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TUTORIAL REVIEW

Molecular spins for quantum information technologies†

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Technological challenges for quantum information technologies lead us to consider aspects of molecular magnetism in a radically new perspective. The design of new derivatives and recent experimental results on molecular nanomagnets are covered in this *tutorial review* through the keyhole of basic concepts of quantum information, such as the control of decoherence and entanglement at the (supra-)molecular level.

1. Introduction

Performances of devices for information technologies are continuously improving. This implies, among many other things, the extreme miniaturization of components and the quest for higher and new performances. Electronic devices have nowadays the size of a few tens of nanometres; a similar size to magnetic bits in hard disks presently in commerce. All these are based on inorganic materials (semiconductors, magnetic media, *etc.*) and on the top-down lithographic processes. There will be a discontinuity in this race as soon as we will scale down all these technologies below 10 nm for several

reasons: the lithographic steps will become extremely demanding and expensive; processing and communication of information at the nanometre scale will be hard to maintain efficient in terms of energy dissipation and speed, just to mention a few technological issues, but more fundamental ones will also rise. Indeed the physical laws governing the functioning of any device with sizes below 10 nm changes dramatically since energy levels are quantized and quantum effects tend to become dominant. At the same time, the classical—and currently used—Boolean logic can be no more valid at nm scale or, maybe better to say, other logics are possible and even more appropriate with quantum devices. In a few words, we cannot think to scale down current information technologies indefinitely. So, the problem is not *just to replace existing materials for doing the same job at a reduced scale*, but probably we have to *deeply rethink materials and their functionalities at the same time for new generations of nano-devices.*

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On the other hand, information technologies provide very interesting challenges and an extremely wide playground in which scientists working in materials science, chemistry, physics and nano-fabrication technologies may find stimuli for novel ideas. Curiously, the nanometre scale is the *molecular scale*. So we may wonder whether, how or simply which functional molecules can be regarded—in some ways—as possible components of nano-devices. The goal is ambitious: it is not just a matter to store information in a molecule, but we may think to *process* information with a molecule and then to *communicate* information at the (supra-)molecular scale.

Spins are alternative/complementary to charges as degrees of freedom to encode information. Recent examples, like for instance the discovery and application of Giant MagnetoResistance, have demonstrated the efficient use of spins for information technologies. Moreover, spins are intrinsically quantum entities and they have therefore been widely investigated in the field of quantum-information processing. Molecular nanomagnets are real examples of finite spin chains (1D) or clusters (0D), and therefore they constitute a new benchmark for testing models of interacting quantum objects.

In this tutorial review, we discuss possible uses of molecular spin clusters for quantum-information processing presenting, firstly, some basic concepts (qubits, quantum gates, entanglement, decoherence); then we make examples based on specific molecular spin systems. Some recent achievements in the fields are mentioned and critically reviewed, but the list is not intended to be exhaustive since the field is in rapid evolution.[1] The interested reader may also refer to textbooks for a deeper presentation of general topics related to quantum information[2] or molecular magnetism.[3] Finally, we take the liberty to present some new ideas which are, at the moment, at an embryonic stage but look very promising.

2. Spin-cluster qubits

Broadly speaking, a **quantum computer** is a physical system that can be initialized to some known state $|\Psi(t_i)\rangle = |\Psi_0\rangle$, and whose dynamics can be controlled so as to induce any unitary transformation of the state vector $|\Psi(t_f)\rangle = U|\Psi(t_0)\rangle$, before this is finally read out.[2] In the standard approach, the computational process is given by the unitary time-evolution operator U of the state vector, and is driven by the application of external stimuli. Most quantum algorithms can be efficiently implemented in systems consisting of weakly coupled and individually addressable two-level subsystems (qubits). Just like its classical counterpart, a quantum bit can take two logical values, 0 and 1, that are physically encoded into the eigenstates of a two-valued observable. For an $s = 1/2$ spin, a typical choice is given by the eigenstates of s_z: $|0\rangle \equiv |\uparrow\rangle$ and $|1\rangle \equiv |\downarrow\rangle$. Unlike a classical bit, a qubit also allows any linear superposition $|\phi\rangle = \alpha|0\rangle + \beta|1\rangle$ of the basis states. While in the initial and final states each qubit is either in its $|0\rangle$ or $|1\rangle$ state, linear superpositions are massively exploited during the dynamics, and play a crucial role in quantum algorithms. The relevance of qubits comes from the fact that any unitary transformation U in the 2^n-dimensional Hilbert space of the n-qubit system can be efficiently decomposed into a discrete sequence of local transformations, such as single and two-qubit gates. The implementation of these quantum logic gates calls for the use of external fields that selectively address the two-level subsystems, and for a switchable coupling between the qubits. In the above mentioned case of the electron spin projection, the quantum gates can be implemented by pulsed magnetic fields. In single- and two-qubit gates, the rotation of the target spin induced by a given pulse is unconditioned by the other qubits and dependent on the setting of a control qubit, respectively. In the latter (former) case, control and target qubits need to be physically (un)coupled. The need for implementing alternatively single- and two-qubit gates, thus calls for the capability of switching on and off the interaction between qubits on a fast time scale. Identifying a good qubit candidate requires to take into account these and other requirements jointly:[4] not any two-level system will do. For example, a system with a ground state doublet that is well separated in energy from the excited states, but where the states $|0\rangle$ and $|1\rangle$ cannot be efficiently rotated one into the other by means of external fields would not represent a good choice.

