in the cluster. The subtle interplay of highly anisotropic exchange coupling tensors ($J$ tensors) and gyromagnetic matrices ($g$ matrices) is the reason for this apparent inconsistency, as explicated by negative gyromagnetic factors $g$ that appear in the effective description of Co$_5$Cl.

In recent years not only the chemical route towards small quantum spin clusters has been advanced, but several beautiful examples of artificially engineered spin clusters also emerged [26, 27, 28]. Here, clusters of magnetic metal ions with desired topologies were fabricated directly on surfaces, and their magnetic properties were studied by means of scanning tunneling microscope (STM) techniques. A particularly relevant example is that of short chains of Mn ions with AFM next-neighbor Heisenberg interactions [26], which from the magnetic point of view are described by the same principles as the short AFM chains realized in some MNMs, such as the Cr$_7$ molecule shown in figure 1(b). Apparently in both fields, that of the MNMs and the artificially engineered spin clusters, one faces very similar scientific questions, yet the technological challenges in putting them forward in real-world applications are quite complementary. It is a second purpose of this review to point out these similarities as well as the complementariness, in a hope to inspire a cross fertilization of these two hitherto disjunct appearing research fields.

The paper is divided as follows: Section 2 discusses the cases of even AFM wheels and even and odd AFM chains and their semiclassical behavior. Section 3 deals with Néel vector tunneling originating in quantum interference in Fe$_{18}$. In section 4 the case of the SMM Co$_5$Cl is explained. Finally, section 5 presents the conclusions and a discussion of the connections between MNMs and artificially engineered clusters.
2. Quantum vs. Classical Description in the Many-Body Physics of Antiferromagnetic Wheels and Chains

The relatively small size of MNMs often enables their theoretical treatment with accuracy not easily attainable for extended systems. As a result, a classification of their properties relative to $N$, $S_i$ and the type of interactions between the spins appears more promising compared to extended systems. However many-body effects, which can also appear for small clusters, merit closer investigation and often perplex such a classification. They also blur the limit between the classical and quantum behavior, as will be demonstrated here. The obvious distinction that exists for the two regimes in extended systems disappears for MNMs, which are zero dimensional and exhibit strong finite-size effects. Hence the states allowed by these small structures can be quite complex.

In AFM wheels the metal ions playing the role of magnetic centers form a close to perfect ring-like arrangement. Nearest-neighbor interactions are not frustrated if all $J_{ij} < 0$ and $N$ is even [15, 29]. The Cr$^{3+}$ and Fe$^{3+}$ ions, which have relatively large spin $S_i = 3/2$ and $5/2$ respectively, are particular useful. The decanuclear wheel [Fe$_{10}$(OCH$_3$)$_{20}$(O$_2$CCH$_2$Cl)$_{10}$], most commonly known as Fe$_{10}h$, is a prototype molecule for this class [30, 31], and there also exist hexanuclear, octanuclear, decanuclear and 18-membered ferric wheels [30, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45]. Their magnetism is generally well described by the Hamiltonian

$$\hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_{i=1}^N D_i \hat{S}_{i,z}^2 + \mu_B \sum_{i=1}^N g_i \hat{S}_i \cdot \mathbf{B},$$

(1)

where three different effects are in competition, the isotropic Heisenberg exchange interactions between the magnetic centers with constants $J_{ij}$, the zero-field splitting (ZFS) term introducing magnetic anisotropy, and a Zeeman term that couples to an external magnetic field. In the case of the AFM wheels, an effective model describing the low-energy physics can be formed by assuming that the effect of quantum fluctuations is not so strong. Hence, grouping spins which are parallel in the classical limit into a single spin will capture the basic physics at least at the semiclassical level [29]. More generally, this situation applies for molecules with magnetic centers that are bipartite, and can be divided in two groups of spins (‘sublattices’) that classically point in opposite directions and all of a spin’s nearest neighbors belong to the other sublattice. This results in two ‘collective’ spins $S_A$ and $S_B$ (with $S_A = S_B = N S_i/2$ for wheels) that effectively describe the low-energy physics as an interacting dimer via the Hamiltonian

$$\hat{H}_{AB} = -a_1 J \hat{S}_A \cdot \hat{S}_B + b_1 D (S_{A,z}^2 + S_{B,z}^2) + g \mu_B \hat{S} \cdot \mathbf{B},$$

(2)

where $a_1 = a_0^c$ and $b_1 = b_0^c$ in the semiclassical limit (see section 3 for wheels), but they can be modified as quantum fluctuations get stronger to provide a more accurate description [29]. Results generated with equation (2) compare very well with the predictions of equation (1) for even AFM wheels, and the semiclassical dimer Hamiltonian $\hat{H}_{AB}$ has proven to be a valuable tool for the calculation of the low-energy behavior for a large number of MNMs [32, 39, 46], see also the next section. It is noted here that this approach can be generalized for more than two sublattices, as is the case for the Fe$_{30}$ Keplerate molecule [8, 9, 10, 11, 47, 48, 49].

The agreement of Hamiltonians (1) and (2) calls for a more systematic comparison of their properties. The ZFS term is typically weaker than the exchange couplings and may be neglected in a first approximation. In the special case where all $D_i = 0$ and uniform AFM interactions $J_{ij} = J < 0$, Hamiltonian (1) simplifies to the AFM Heisenberg Model (AHM)

$$\hat{H} = -J \sum_{i<j} \hat{S}_i \cdot \hat{S}_j,$$

(3)
written here in the absence of a magnetic field. The AHM, which is isotropic in spin space, has been the object of intense investigation over the years on different types of lattices as a prototype of strongly correlated electronic behavior in extended systems. In particular, it is closely associated with the investigation for the existence or not of long-range order in two-dimensional lattices at zero temperature [50]. In the case of the square lattice, the AHM has been used to describe the behavior of the superconducting carriers above the critical temperature [51]. Existing evidence strongly points to a ground state where quantum fluctuations weakly renormalize the classical Néel state. The AHM has also been of great interest for frustrated lattices, where nearest-neighbor spins are not aligned in an antiparallel fashion at the classical level. Standard examples are the triangular and the Kagomé lattice [52]. These have been intensively studied with the hope of realizing the elusive spin-liquid ground state proposed by Anderson [53], which has pure quantum mechanical character and possesses no long-range order.

AFM wheels have been extensively studied within the framework of the AHM. Energy levels are characterized by $S$ and $M$, the expectation values respectively of $\hat{S}^2$ and $\hat{S}_z$, the projection of the total spin along the z-axis. AFM wheels and chains provide a direct comparison with the infinite one-dimensional chain, their extended systems counterpart, by simply taking the limit $N \to \infty$. The infinite chain has been theoretically conjectured by Haldane to possess different physics depending on $S_i$ being integer or half-integer [54, 55]. In the former case excitations are gapful, while in the latter gapless. In the infinite chain the distinction between the classical and quantum regimes is clear. Classical nearest neighbors are pointing in opposite directions, forming a state with perfect Néel long-range order in the staggered magnetization. In the full quantum limit $S_i = 1/2$ the correlations do not have long-range order, but rather decay exponentially as the ground state is in a critical phase (the ground-state energy can exactly be calculated with the Bethe ansatz [56]). This is in accordance with the Mermin-Wagner theorem [50], which states that quantum fluctuations are so strong in one dimension that they destroy any order for any temperature $T$.

In the case of AFM wheels, their finite size perplexes the problem. As their size is of the order of tenths of magnetic centers they are nowhere near the thermodynamic limit, but this size can be long enough to generate non-trivial many-body effects. The AFM interactions in equation (3) minimize the total spin $S$ in the ground state, which is a singlet $S = 0$ for even AFM wheels. The lowest energies in the different $S$ sectors follow Landé’s interval rule $E(S) \propto S(S + 1)$ [30]. In fact, several parallel rotational bands were identified [14, 15, 57], see figure 2. The lowest

Figure 2. Energy spectrum of the $N = 6$, $S_i = 5/2$ AFM wheel. It is divided in the $L$ band, the $E$ band and the quasi-continuum.
band is called $L$, while the next higher bands collectively form the $E$ band, with the remaining states collected together in the so-called quasi-continuum, of little relevance for temperatures $T$ less than $\sim |J|$ [14]. The two lowest bands have a simple physical interpretation. For an infinite antiferromagnet, arbitrary rotations in spin space are allowed but are extremely unlikely to be realized experimentally, as the size of the system implies a very large experimental time for such an observation. However for finite wheels these classical-type states are physically accessible and correspond to the $L$ band. The $E$ band is associated with the discretized versions of the familiar spin-wave excitations where a single spin is flipped from the ground state and allowed to propagate in the whole cluster [58]. The $E$ band includes all the states accessible with significant probability from the $L$ band by single-spin excitations, as observed for instance in inelastic neutron scattering experiments. Interestingly enough and unlike the infinite chain, the lowest energy excitations that determine the low-temperature magnetization such as the magnetization steps in an external field [15, 30, 38], relate to the $L$ band and rotations of the Néel vector rather than the magnon type excitations.

The classical nature of the low-energy spectrum allows one to describe the low-energy physics of the $L$ band with equation (2), written in the absence of magnetic anisotropy and external field,

$$
\hat{H}_{AB} = -a_1 J \hat{S}_A \cdot \hat{S}_B.
$$

(4)

This is in contrast with the extended AFM chain where quantum fluctuations are so strong that drive the system out of order. $\hat{H}_{AB}$ can be diagonalized and by construction its low-energy spectrum consists of an $L$ and an $E$ band and agrees with Hamiltonian (3) in first order in perturbation theory. It turns out that $\hat{H}_{AB}$ is a very good approximation for the AHM for small $N$ and large $S_i$. This can be seen in figure 3(a), where the energy difference $\Delta E_L(S) = \frac{1}{2} \Delta_0 (S + 1) - E_{S,0}$ between the energy extrapolated from the two lowest states with $S \leq 1$ using the Landé rule (which determines $\Delta_0$) and the lowest energy state with $S$ is plotted for $S = 2$ [29]. This difference goes to zero as $S_i$ increases towards its classical limit. The signature of the Haldane conjecture for larger spins with the oscillations as $S_i$ alternates between integer and half-integer can also be seen [54, 55], however these oscillations also disappear as $S_i$
Figure 4. Properties of the AFM Heisenberg wheels as a function of their size $N$ and the spin length $S_i$. The area in which the results of this work apply is blue shaded and marked by $\hat{H} \approx \hat{H}_{AB}$ and exact.

approaches the classical limit.

The behavior of even AFM wheels as function of $N$ and $S_i$ is summarized in figure 4 [29]. For large $N$, the system goes to the thermodynamic limit and the Haldane conjecture appears. For $S_i = 1/2$ the elementary excitations are spinons. As $N$ is getting smaller the system behaves more and more classically, and for small $N$ and large $S_i$ $\hat{H}_{AB}$ provides an effective semiclassical description of the physics (for $N \leq 4$ Hamiltonian (3) can exactly be solved with the spin-coupling method [59]). This is the region where the correlation length of the Heisenberg wheels is much larger than the size of the system.

It appears quite natural that the semiclassical Hamiltonian (4) becomes more successful as the spins acquire a more classical character with increasing $S_i$. The reduction of $N$ brings about a characterization of the states in terms of $S$, rather than the momentum $k$ which is appropriate for large or infinite systems. In this regime the energies and the expectation values of operators are very well reproduced by equation (4) and the wavefunctions generated by it, however, the wavefunctions themselves, maybe surprisingly, do not approach the exact wavefunctions of equation (3), i.e. the overlap with the exact wavefunctions does not go to unity (figure 3(b)). It rather approaches a limiting value with decreasing $N$ and increasing $S_i$, which is not very close to unity. Consequently the apparent semiclassical behavior of the AHM model (3) is not carried to a full extent, and there are still features of the system that call for a treatment where quantum fluctuations are more systematically taken into account.