In the following, we shall specifically refer to the use of low-spin molecular nanomagnets for the qubit encoding. Here, the overall quantum hardware is represented by a collection of such molecular nanomagnets, weakly coupled to each other by means of super-exchange bridges. Not all quantum algorithms, however, need qubits and a decomposition in terms of local operations in order to outperform classical algorithms. Grover's algorithm for searching in an unsorted database, for example, can be efficiently implemented in a single (*i.e.* non-composite) system. Single high-spin molecules have in fact been proposed for the implementation of Grover's algorithm by sequences of multi-frequencies EPR pulses.[5]

Single electron spins represent quite a natural choice for the implementation of a quantum bit. In fact, they are "true" (as opposed to "effective") two-level systems. Besides, as compared to other degrees of freedom in solid-state or molecular systems, they are relatively decoupled from the environment, and thus have longer relaxation and dephasing times. These basic motivations also support the choice of spin-cluster qubits,[6] where the logical states $|0\rangle$ and $|1\rangle$ are identified with the two lowest eigenstates of a spin cluster (see Fig. 1).

Molecular nanomagnets[3] (MnM) represent prototypical implementations of spin-clusters; their magnetic properties result from the combined interactions between the constituent ion spins, and can be largely engineered by chemical synthesis. In particular, MnMs with an $S = 1/2$ ground state are potential candidates for the implementation of a spin-cluster qubit, for the $|\Uparrow\rangle = |S = 1/2, M = 1/2\rangle$ and $|\Downarrow\rangle = |S = 1/2, M = -1/2\rangle$ eigenstates provide a natural encoding of the qubit logical states (hereafter, the thick arrows will be used to highlight the composite character of these effective two-level systems). The presence of a well-defined $S = 1/2$ ground state requires not only an antiferromagnetic coupling between the magnetic ions, but also a detailed control of their number and spatial arrangement; specific chemical substitutions can also be required.

The use of a nanomagnet, rather than a single electron or $s = 1/2$ ion, for encoding a qubit offers further opportunities
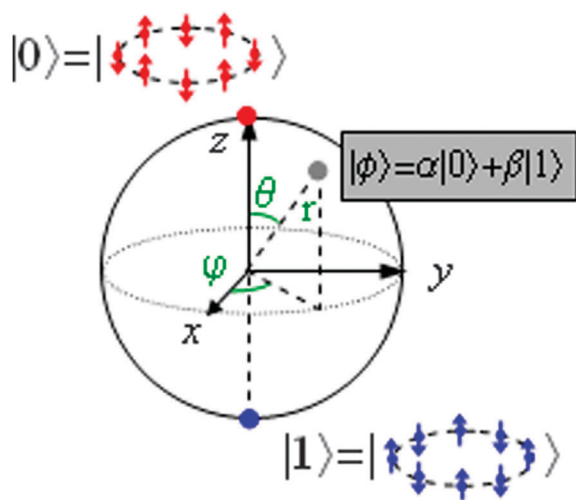
Fig. 1 Bloch sphere representation of the (spin-cluster) qubit state. Pure and mixed states of the two-level system correspond to points on the sphere ($r = 1$) and inside it ($r < 1$), respectively. Completely incoherent mixtures of the basis states $|0\rangle$ and $|1\rangle$ correspond to points along the z axis.

and implies some possible complication.[7] The larger size of a nanomagnet with respect to a single ion reduces the spatial resolution required in order to selectively address the qubit by means of both external fields and measuring apparatuses. Besides, molecular nanomagnets, being relatively complex systems, are more widely engineerable at the chemical level. This is the case of, *e.g.*, the effective *g*-tensor of molecular spin that results from the average of the constituent ions *g*-tensors, weighted by the spin density. Differences in the *g*-tensors between neighbouring nanomagnets, for example, would allow their selective addressing without the need for spatially modulating the magnetic field on the molecular length scale. Another substantial difference between nanomagnets and single-ions is represented by the presence, in the former, of excited spin states. The population leakage from the two lowest states, $|0\rangle$ and $|1\rangle$, to the excited states represent a possible source of error in the quantum algorithm, and should in general be avoided. Undesired occupation of such states might result initially from thermal distribution, if the temperature is not sufficiently low compared to the energy splitting between ground and excited states. Leakage can also occur during the manipulation of the qubit state, due to transitions unintentionally induced by the e. m. pulses. For these reasons it is in general preferable that the ground state doublet of the molecule is well separated in energy from the excited states. On the other hand, these can also be used as auxiliary levels in specific computational sequences: here, the state of the molecule is in the subspace $\{|0\rangle,|1\rangle\}$ at the beginning and at the end of each quantum gate, but excited states can be controllably involved during the implementation of specific operations. The additional resource provided by the auxiliary states can be used, *e.g.*, for effectively switching on and off the coupling between two nanomagnets even in the impossibility of switching the underlying physical interaction. This can be achieved in suitably engineered systems if the inter-molecular interaction terms have vanishing or finite expectation values

depending on whether the system is in the ground-state doublet or in the excited multiplet states[8] (Fig. 2). Along these lines, auxiliary states can also be used in order to implement global-field approaches, where the requirement of selectively addressing each qubit is relaxed, at the expense of using a number of additional auxiliary qubits. The presence of excited states within the physical qubits allows to reduce the number of auxiliary qubits, and simplifies the implementation of the quantum logic gates. Crucial within such a scheme is the interplay between the symmetry of the molecular nanomagnet and the microscopic details of the intermolecular exchange.[9]