Further insight into why the effective Hamiltonian (4) works to the extent it does comes from short AFM chains. In contrast to wheels, MNMs in the form of chains have open boundary conditions with free spins at their edges, and have been considerably less studied. Open boundary conditions combined with finite-size effects complicate the physics. The Cr$_6$ and Cr$_7$ horseshoes are AFM chains with an even and odd number of $S_i = 3/2$ magnetic centers [60]. The Cr$_7$ molecule is displayed in figure 1(b). Apart from their expected different ground-state spin of $S = 0$ and $S = 3/2$ respectively [61], the excited energy spectra are also intrinsically different. This difference is a more general feature of even and odd AFM chains [62]. In particular, for odd chains the Landé rule for the lowest states in each $S$ sector is very weakly renormalized. In contrast, it is strongly renormalized for the even chains. It is the lowest states in the AFM region, where $S$ is minimal, that deviate from the rule. This is due to a low-lying first excited state with
Figure 5. Overlap of approximating wavefunctions for the ground state of the AFM chain as functions of \( N \) for (a) \( S_i = 1 \) and (b) \( S_i = 2 \). Plotted are the overlap of the ground state of the AHM with the ground state of \( \hat{H}_{AB} \), \( |\langle \Psi_{AB} | \Psi \rangle|^2 \) (blue), with the VBS state, \( |\langle \Psi_{VBS} | \Psi \rangle|^2 \) (green), and the overlap of the ground state of \( \hat{H}_{AB} \) with the VBS, \( |\langle \Psi_{AB} | \Psi_{vbs} \rangle|^2 \) (red).

\( S = 1 \), which leads to a strong curvature in the band of the lowest \( S \) states. Consequently, the effective Hamiltonian \( \hat{H}_{AB} \) approximates better the excited states for odd chains. Nevertheless, the quality of approximation of the ground state of equation (3) by \( \hat{H}_{AB} \) is similar for chains as it is for even wheels. Another consequence of the open boundary conditions is that the \( E \) band is different for chains compared with even wheels, as the open boundary conditions split the running spin waves of the wheels to standing spin waves for the chains [63].

An alternative approach comes about naturally for AFM chains when considering the valence-bond-solid (VBS) model [64, 65]. A valence bond is a singlet coupling between two spins 1/2. If each spin \( S_i \) of a chain is considered to be made up of 2\( S_i \) spin-1/2 objects, then valence bonds can be formed between objects belonging to neighboring sites. The VBS model has been developed especially as a model for AFM chains and its ground state is the VBS state, which is named like this because its structure mimics the one of the lattice. If it has spin \( S \), apart form the singlet bonds between nearest-neighbor spins there exist 2\( S \) unpaired spin-1/2 objects. If \( S = 0 \), the ground state is the same for AFM wheels. The VBS ground state can be generated by recursion or parent Hamiltonian techniques. Then it can be compared with the exact ground state of the AHM, by means of energy and overlap. The same can be done for the ground state of the semiclassical Hamiltonian \( \hat{H}_{AB} \).

It turns out that both agree very well with the exact ground state for small \( N \), which considering the apparently very different structure of the semiclassical and VBS wavefunctions is very surprising, and a main finding in this work. As \( N \) increases and \( S_i \) decreases the VBS state provides a better approximation for the energy and wavefunction. This is expected since when the AFM chains become larger than their correlation length the VBS model gives a better result, as it has exponentially decaying correlations in contrast to the infinite correlations of \( \hat{H}_{AB} \). The overlaps of the ground states of the two models with the exact ground state of the AHM are shown in figure 5 for \( S_i = 1 \) and 2, and underpin the observation that for smaller \( N \) and larger \( S_i \) both approximate the ground state wavefunction equally well. It is also seen that their mutual overlap is also decreasing significantly with \( N \), which points to the fact that even though the semiclassical and the VBS wavefunctions come from exactly opposite limits, the ‘classical’ and the ‘quantum mechanical’ respectively, they are almost equally successful in describing the physics of the short AFM chains. The even AFM wheels and the AFM chains
Figure 6. (a) Schematics of a classical ground state configuration for the AFM wheel Fe$_{18}$ (red and blue arrows are the spins of the two sublattices) with the resulting Néel vector $\mathbf{n}$ (green arrow, length not scaled). (b) Shape of the potential $V(\mathbf{n})$ in the high field regime. The two tunneling paths of the Néel vector (green arrow) are indicated by the red arrows.

present therefore a class of MNMs where the distinction between classical and quantum behavior is not well-defined. Further investigations are needed for a full understanding of the complex finite-size many-body physics.

3. Quantum Phase Interference Effects in AFM Molecular Nanomagnets

Observing quantum phase interference effects (QPIEs), which may occur in the coherent tunneling between two classically degenerate magnetization directions, is difficult for mesoscopic particles. QPIE in a MNM was first observed in the molecule [Fe$_8$O$_2$(OH)$_{12}$/tacn]$^{8+}$, known as Fe$_8$, which has an $S = 10$ ground state [24]. By applying a magnetic field along the anisotropy hard axis at very low temperatures oscillations in the tunneling splitting were observed. They correspond to QPIE due to different tunneling paths between the degenerate $M = \pm 10$ ground states. It took another 10 years to observe a similar phenomenon, this time in antiferromagnetically coupled MNMs with compensated magnetic moments. This is not only because of the experimental challenge to characterize a system with zero ground-state magnetization, but also due to chemical difficulties to synthesize an MNM with the ‘right’ physical properties [21, 22, 23]. The meaning of ‘right’ properties will be explained on a series of AFM wheels that seemed to be promising candidates to observe QPIE in the Néel vector tunneling (NVT). In NVT the Néel vector $\mathbf{n} = (\mathbf{M}_A - \mathbf{M}_B)/(2M_0)$, with sublattice magnetizations $\mathbf{M}_A$ and $\mathbf{M}_B$ of length $M_0$, has two tunneling paths through an anisotropy barrier (figure 6).

The phase of the ground-state wavefunction can generate interference which leads to oscillations of the tunnel splitting as function of an applied magnetic field. A generic spin Hamiltonian for AFM wheels is given by equation (1). For a magnetic field $\mathbf{B}$ parallel to the $x$ axis and $D > 0$ the Néel-vector dynamics in a semiclassical theory (SCT) [21, 23] are governed by the effective semiclassical potential $V(\mathbf{n}) = N/|8J|(g\mu_B B)^2 n_z^2 + NS^2 D n_z^2$, which separates two minima at $\mathbf{n} = \pm y$ by an energy barrier $\Delta U = NS \sqrt{2D|J|}$. If this energy barrier is much larger than the attempt frequency $\hbar \omega_0 = S \sqrt{8D|J|}$, which relates to an exponentially small tunnel splitting $\Delta$ in the quantum-mechanical energy spectrum, NVT between the two ground states with opposite orientations of the Néel vector (or sublattice magnetization vectors) can occur. The phase of the ground-state wavefunction contains a $\pi/2$ term due to quantum fluctuations.
plus a topological term $\pi N g \mu_B B/[4J]$, which is proportional to the magnetic field [23]. Therefore one can repeatedly tune the phase through destructive and constructive interference by tuning the magnetic field. This results in tunneling splitting oscillations according to

$$\Delta(B) = \Delta_0 \left| \sin \left( \frac{\pi N g \mu_B B}{4|J|} \right) \right|$$

with the tunneling amplitude $\Delta_0 = 8\hbar \omega_0 \sqrt{S_0/\hbar} \exp(-S_0/\hbar)$ and the tunneling action $S_0/\hbar = NS_i\sqrt{2D/|J|}$. In these quantities the condition for NVT reads $S_0/\hbar > 2$. It is important to point out that tunneling affects also the ground-state energy $\epsilon_0(B) = \epsilon(B) - \Delta(B)/2$. Hence, tunneling oscillations can be observed by static magnetization or torque measurements at zero temperature.

Since the Hilbert space of mesoscopic particles can be prohibitively large it is often necessary to use approximations to connect theory and experiment. One such approximation is to use the semiclassical two-sublattice Hamiltonian (2) (with $S_A = S_B = 45/2$ for Fe$_{18}$) [29]. This reduces the Hilbert space drastically so that exact numerical diagonalization may become possible. Another approximation is to use the SCT of the microscopic Hamiltonian (1) [23].

The QPIE in the NVT has been observed in the AFM wheel [Fe$_{18}$(pd)$_{12}$-(pdH)$_{12}$(O$_2$C$\text{Et}$)$_6$(NO$_3$)$_6$](NO$_3$)$_6$, or Fe$_{18}$, shown in figure 1(a) [43]. The experimentally measured magnetization curves for the magnetic field $\mathbf{B}$ parallel and perpendicular to the anisotropy axis $z$ followed the predictions in [23], and thus provided strong indication for NVT in Fe$_{18}$. The measured torque (figure 7) for $\mathbf{B} \perp z$ however, provided a clear-cut demonstration of the QPIE: after a first step it exhibits wiggles which directly correspond to the oscillations of the NVT splitting [66].

In the interpretation of the data and the simulation of the torque and magnetization curves in particular, it has to be realized that the two-sublattice Hamiltonian (2) and the SCT are approximations of equation (1), but at different levels. That is, they give quantitatively different results compared to each other and to equation (1) if one uses the same values for $J$ and $D$ in all three models. These values need to be ‘adjusted’ properly, which may be accomplished by using the appropriate values for $a_1$ and $b_1$ in equation (2). Then and only then do $\hat{H}_{AB}$ and SCT work with high accuracy.

Highly accurate results for $\hat{H}_{AB}$ are obtained by choosing $a_1$ and $b_1$ such that the lowest energies of equation (2) match the exact energies of equation (1), resulting in $a_1 = a_1^{em} = 0.27$.
and $b_1 = b_1^{qm} \approx 0.07$ for Fe$_{18}$ (as derived from quantum Monte Carlo calculations [67]). If $\hat{H}_{AB}$ is derived in first-order perturbation theory the values $a_1 = a_1^{AB} = 4/N$ and $b_1 = b_1^{AB} = (2S_i - 1)/(NS_i - 1)$ are found [29]. The SCT provides $a_1 = a_1^{sc} = 4/N$ and $b_1 = b_1^{sc} = 2NS_i^2/[NS_i(NS_i + 2) - 3]$. Obviously these three results do not coincide with each other, and a careful analysis is needed to determine which set is to be used, since the experiment 'only' allows to determine the quantities $j = a_1J$ and $d = b_1D$. Hence different values for $J$ and $D$, and thereby for $S_0/\hbar$, $\Delta U$, $\hbar\omega_0$ and $\Delta_0$, which are the key characteristics for NVT, may be derived and the question arises which set of parameters is the most appropriate one. For Fe$_{18}$ the three resulting sets are collected in table 1.

### Table 1. Comparison of the results of some key NVT quantities for Fe$_{18}$, as derived with the $qm$, $AB$, and $sc$ values for $a_1$ and $b_1$.

| $a_1$ | $b_1$ | $J$ (K) | $D$ (K) | $S_0/\hbar$ | $\Delta U$ (K) | $\hbar\omega_0$ (K) | $\Delta$ (K) |
|------|------|--------|--------|-------------|----------------|-----------------|-------|
| $qm$ | 0.27 | 0.07   | -18.9 | 0.300 | 8.02 | 33.8 | 16.8 | 0.050 |
| $AB$ | 0.2222 | 0.0099 | -23.0 | 0.231 | 6.38 | 26.0 | 16.3 | 0.222 |
| $sc$ | 0.2222 | 0.1065 | -23.0 | 0.197 | 5.90 | 22.2 | 15.0 | 0.320 |

It turns out that the $J$ and $D$ values that have to be inserted in the microscopic Hamiltonian (1) should be derived from the values $a_1^{qm}$ and $b_1^{qm}$. However, importantly, to use the formula of the SCT the 'corrected' $J$ and $D$ values should be inserted as derived with $a_1^{sc}$ and $b_1^{sc}$ in order to obtain quantitatively accurate results. The latter fact can be made plausible by looking for instance at the fields at which the magnetization/torque steps or zeros in the oscillation of the tunneling splitting respectively occur. In SCT these fields are controlled by the period $Ng\mu_B B/|4J]$ but actually appear with period $g\mu_B B/|j|$. Therefore, $J = j/a_1^{sc}$ should be inserted and not $J = j/a_1^{qm}$, and similarly $D = d/b_1^{sc}$, and not $D = d/b_1^{qm}$.