Therefore, two of the main problems in the implementation of quantum-information processing in molecular nanomagnets, namely the switchability of intermolecular interaction and the selective addressability of the molecules, can be possibly tackled by a suitable exploitation of the spin-cluster excitations. The composite character of these systems can in principle also affect the coupling of the electron spin with the environment (nuclear spins, phonons) and the resulting decoherence. However, it is not obvious *a priori* whether or not molecular spin-clusters imply advantages in this respect.[6]

3. Entanglement

Definition

Entanglement is probably the most peculiar feature of quantum-mechanical systems;[10,11] besides, it represents a fundamental resource in quantum-information processing. Two spins s_1 and s_2 are entangled if the two-spin states $|\psi\rangle$ can be, by no means, written as a product of single-spin states: $|\psi\rangle \neq |\phi_1\rangle \otimes |\phi_2\rangle$, for any $|\phi_1\rangle$ and $|\phi_2\rangle$. For mixed states ρ, the above criterion translates into the impossibility of
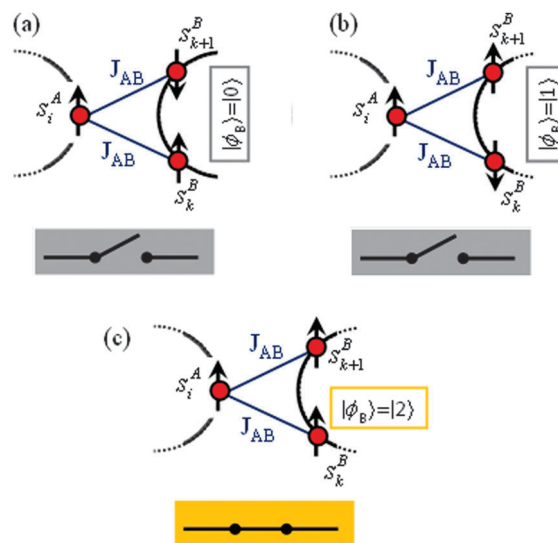

Fig. 2 Example of a state-dependent (effective) coupling between the spin rings A and B. An Ising interaction between spin i of ring A and spins k and $k + 1$ of B results in an effective coupling: $\langle \phi_A,\phi_B|H_{AB}|\phi_A,\phi_B\rangle = J_{AB}\langle \phi_A|s_{i,z}{}^A|\phi_A\rangle \ (\langle \phi_B|s_{k,z}{}^B|\phi_B\rangle + \langle \phi_B|s_{k+1,z}{}^B|\phi_B\rangle)$. If $s_{k,z}{}^B$ and $s_{k+1,z}{}^B$ are antiparallel when B is in $|0\rangle$ (a) or $|1\rangle$ (b), but not for $|\phi_B\rangle = |2\rangle$ (c), the excitation of B from one of the former states to the latter ones switches on the effective coupling between (the total spins of) A and B.

decomposing the density matrix in terms of separable states: $\rho \neq \sum_i p_i \rho^1{}_i \otimes \rho^2{}_i$. Such definitions are easily generalized to multi-spin states.

One of the most counter-intuitive consequences of entanglement is that the complete specification of the system state does not prevent the state of its components from being at least partially unspecified. In other words, the state of each subsystem cannot be described independently of the state of the other one. This is the case of, *e.g.*, two $s_1 = s_2 = 1/2$ spins in a singlet state $|\psi\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$. The state of spin 1, averaged over all possible states of spin 2, is given by its reduced density matrix $\rho_1 = \mathrm{Tr}_2\{|\psi\rangle\langle\psi|\} = 1/2(|\uparrow\rangle\langle\uparrow| + |\downarrow\rangle\langle\downarrow|)$, which corresponds to a completely undetermined state.

Entanglement *vs.* coupling

In order to allow the investigation of entanglement, a physical system should consist of a collection of well-defined and (weakly) interacting subsystems. The possibility of generating entangled states depends in practice on such coupling between the subsystems. Coupling and entanglement are however conceptually distinct (the coupling is a property of the system and of its Hamiltonian, whereas entanglement is a property of the quantum state) and one thing does not imply the other.

The generation of entangled states can follow distinct approaches. In the first one, the coupling between the subsystems is engineered in such a way that the ground state of its Hamiltonian H coincides with some remarkable entangled state; the system is then cooled down in order for the equilibrium density matrix to approach such ground state. In the second approach, the system is initialized in some defined state, and this is then rotated by pulsed external fields into the entangled state of interest that needs no longer to coincide with an eigenstate of H. On the one hand, this latter procedure makes the requirements on the coupling between subsystems less stringent; on the other hand, however, it requires coherent control of the state vector and time-resolved measurement of the spin.

Different approaches can also be followed to detect and possibly **quantify entanglement** experimentally. Ideally, these objectives call for a selective addressing of the subsystems, and require the measurement of correlations between their observables. In quantum state tomography,[2] a complete set of correlation functions is used to reconstruct the overall density matrix. This procedure has been followed, *e.g.*, to demonstrate entanglement between two or more photons. An experimentally less demanding approach for detecting entanglement (*i.e.* for simply distinguishing an entangled state from a separable one) is based on the so-called *entanglement witnesses* (Fig. 3). An entanglement witness is an observable W whose expectation value is always positive if the density matrix ρ is factorizable ($\rho = \sum_i p_i \rho^1{}_i \otimes \rho^2{}_i \rightarrow \langle W \rangle = \mathrm{Tr}\{\rho W\} \geq 0$), and negative for some class of entangled states. Therefore, if the expectation value of W is negative, one can conclude that the system density matrix ρ is not factorizable. The main advantage of such approach is that it does not require the knowledge of the system state, nor that of its Hamiltonian. It is quite remarkable that some of the quantities that are routinely measured in (molecular) magnetism correspond to

entanglement witnesses, under relatively broad conditions. In particular, magnetic susceptibility can play such a role for a system of N spins s, provided that this is isotropic (*i.e.* that the Hamiltonian is invariant under arbitrary rotations of the total spin). In this case, $\chi \geq cNs/k_B T$ for any factorizable ρ (where c is a dimensional constant). The use of magnetic susceptibility as an entanglement witness has allowed the detection of equilibrium state entanglement between Ho^{3+} ions in a bulk magnetic salt $LiHo_xY_{(1-x)}F_4$.[12]

In the following, we focus on the case of **intermolecular entanglement**, *i.e.* on entanglement between the total spins of two low-spin ($S = 1/2$) nanomagnets.[13] As with most genuine quantum-mechanical features, entanglement is also more difficult to observe in systems of increasing complexity. In the case of coupled nanomagnets, a preliminary and non-trivial requirement is that of chemically and magnetically coupling the molecules, while leaving their individual properties substantially unaffected (hence the requirement that the coupling between the subsystems should be weak). More specifically, the intermolecular coupling needs to be large with respect to, *e.g.* the working temperatures, but small compared to the intra-molecular interactions, so that each molecule can still be regarded as an effective two-level system. An exchange interaction that fulfils the above requirements was recently demonstrated in a dimer of antiferromagnetically coupled heterometallic wheels.[14] Here, in order to have an entangled equilibrium state, also the sign of the exchange coupling J and its magnitude play a fundamental role. In fact, if the inter-molecular exchange had a ferromagnetic character, the population of the dimer in the limit $|J| \gg T$ would have been distributed amongst the triplet states $|S = 1, M = 0\rangle$ and $|S = 1, M = \pm1\rangle$, resulting in a factorizable density matrix at any temperature and applied magnetic field. An antiferro-magnetic exchange between the nanomagnets, combined with a temperature $T \ll |J|$, allows the equilibrium density matrix to resemble the singlet ground state. The entangled character of the equilibrium state has been detected by using magnetic susceptibility as an entanglement witness.[14] It is worth noticing that the use of experimental observables as entanglement witnesses requires the determination of their absolute value per molecule that has to be compared to the threshold value. Such requirement might be rather demanding in the case of, *e.g.*, energy, which is also an entanglement witness for systems of antiferromagnetically coupled spins.

Quantum entanglement between nanomagnets in out-of-equilibrium states has not been demonstrated so far. In this case, the role of intermolecular interaction would be that of enabling the implementation of a genuine two-qubit operation by pulsed magnetic fields. Liquid NMR and nitrogen-vacancy defects in silicon provide examples of how these operations can be implemented in spin systems.[2]

4. Decoherence

Communication and processing of quantum information is based on the **coherent evolution** of the system state vector: $|\Psi(t)\rangle = e^{-iHt/\hbar}|\Psi_0\rangle$. If the system consists of N_e electron spins s_i, this implies that the Hamiltonian H depends only on the spin degrees of freedom and on external control parameters

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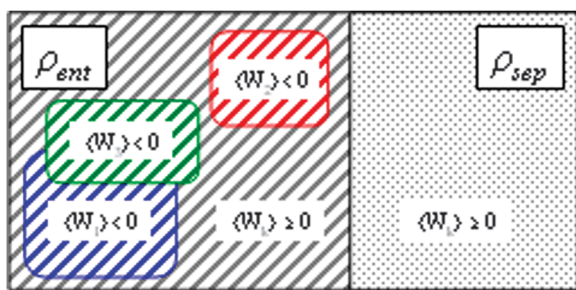
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Fig. 3 An entanglement witness allows to discriminate between a separable (dotted area) and an entangled (striped area) density matrix. Different entanglement witnesses W_k detect different classes of entangled states, for which their expectation value is negative.

α_k (classical fields): $H = H(s_1, \ldots, s_{Ne}; \alpha)$. In real systems, however, the coupling to the environment ($\mathcal{E}$) tends to spoil the coherent character of the system ($\mathcal{S}$) dynamics. This process is known as *decoherence*, and its characteristic time-scale is the (de)coherence time τ_d.[15] In the perspective of quantum-information processing, the relevant **figure of merit** is given not by the absolute value of such parameter, but rather by the ratio between τ_d and the characteristic timescale of the coherent manipulation (*e.g.*, the typical duration τ_g of a quantum gate). In fact, the errors induced by decoherence can be corrected and the computation can be made fault-tolerant, provided that the ratio τ_d/τ_g is lower than a given threshold; a typical value of the threshold is 10^{-4}, but such value can change, depending on the general features of the decoherence process. The environment can induce transitions between different eigenstates of the system Hamiltonian H: $|\phi_i\rangle \rightarrow |\phi_k\rangle$. Such energy exchange with the environment takes place in relaxation ($E_i > E_k$) and incoherent excitation ($E_i < E_k$). These processes can be made relatively inefficient by introducing a large energy mismatch between the system and the environment excitation energies.