The next step is to consider the 'right' conditions for observing NVT, and in particular compare the situations for Fe$_{18}$ and the two most promising previously studied AFM wheels, [CsFe$_3$(N(CH$_2$-CH$_2$O)$_3$)$_8$]Cl or CsFe$_8$ [68], and [Fe(OMe)$_2$(O$_2$CCH$_2$Cl)]$_{10}$ or Fe$_{10}$ [69]. As mentioned, the Néel-vector dynamics in the SCT are characterized by the following quantities:

- **tunneling action**: $S_0/\hbar = NS_i\sqrt{2|D/J|}$,  
  \[ (6) \]
- **attempt frequency**: $\hbar\omega_0 = S_i|/8|DJ|$,  
  \[ (7) \]
- **energy barrier height**: $\Delta U = NS_i^2|D|$,  
  \[ (8) \]
- **tunneling amplitude**: $\Delta_0 = 8\hbar\omega_0 \sqrt{S_0/\hbar} \exp(-S_0/\hbar)$.  
  \[ (9) \]

Fe$_{18}$ has a hard-axis single-ion anisotropy ($D > 0$), while Fe$_{10}$ and CsFe$_8$ easy-axis type ($D < 0$). Furthermore, Fe$_{18}$ has been investigated in the high-field regime, while the other two wheels in zero field (systems with a hard-axis anisotropy do not exhibit NVT in zero field). NVT is realized if the anisotropy barrier $\Delta U$ is larger than the ground state energy, which is $\hbar\omega_0/2$ for Fe$_{18}$ and $\hbar\omega_0$ for Fe$_{10}$ or CsFe$_8$. This criterion can be translated into $S_0/\hbar > 2$ and $S_0/\hbar > 4$, respectively. For Fe$_{18}$ the tunneling splitting $\Delta$ shows an oscillation as function of field according to equation (5). For Fe$_{10}$ and CsFe$_8$, to the best of our knowledge, $\Delta$ has not yet been calculated analytically, however numerical calculations indicate $\Delta \approx 2\Delta_0$. For a better comparison of the three wheels a constant $c$, with $c = 1$ for Fe$_{18}$ and $c = 2$ for Fe$_{10}$ and CsFe$_8$, is introduced such
that the quantities to look at become $c\hbar \omega_0/2$, $\Delta = c\Delta_0$, and the NVT criterion $(S_0/\hbar)/c > 2$. With the experimentally determined values for $j$ and $d$ for each of the three AFM wheels, the NVT characteristics compiled in Table 2 are obtained from the above relations (in the case of Fe$_{10}$ one has to additionally take into account that it exhibits a significant $E$ term and is far from uniaxial, its $d$ value was hence determined as if it would be uniaxial).

Table 2. Comparison of the characteristic parameters for NVT in Fe$_{18}$, CsFe$_8$, and Fe$_{10}$. The last row sketches the energetic situation in the three AFM wheels. The solid line represents the potential barrier of height $\Delta U$, the left and right bar the classical Néel vector states at energy $c\hbar \omega_0/2$, and the bars in the middle the tunneling-split quantum states at energies $c\hbar \omega_0/2 \pm c\Delta_0/2$.

|                  | Fe$_{18}$ [66] | CsFe$_8$ [68] | Fe$_{10}$ [69] |
|------------------|---------------|---------------|---------------|
| experimental     |               |               |               |
| values (K)       | $j = -5.1$    | $j = -11.1$   | $j = -6.31$   |
|                  | $d = 0.021$   | $d = -0.104$  | $d = -0.0276$ |
| $\Delta$ not     |               |               |               |
| directly measured|               |               |               |
| $a_1^\text{nc}$  | 0.2222        | 0.5           | 0.4           |
| $b_1^\text{nc}$  | 0.1065        | 0.2288        | 0.1860        |
| $J$ (K)          | -23.0         | -22.2         | -15.8         |
| $D$ (K)          | 0.197         | -0.454        | -0.148        |
| $S_0/\hbar$      | 5.90          | 4.03          | 3.42          |
| $c\hbar \omega_0/2$ (K) | 7.52      | 22.3          | 10.8          |
| $\Delta U$ (K)   | 22.2          | 22.5          | 9.25          |
| $\Delta = c\Delta_0$ (K) | 0.320 | 5.08          | 4.18          |
| $(S_0/\hbar)/c$  | 5.70          | 2.02          | 1.72          |

A further property that characterizes NVT is the 'localization' of the Néel vector. It can be measured e.g. by the matrix element $\langle 0|\hat{n}_y|1\rangle^2$ with the Néel-vector operator defined as $\hat{n} = (\hat{S}_A - \hat{S}_B)/(S_A + S_B)$. The SCT yields the estimate $\langle 0|\hat{n}_y|1\rangle^2 \approx 1 - 1/(S_0/\hbar)$. For Fe$_{18}$ this gives $\langle 0|\hat{n}_y|1\rangle^2 \approx 0.83$, i.e. the Néel vector is localized in Fe$_{18}$ to 83%. For Fe$_{10}$ and CsFe$_8$ the SCT yields the estimate $\langle 0|\hat{n}_y|1\rangle^2 \approx 1 - 2/(S_0/\hbar)$, or $\langle 0|\hat{n}_z|1\rangle^2 = 0.42$ and 0.50 respectively.

Apparently, while for Fe$_{10}$ the NVT is at best only approximately fulfilled and similarly for CsFe$_8$, the AFM wheel Fe$_{18}$ fully satisfies the criteria for it. This is probably most convincingly demonstrated by the energy diagrams in Table 2.
Figure 8. (a) Magnetic core of the molecule Co$_5$Cl. Turquoise: Co$^{2+}$, blue: nitrogen, red: oxygen, green: chloride. Carbon and hydrogen atoms are omitted for clarity. (b) Measured $\chi T$ versus $T$ curves for Co$_5$Cl (black dots) compared with the two simulations with a negative $g_i$ factor as obtained in the best fit (blue line), and with the $g_i$ factor set to be positive (red line). The other parameters were as found for the best fit.

4. Negative $g$-Factors and Apparent AFM Susceptibility for Ferromagnetically Coupled Co$^{2+}$ Clusters

The studies of SMMs were mainly restricted in the past to molecules containing manganese or iron ions. Compared to them only a few SMMs have been reported in the literature which consist of high-spin Co$^{2+}$ ions [70]. In principle Co$^{2+}$ ions should be ideal for building SMMs, as they typically possess large magnetic anisotropy as a result of their unquenched orbital angular momentum. Due to this unquenched orbital angular momentum a spin-only approach for describing the magnetism, as in the cases of the previous sections, becomes invalid, and this complication is one of the major reasons why magnetic models were developed only for a few Co$^{2+}$ clusters. Fortunately, the unquenched orbital angular momentum allows for a simplification in as much as that the low-temperature magnetism can be described by an effective spin-1/2 model. The ground state of a Co$^{2+}$ ion is a Kramer’s doublet and at temperatures below ca 40 K only this doublet is populated, consequently the dynamics of the ion may be described as that of an effective spin 1/2 [71]. The drawback is that this leads to highly anisotropic exchange coupling tensors $J$ as well as $g$ matrices, and hence to a large number of magnetic parameters even for the simplest clusters [72]. In many cases the anisotropy is thus restricted to uniaxial type [73, 74].

In our group the magnetic properties of three Co$^{2+}$ clusters with similar core motif but surprisingly large differences in their magnetic properties, especially their SMM behavior, were studied [75]. The clusters contain five Co$^{2+}$ ions arranged in a square-pyramidal fashion. [Co$_5^{2+}$($\mu_4$-N$_3$)(Cl)(tbea)$_2$(piv)$_4$(H)$_2$, or Co$_5$Cl in short, is shown in figure 8(a). In its magnetic susceptibility curve, plotted as $\chi T$ versus $T$, Curie behavior was observed at the highest measured temperature of 250 K. With decreasing temperature $\chi T$ decreases, which is usually taken as a clear signal of dominant AFM couplings in the cluster. The AC susceptibility measurements revealed an out-of-phase signal at the lowest temperatures, strongly evidencing SMM behavior of Co$_5$Cl. In view of the AFM type of behavior one would expect that the ground state of this system is weakly magnetic, and in particular that an energy barrier for spin reversal is small, disfavoring SMM behavior. After intense and careful efforts the appropriate model for Co$_5$Cl was established, and it describes the molecule as a cluster of five spin-1/2 centers. The model reproduces the magnetic data, i.e. the magnetization curves as well as the
magnetic susceptibility below 40 K, excellently. Surprisingly it revealed dominant ferromagnetic couplings, and accordingly the simulated energy spectrum is characterized by a ferromagnetic ground state. Furthermore, it exhibits a sizeable energy barrier of ca 15 K, which explains the SMM behavior observed in the AC susceptibility measurements.

Ferromagnetic couplings and a ferromagnetic ground state are intuitively inconsistent with the apparent AFM curvature of $\chi_T$. This contradiction is a result of the interplay of the highly anisotropic $J$ tensors and $g$ matrices, as they are typical for effective spin models. In fact, in the present magnetic model one component of the $g$ matrix of the apical $\text{Co}^{2+}$ ion was obtained as negative. Usually the possibility of negative $g$ factors is not considered, with arguments that the $g$ values enter only quadratically in measured observables such that the sign becomes irrelevant or that negative $g$ values are unphysical. However, both arguments are incorrect and it was recently demonstrated that negative $g$ factors can appear quite naturally in effective spin descriptions [72]. Indeed, as the $\chi_T$ curve was simulated for the $\text{Co}_5\text{Cl}$ molecule with all entries $g_{i,xy}$ and $g_{i,z}$ in the local $g_i$ matrices artificially set to positive, the typical increase at low temperatures in the $\chi_T$ curve was obtained as expected for dominant ferromagnetic couplings, see figure 8(b). The effect of the sign of $g$ factors may be understood by analyzing the low-temperature value of $\chi_T$. At these low temperatures only the ground state of the $\text{Co}_5\text{Cl}$ cluster is populated, which because of the odd number of magnetic electrons in the molecule is again a Kramer’s doublet, and may hence also be described by an effective spin-1/2, $\tilde{S} = 1/2$. This however should not be confused with the effective spin-1/2 introduced for each $\text{Co}^{2+}$ center. The Zeeman splitting of this Kramer’s doublet is described by the gyromagnetic factors

$$\tilde{g}_x = \tilde{g}_y = 0$$

$$\tilde{g}_z = \sum_{i=1}^{5} g_{i,z}$$

and the Curie constant or $\chi_T$ constant can be calculated as

$$\chi_T|_{T \to 0} = \frac{1}{8} \tilde{g}_x^2 + \tilde{g}_y^2 + \tilde{g}_z^2 (\tilde{S} + 1) = \frac{1}{32} \tilde{g}_z^2$$

Importantly, the $\tilde{g}_z$ value is given as as sum of the $g_{i,z}$ components of all $\text{Co}^{2+}$ ions. Hence, if one or more of the $g_{i,z}$ factors have negative sign, then this tends to reduce the cluster $g$ factor and thereby the $\chi_T$ constant. If it happens as in the case of $\text{Co}_5\text{Cl}$ that this $\chi_T$ value is smaller than the $\chi_T$ value at high temperatures, then apparently the $\chi_T$ curve will show a drop towards lower temperatures reminiscent of an AFM coupling. In passing it is noted that the described effect may not only be produced by negative entries in the local $g_i$ matrices. A negative $g$ value is only the simplest representation of a different orientation of a $g_i$ matrix with respect to the other $g_i$ matrices. Indeed model calculations with anisotropic $g_i$ matrices showed that this effect can be obtained even with $g_i$ matrices with only positive entries, if they are rotated with respect to each other.