A major problem is typically represented by dephasing, resulting from elastic interactions between $\mathcal{S}$ and $\mathcal{E}$. **Dephasing** consists of the loss of phase coherence between the components of a linear superposition, and implies the evolution of a pure state into a statistical mixture: $|\psi\rangle = \sum_i c_i |\phi_i\rangle \rightarrow \rho = \sum_i |c_i|^2 |\phi_i\rangle\langle\phi_i|$. If the system–environment interaction has a Markovian character, both excitation/relaxation and dephasing display an exponential dependence on time. These are characterized by the so-called longitudinal (T_1) and transverse (T_2) relaxation time constants, with $T_2 \leq 2T_1$.

Decoherence is an ubiquitous phenomenon, yet its features and timescales depend strongly on the system, the experimental conditions, and on the specific linear superpositions under consideration. From the experimental point of view, the coherent transition from a coherent to an incoherent dynamics can be probed by the observation of Rabi oscillations between two quantum states, driven by a coherent beam of e. m. radiation, or by free rotations (*e.g.*, a spin precessing in a static magnetic field).

In molecular nanomagnets, decoherence of the electron spin mainly arises from **the coupling to phonons and nuclear spins**. In addition, with most experiments performed on ensembles of nanomagnets, dipolar interactions between different replicas

of the system can result in decoherence. While **dipolar interactions** and coupling to phonons depend on the arrangement of the nanomagnets within the sample, and can be possibly reduced by modifying such arrangement, the coupling between electron and nuclear spins of each molecule represent an intrinsic source of decoherence. Hyperfine interactions might therefore represent the fundamental limitation of the electron-spin coherence.

Interaction with the nuclear bath

We consider the case of a nanomagnet with an $S = 1/2$ ground state doublet that is initialized into a linear superposition: $|\psi_0\rangle = (|\Uparrow\rangle + |\Downarrow\rangle)/\sqrt{2}$, where $|\Uparrow\rangle$ and $|\Downarrow\rangle$ are the lowest eigenstates of the molecule spin Hamiltonian H. In the presence of a static magnetic field $\boldsymbol{B}_0$ along z, the molecule spin tends to precess in the xy plane. The coupling between the electron (s_i) and the nuclear (I_k) spins modifies such idealized dynamics in different respects. Firstly, the nuclear bath generates a magnetic field (the so-called Overhauser field $\boldsymbol{B}_N$); $\boldsymbol{B}_N$ adds to $\boldsymbol{B}_0$ a contribution that depends on the state of the nuclei, $\boldsymbol{B}_N^k = \boldsymbol{B}_N(|\mathcal{E}_k\rangle)$, thus renormalizing the Larmor frequency of the nanomagnet spin $\boldsymbol{S}$. For temperatures larger than the nuclear Zeeman energy ($T \sim 1$ mK for $B_0 \sim 1$ T), the nuclear bath is not in a defined (*i.e.* pure) state, but rather in a statistical mixture of different states ($\rho_n = p_k|\mathcal{E}_k\rangle\langle\mathcal{E}_k|$). As a consequence of the statistics in the Overhauser field, and thus of the Larmor frequency, the state of the nanomagnet evolves from $\rho_e = |\psi_0\rangle\langle\psi_0|$ into mixture $\rho_e = p_k|\psi_k(t)\rangle\langle\psi_k(t)|$, with $|\psi_k(t)\rangle = (|\Uparrow\rangle + e^{i\phi_k(t)}|\Downarrow\rangle)/\sqrt{2}$ and $\phi_k = \omega_L t + \delta_k(t)$.

If the dynamics of the nuclear bath is frozen, the above effect is analogous to that produced by inhomogeneities between different replicas within an ensemble. As in the case of inhomogeneous broadening, the phase coherence can be ideally recovered by refocusing techniques.[16] On timescales where the nuclear bath dynamics cannot be neglected, the electron spin decoherence tends to be irreversible, due to spectral diffusion and electron–nuclear entanglement. The first phenomenon, that can be understood also in classical terms, consists of the fluctuations of the Overhauser field $\boldsymbol{B}_N^k$ resulting from the time evolution of $|\mathcal{E}_k\rangle$. Here, the effect on the precession of the electron spin cannot be cancelled by spin echo techniques, because the nuclear contribution to the phase difference $\delta_k(T)$ accumulated between $t = 0$ and $t = T$ need not coincide with $\delta_k(2T) - \delta_k(T)$. The second phenomenon—electron–nuclear entanglement—has no classical interpretation nor counterpart. It arises from the fact, that, even if the nuclei cannot efficiently induce transitions between electron spin states (due to the large mismatch between the electron and the nuclear Zeeman energies), these can in turn affect the nuclear dynamics. In first order in the hyperfine coupling, such dependence results from the chemical shift, *i.e.*, from the magnetic field generated by the spins s_i on the I_k. Higher-order processes can also contribute, such as those where a (real) transition between nuclear states involves a virtual transition of the electron state: $|\phi_i, \mathcal{E}_i\rangle \rightarrow |\phi_k, \mathcal{E}_l\rangle \rightarrow |\phi_i, \mathcal{E}_f\rangle$. The evolution of the nuclear bath state, resulting from the interplay between such hyperfine interactions and the (dipole–dipole) ones between nuclei, is different if the electron spin of the

nanomagnet points in one direction or in the opposite one. As a consequence, electron–nuclear correlations arise, and an initial state which is factorizable into the product of an electron and a nuclear state (e.g., $|\Psi_{en}(0)\rangle = (|\Uparrow\rangle + |\Downarrow\rangle)/\sqrt{2} \otimes |\mathcal{E}_k\rangle)$, evolves into an entangled state $(|\Psi(t)\rangle = (|\Uparrow\rangle \otimes |\mathcal{E}_{k,\Uparrow}\rangle + |\Downarrow\rangle \otimes |\mathcal{E}_{k,\Downarrow}\rangle)/\sqrt{2})$, where $|\mathcal{E}_{k,\Uparrow}\rangle$ and $|\mathcal{E}_{k,\Downarrow}\rangle$ are the states of the nuclei conditioned upon the electron spins being in $|\Uparrow\rangle$ and $|\Downarrow\rangle$, respectively. The state of the electron spins alone is defined by the reduced density matrix, which is obtained by tracing away the nuclear degrees of freedom, i.e., by averaging over the nuclear spins state. The result is given by: $\rho_e = Tr_n\{|\Psi_{en}\rangle\langle\Psi_{en}|\} = 1/2(|\Uparrow\rangle\langle\Uparrow| + |\Downarrow\rangle\langle\Downarrow|) + 1/2(\langle\mathcal{E}_{k,\Uparrow}|\mathcal{E}_{k,\Downarrow}\rangle|\Uparrow\rangle\langle\Downarrow| + h.c.)$. Therefore, the stronger the dependence of the nuclear state on the electron state, the smaller $r_k \equiv |\langle\mathcal{E}_{k,\Uparrow}|\mathcal{E}_{k\Downarrow}\rangle|$, the more ρ_e differs from the initial pure state and resembles a mixture of $|\Uparrow\rangle$ and $|\Downarrow\rangle$. The degree of purity of ρ_e and the electron–nuclear entanglement respectively decrease and increase with r_k.

Polarization of nuclear spins reduces both the inhomogeneous broadening and the nuclear dynamics, for this is mainly induced by Zeeman energy-conserving processes (such as flip-flop transitions), and the more the nuclei are polarized, the smaller the number of final states towards which their initial state can evolve.[17] Theoretical simulations have shown that spin-echo pulse sequences can partially disentangle electron and nuclear spins, thus inducing a partial recovery of the electron spin coherence.[18] In the simplest case (Hahn-echo sequence), the spin echo resulting from the refocusing of inhomogeneous spins within an ensemble or from the static component of the Overhauser field takes place at a time $t = 2\tau$, being τ the time of the refocusing pulse. The electron–nuclear disentangling, instead has a maximum at earlier times (typically $t \approx 1.5\tau$). In order to make this effect experimentally observable, spin-echo sequences are required where the two effects coincide in time.[19]

The control of decoherence represents indeed one of the key challenges for the implementation of quantum information processing. In order to maximize the decoherence time, a detailed understanding of the process is in order. This represents the prerequisite for engineering the system by chemical synthesis; besides, it allows to identify the degrees of freedom that are more robust with respect to decoherence, and that are thus more suitable for encoding quantum information.

The simulation of the nuclear dynamics in Cr_7Ni rings,[20] for example, has allowed to highlight the following features. The decoherence time is in the order of few microseconds, and is mainly induced by the H nuclei, that represent the majority of the nuclear spins in the molecule. These evolve under the effect of the dipole–dipole interactions, combined with the diagonal part of the hyperfine coupling to the electron spins (this originates mainly from the electron–nuclear dipole–dipole interactions, being the electron spin density localized away from the H nuclei). A minor role is played by the F nuclei (fewer, but localized close to the magnetic ions) and by the electron-spin mediated couplings between nuclear spins. The role of the H nuclei that are present in the solvent is reduced—as compared to other nanomagnets—by the shell of organic ligands that surrounds the magnetic ions.

Quantum-information processing heavily relies on linear superpositions of multi-qubit states. The decoherence of such states is therefore also relevant, and in general cannot be simply reduced to that of the single qubit. Let us consider the case of two exchange-coupled $S = 1/2$ nanomagnets, to which we refer as A and B. A linear superposition of two eigenstates of the dimer such as $(|\Uparrow\Uparrow\rangle + |\Downarrow\Downarrow\rangle)/\sqrt{2}$, which is also an entangled state, decoheres under the effect of hyperfine interactions. In particular, the electron spins affect the nuclear dynamics through the different chemical shift induced by the $|\Uparrow\rangle$ and $|\Downarrow\rangle$ components. In pictorial terms, one can say that the nuclear environment "reads" efficiently the spin projection of the electron spin. This suggests that linear superpositions between states with equal state projection of the spin might be more robust with respect to decoherence. The singlet and triplet ($M = 0$) eigenstates of the dimer fulfil this condition. In both cases, the expectation values of the electron spins vanishes. As a consequence, neither state induces a chemical shift in the nuclear energies. The main contribution to the electron–nuclear entanglement is thus represented by processes that are second order in the hyperfine couplings. More specifically, these consist of flip-flop transitions between pairs of nuclei mediated by virtual transitions of the electron spin state. These processes involve the nuclei that are located closer to the electron spin density, namely the F nuclei.[21] This shows how decoherence can depend not only quantitatively, but also qualitatively on the specific linear combination in question.

5. Molecular candidates as compared to the DiVincenzo criteria

In order to exploit the quantum features for information processing, molecular spin clusters have to fulfil some basic requirements. It is generally accepted that the DiVincenzo criteria[22] establish the basic requests for a quantum system to be considered as a good candidate for performing quantum computation within the standard approach.[23] These criteria can be summarized as follows:

1. Well-defined qubits forming a *scalable* quantum register. For molecular spin clusters this implies the definition of molecular states to be used for encoding quantum information.