It is thus concluded that in clusters where ions may have different and anisotropic $g_i$ matrices the usual interpretation of the curvature of the $\chi_T$ curve versus $T$ as to indicate ferromagnetic or aniferromagnetic interactions may be misleading, as in such cases an ‘AFM’ curvature can, opposite to common sense, be a result of the details of the individual $g_i$ matrices and not the exchange couplings.

5. Conclusions

MNMs constitute an exciting class of relatively small systems where the combination of unusual magnetic properties and synthetic chemistry appears very promising for future applications.
Their comparatively small size places them away from the thermodynamic limit, while the relatively large spin of their centers is inbetween the classical and the full quantum limit, defining a mesoscopic scale. Consequently these molecules may support unusual complex quantum states. This is the main point demonstrated in this article. It may even happen that their properties do not have a predominant classical or quantum character, and rather belong to an intermediate regime. Hence, MNMs are obviously attractive objects for studying fundamental questions in basic sciences, but could also be potentially very useful in applications where classical or quantum behavior could be adjusted by the topology and spin length of the magnetic centers.

In this review a few examples of MNMs were considered, which showcase the unusual many-body character that comes about in this mesoscopic regime and borders between classical and quantum physics. Even AFM wheels as well as AFM chains were shown to behave classically in some aspects as $N$ decreased and $S_i$ increased, however their ground state is not exactly in the classical or quantum regime and the intuitively clear distinction between these two regimes becomes in fact blurred. The Fe$_{18}$ AFM wheel has been shown to be one of the few magnetic examples where quantum phase interference effects occur, associated with tunneling of the Néel vector, a concept originating in semiclassical physics. Finally, a MNM incorporating high-spin Co$^{2+}$ ions which behaves as a weak SMM was also considered. There the unquenched orbital angular momentum leads to highly anisotropic magnetic interactions and gyromagnetic matrices. The anisotropic $g$ matrices lead to effects usually associated purely with the exchange coupling.

MNMs may also be important as magnetic units that can be potentially deposited on surfaces while preserving their magnetic properties. They are in general particularly fit for this purpose as the typical energy scale of their magnetic excitations is of the order of some Kelvins, which supersedes by orders of magnitude the tunneling gap of SMMs [5]. The latter is of the order of e.g. $10^{-7}$ K in the archetype SMM Mn$_{12}$-acetate [5], and therefore expected to be very easily influenced by environmental perturbations such as thermal vibrations or the different conditions found on surfaces as compared to in crystals. Indeed, observing magnetic hysteresis of a SMM deposited on a surface could only very recently be achieved [76, 77]. In contrast, the magnetism in MNMs is expected to be a lot more robust and to survive the change in environment on a surface.

A MNM will in general not exhibit a magnetic function obviously suitable for application as the magnetic hysteresis and/or QTM in the case of SMMs. This raises a serious question, and indeed innovative novel schemes need to be developed. A 'simple' example of a possible application for MNMs is their usage in magnetic refrigeration, where 'simple' refers to the fact that the 'complex quantum state' which is envisaged here is a ground state with a large spin and low magnetic anisotropy. By application of the magneto-caloric effect it is in principle possible to reach temperatures beyond the reach of liquid helium, by cooling on a molecular level [78]. However, more involved refrigeration schemes exploiting e.g. quantum spin frustration effects have also been suggested [79]. This points to the general idea of exploiting, yet to be identified, complex quantum states promoted by particular spin topologies for novel application schemes. This subject is currently much studied but still in its infancy. An example would be the chiral quantum spin states in spin triangles [80, 81, 82]. Obviously, MNMs may be the candidates of choice to realize experimentally such scenarios.

At this point it is interesting to note a potential link with another emerging research field. Recently, artificially engineered magnetic structures like AFM spin chains have been assembled on insulating layers, and their low-energy spectra have been measured with STM techniques with atomic scale precision [26]. In comparison with artificially formed atomic-scale magnetic structures, MNMs can be easily manipulated in size or spin length resulting in a wide variety of different topologies. In fact, hundreds of potentially interesting MNMs were already synthesized by chemists and are currently available for searching for complex quantum states, with potential for applications. In addition, the ground-state properties as well as the spin excitations can be
Artifically Engineered Spin Systems are on surfaces are addressable which quantum states? which topology? Molecular Nanomagnets available in many topologies excitations can be studied in detail function on surface? how to address function?

Figure 9. Comparison of achievements and opportunities as well as the challenges regarding application of artificially engineered atomic-scale spin systems and molecular nanomagnets, demonstrating the similarities as well as complementariness of these two research fields.

studied in any detail in such topologies thanks to the applicability of a full set of experimental techniques and bring about interesting effects, as were the ones discussed in this review. From this point of view MNMs have an advantage over artificial nanostructures. However, the latter have already been grafted on surfaces while maintaining their magnetic properties. Also, implicit in the use of the STM technique, the nanostructures and their magnetic function could be addressed individually, which is still a major obstacle in the case of MNMs.

In any case, both classes of systems are characterized by magnetic interactions of the order of few Kelvins or larger, thus they are quite robust when put on the surface against thermal vibrations and other types of external perturbations. MNMs and artificially engineered spin systems are complementary, as the former can be manipulated to many different topologies and assume complex many-body states, while the latter have already been shown to maintain their magnetic properties and their function to be addressable on the surface. Hence the advantages of each class can be an example for the other to overcome its problems, as summarized in pictorial fashion in figure 9.