2. Initialization of the qubits in a defined state at time $t = 0$. For molecular spin clusters this may imply a simple cooling in an external magnetic field that brings the molecule into its ground state.

3. Implementation of a *universal* set of quantum gates. These implies the capability of selectively addressing the nanomagnets by means of external stimuli, and of switching the coupling between nanomagnets on a timescale faster than the decoherence time.

4. In order to keep the time evolution unitary, it is necessary that coherence is kept for times much longer than the typical gating time. As mentioned before, it is in general required that the *figure of merit* τ_d/τ_g is lower than 10^{-4}.

5. Finally, the spin state of each nanomagnet needs to be read out.

Scalability implies that the resources that are necessary in order to fulfil the above requirements scale polynomially with the number of qubits. Moreover, since errors are always present, *scalability* also implies the possibility to correct these errors efficiently and that these do not increase

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exponentially with the increasing complexity of the whole quantum processor.

In principle, many molecular spin clusters have the potentialities to encode qubits. In practice only very few of them have been tested against the DiVincenzo criteria and much work still need to be done. It is probably worth to critically review some important achievements obtained so far in the field. We start by comparing the use of *high spin* Single Molecule Magnets (SMM) with that of *low spin* molecular clusters.

High spin SMM may certainly act as multiple registers, for instance by exploiting sublevels M_S of the ground state multiplet. This may allow the encoding of a specific quantum (Grover's) algorithm as proposed by Leuenberger and Loss[5] for Mn_{12} or Fe_8. In this approach, the dimension N of the computational space is fixed by the value of S in the ground state multiplet ($N = 2S + 1$); this might represent the main limitation towards scalability. The coherence time in ensembles of SMM is presently limited by the intermolecular dipolar interaction, resulting from the high values of their total spin in the ground state. For Fe_8 a decoherence time T_2 of 712 ns at 1.3 K has been reported.[24] In practice, the spectral resolution within the ground multiplet required for encoding the Grover's algorithm and the presence of quantum tunneling of the magnetization make experiments difficult for Mn_{12} and Fe_8 although attempts to encode qubits in these molecules are still in progress. Experimental conditions seem to be better for Fe_4 SMM for which direct experimental evidence for long-lasting, $T_2 = 640$ ns, quantum coherence and quantum oscillations between two M_S states has been reported by using pulsed W-band ESR spectroscopy.[25]

Quantum oscillations have been reported for some Single Ion Magnets like for instance Er^{3+} ions ($J = 15/2$ and $g_J = 6/5$) diluted in a single crystalline matrix of $CaWO_4$.[26] A general problem for diluted impurities is the lack of control in their positioning in real devices. More recently, coherent oscillations, with some resonances between electron and nuclear spins, have been observed in single RE ions (Ho^{3+}) embedded in polyoxometallates (POM).[27] In the case of POM different ways to deposit and position such molecules have been shown by the group of Prof. E. Coronado in Valencia. A possible issue is the fact that methods/strategies to couple two or more such RE ions or the chemistry necessary to couple two or more POM in a controlled way are not evident at the moment. Moreover, besides the Grover's algorithm, the presence of multiple registers (electronic sublevels) in the lowest multiplet is not strictly required for the implementation elementary quantum gates while the interplay between electronic and nuclear spins needs to be controlled. Finally it is worth mentioning the activity of the group of Dr G. Aromi who is using β-diketonates ligands to synthesise linked SMMs designed under different gate schemes.[28,29]

Low spin ($S = 1/2$) ***molecular clusters*** appear as the most straightforward implementation of the two level systems necessary for the qubit encoding. Since a universal set of unitary transformations can be, in principle, encoded in an array of two level systems, this scheme is scalable as far as we are able to dispose molecules within our quantum machine with no particular limitation. In this respect, positioning of a molecule in a specific place over the surface can be one

additional requirement. Molecular units need to identical otherwise (for instance, in case of isomers or misalignment) this may introduce errors in an uncontrolled manner, limiting scalability. As regard to this point, the presence of a Kramer doublet with no preferential orientation (anisotropy) for the ground state is certainly one advantage of low spin molecules. Moreover, the low spin limits cross talk (dipolar interaction) between independent units and this is a further advantage in view of dense packing in scalable architectures.

A first prototypical example is V_{15} whose ground state comes out from the coupling of fifteen V^{4+} in a spherical arrangement. The lowest lying states are two doublets split by only 80 mK and separated by 3.8 K from the first $S = 3/2$ excited state. Rabi oscillations within the $S = 3/2$ multiplet have been observed on V_{15} with a coherence time estimated to be a few hundreds of ns at 4 K.[30]

Heterometallic rings have been engineered by Dr G. Timco in the group of Prof. R.E.P. Winpenny at Manchester University in order to have a non-degenerated doublet as the ground state. That was the case of molecular Cr_7Ni[31] for which quantum oscillations within the ground doublet have been measured to be as long as 3 μs at 2 K.[32] The main mechanism for decoherence at low temperature is a hyperfine interaction with nuclei present in the molecule while a new variant of this macro-cycle[33] seems to have a longer coherence time as expected from the reduced amount of Fluorine nuclei. This molecule can be successfully grafted on different substrates including gold[34] and graphite[35] showing to be robust enough to suffer only minor changes in the pattern of its low lying levels when single units are anchored on the surface.[36] More recently two or a few more Cr_7Ni rings have been linked together and the chemistry behind this seems to provide great flexibility in the choice of linker (including switchable ones) and therefore tuneability of the magnetic coupling.[37] Spin entanglement at the supramolecular level has been proven and discussed in different cases.[14,38] The presence of different Cr_7Ni variants in principle leads to spectroscopic diversity of each species. Different approaches can in principle be followed in order to allow the implementation of logical gates. The required individual addressing of each molecule is however still an open issue.