References
[1]Gatteschi D and Sessoli R 2003 Angew. Chem. Int. Ed. 42 268
[2] Cavallini M, Gomez-Segura J, Ruiz-Molina D, Massi M, Albonetti C, Rovina C, Veciana J and Biscarini F 2005 Angew. Chem. Int. Ed. 44 888
[3] Affronte M 2009 J. Mater. Chem. 19 1731
[4] Leuenberger M N and Loss D 2001 Nature 410 789
[5] Gatteschi D, Sessoli R and Villain J 2006 Molecular Nanomagnets (Oxford: Oxford University Press)
[6] Waldmann O 2007 Inorg. Chem. 46 10035
[7] Ruiz E, Cirera J, Cano J, Alvarez S, Loose C and Kortus J 2008 Chem. Commun. 52
[8] Schröder C, Nojiri H, Schnack J, Hage P, Luban M and Kögerler P 2005 Phys. Rev. Lett. 94 017205
[9] Roussochatzakis I, Läuchli A M and Mila F 2008 Phys. Rev. B 77 094420
[10] Schmidt R, Schnack J and Richter J 2005 J. Magn. Magn. Mater. 295 164
[11] Kortz U, Müller A, Slageren J V, Schnack J, Dalal N S and Dressel M 2009 Coord. Chem. Rev. 253 2315
[12] Anderson P 1952 Phys. Rev. 86 694
[13] Bernu B, Lhuillier C and Pierre L 1992 Phys. Rev. Lett. 69 2590
[14] Waldmann O, Guidi T, Carretta S, Mondelli C and Dearden A L 2003 Phys. Rev. Lett. 91 237202
[15] Waldmann O 2002 Phys. Rev. B 65 024424
[16] Dreiser J, Waldmann O, Dobe C, Carver G, Ochsenbein S T, Sieber A, Güdel H U, van Duijn J, Taylor J and Podlesnyak A 2010 Phys. Rev. B 81 024408
[17] Carretta S, Santini P, Amoretti G, Guidi T, Copley J R D, Qiu Y, Caciuffo R, Timco G and Wernpenny R E P 2007 Phys. Rev. Lett. 98 167401
[18] Candini A, Lorusso G, Troiani F, Ghirri A, Carretta S, Santini P, Amoretti G, Mury C, Tuna F, Timco G, McInnes E J L, Wernsdorfer W and Affronte M 2010 Phys. Rev. Lett. 104 037203
[19] Affronte M, Carretta S, Timco G A and Wernpenny R E P 2007 Chem. Commun. 1789
Laye R H, Larsen F K, Overgaard J, Muryn C A, McInnes E J L, Rentschler E, Sanchez V, Teat S J, Güdel H U, Waldmann O, Timco G A and Winpenny R E P 2005 Chem. Commun. 1125

Barbara B and Chudnovsky E 1990 Phys. Lett. A 145 205

Tejada J, Garg A, Gider S, Awwalomal D D, DiVincenzo D P and Loss D 1996 Science 272 424

Chiolerio A and Loss D 1998 Phys. Rev. Lett. 80 169

Wernsdorfer W and Sessoli R 1999 Science 284 133

Palii A, Tsukerblatt B S, Coronado E, Clemente-Juan J M and Borrás-Almenar J J 2003 Inorg. Chem 42 2455

Hirjibehedin C F, Lutz C P and Heinrich A J 2006 Science 312 1021

Barbara B and Chudnovsky E 1990 Phys. Lett. A 145 205

Huang G, Qiao R J and Chklovskii D B 2001 Phys. Rev. B 63 245109

Haldane F D M 1983 Phys. Rev. Lett. 50 1153

Bethe H 1931 Z. Phys. 71 205

Bencini A and Gatteschi D 1990 Electron Paramagnetic Resonance of Exchange Coupled Clusters (Berlin: Springer)

Ochsennbein S T, Wallding O, Sieber A, Carver G, Bircher R, Davies R S G, Timco G A, in preparation.
Winpenny R E P, Mutka H and Fernandez-Alonso F 2007 *Europhys. Lett.* **79** 17003

[64] Affleck I, Kennedy T, Lieb E H and Tasaki H 1987 *Phys. Rev. Lett.* **59** 799

[65] Affleck I 1989 *J. Phys. Cond. Matt.* **1** 3047

[66] Waldmann O, Stamatatos T, Christou G, Güdel H U, Sheikin I and Mutka H 2009 *Phys. Rev. Lett.* **102** 157202

[67] Engelhardt L and Luban M 2006 *Phys. Rev. B* **73** 054430

[68] Waldmann O, Dobe C, Güdel H U and Mutka H 2006 *Phys. Rev. B* **74** 054429

[69] Santini P, Carretta S, Amoretti G, Guidi T, Caciuffo R, Caneschi A, Rovai D, Qiu Y and Copley J R D 2005 *Phys. Rev. B* **71** 184405

[70] Murrie M 2010 *Chem. Soc. Rev.* **39** 1986

[71] Palii A, Tsukerblatt B S, Clemente-Juan J M and Coronado E 2010 *Int. Rev. Phys. Chem.* **29** 135

[72] Chibotaru L F, Ceulemans A C and Bolvin m H 2008 *Phys. Rev. Lett.* **101** 033003

[73] Waldmann O, Hassmann J, Müller P, Hanan G S, Volkmer D, Schubert U S and Leh n J M 1997 *Phys. Rev. Lett.* **78** 3390

[74] Alley K G, Bircher R, Waldmann O, Ochsenbein S T, Güdel H U, Moubaraki B, Murray K S, Fernandez-Alonso F, Abrahams B F and Boskovic C 2006 *Inorg. Chem.* **45** 8950

[75] Klöwer F, Lan Y, Nehrkorn J, Waldmann O, Anson C E and Powell A K 2009 *Chem. Eur. J.* **15** 7413

[76] Mannini M, Pineider F, Danieli C, Totti F, Sorace L, Sainctavit P, Arrio M A, Otero E, Joly L, Cezar J C, Cornia A and Sessoli R 2010 *Nature* **468** 417

[77] Mannini M, Pineider F, Sainctavit P, Danieli C, Otero E, Sciancalepore C, Talarico A M, Arrio M A, Cornia A, Gatteschi D and Sessoli R 2009 *Nature Mater.* **8** 194

[78] Nayak S, Evangelisti M, Powell A K and Reedijk J 2010 *Chem. Eur. J.* **16** 12865

[79] Schnack J, Schmidt R and Richter J 2007 *Phys. Rev. B* **76** 054413

[80] Trif M, Troiani F, Stepanenko D and Loss D 2008 *Phys. Rev. Lett.* **101** 217201

[81] Luzon J, Bernot K, Hewitt I J, Anson C E, Powell A K and Sessoli R 2008 *Phys. Rev. Lett.* **100** 247205

[82] Georgeot B and Mila F 2010 *Phys. Rev. Lett.* **104** 200502