Finally it is worth mentioning recent achievements in the use of simple radicals as elementary molecular two level systems. These present several advantages starting from the simple and flexible chemistry, to the easy of their deposition on surfaces and more deeply they are free from metal centres that, due to their single ion anisotropy, may represent an intrinsic limitation for qubits encoding. The group of Prof. T. Takui at Osaka City University is carrying out an intense research program on (malonyl) radicals.[39] Preliminary results obtained by Prof. Gatteschi's group on a frozen solution of NitRin CH_2Cl_2 have shown that the relaxation times observed at 70 K were 3 μsec for T_2 and 500 μsec for T_1, respectively.[40]

6. Alternative ways to perform spin manipulation and spin logic

Spin manipulation with electric fields

The projection of the nanomagnet spin is not the only degree of freedom that can be used for encoding quantum

information. A potentially powerful—yet largely unexplored—alternative is represented by the chirality.[41] While the projection of the nanomagnet spin can be manipulated by oscillating magnetic fields,[39] the control of spin chirality can be achieved by means of oscillating electric fields.[42] Magnetic wheels consisting of an odd number N of identical spins represent ideal systems for exploring the potentialities of spin–electric coupling. In the presence of antiferromagnetic coupling between neighbouring spins, $H = \sum_i J_i s_i \cdot s_{i+1}$ with $J_i \equiv J$, these frustrated systems exhibit a four-fold degenerate $S = 1/2$ ground state. Hereafter, we refer for simplicity to the case of a triangle of $s = 1/2$ spins[43] (Fig. 4). The states that span such low-energy subspace can be labelled in terms of their spin projection S_z and of the chirality $C_z = s_1 \cdot s_2 \times s_3$. Spin–orbit (Dzyaloshinskii–Moriya) interaction couples these two degrees of freedom, thus partially removing the degeneracy of the $S = 1/2$ quadruplet. An electric field can couple states of opposite chirality (and equal S_z), by modulating inhomogeneously the exchange couplings within the ring ($\delta J_i \neq \delta J_k$). The electric field E renormalizes J by affecting the electron hopping between the magnetic sites that effectively couples the spins. In order for the renormalizations δJ_i of the exchange coupling to depend linearly on the electric field intensity, E must possess a component along the permanent dipole of the exchange bridge(s) that couple s_i and s_{i+1}. In order for the δJ_i to differ from one another, such dipoles must point in different directions (an homogeneous perturbation $\delta J_i \equiv \delta J$ would not couple states of different chirality). Very little is still known on spin–electric coupling in nanomagnets and on the values of the coupling constants.[44] In order to use the spin chirality for encoding and manipulating quantum information, the renormalizations δJ_i need to be sizeable. Unlike the case where spin–electric coupling is used for inducing spin–electric crossover,[45] however, the reference value for δJ_i is not represented by the unperturbed value of J, but rather by the inverse of the decoherence time $\hbar/\tau_d$ (which is still unknown for the chirality degree of freedom).
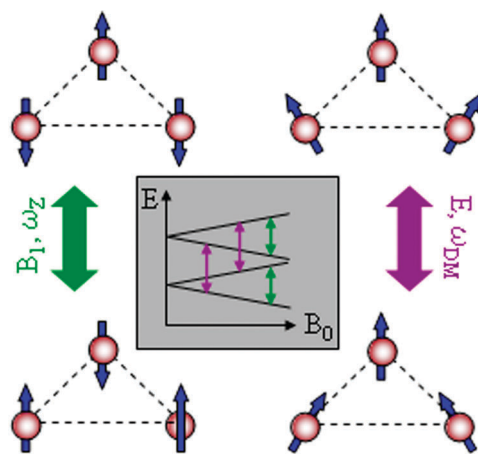

Fig. 4 Spin projection (S_z) and spin chirality within a frustrated spin ring can be manipulated by pulsed magnetic and electric fields, respectively. In the case of S_z (green arrows) the transition energy ω_Z is given by the Zeeman splitting, whereas in the case of chirality (purple arrows), it is fixed by the Dzyaloshinskii–Moriya interaction. Central inset: low-energy $S = 1/2$ quadruplet.

In fact, just like in pulsed EPR, the rotations of the quantum state is induced by resonant pulses; unlike the case of EPR, the frequency of the oscillating field is determined not by the static magnetic field (Zeeman splitting) but rather by the spin–orbit interaction, that splits states of opposite chirality.

The use of electric fields for manipulating the nanomagnet state offers technological advantages. These include the possibility of coupling the spin with photons confined in stripline cavities, and of using such spin–photon coupling in order to induce long-range interactions between nanomagnets. Indeed, the coupling between (ensembles of) spins and confined electromagnetic modes represents one of the potential frontiers in the use of nanomagnets for quantum-information technology.

Quantum cellular automata

Very attracting model systems in computing science are *cellular automata*. These are often used in statistical mechanics to simulate the behaviour of complex systems like, for instance, crystal growth or conformation of biological systems. Their power resides in the simplicity of the basic rules that one needs to define, as pointed out by Stephen Wolfram,[46] one of the pioneers of this field.

Essentially, we need to define a discrete system made of *cells*, for instance squares in graph paper or, more in general, in N dimensions. Each *cell* can be set in two well-defined states such as *black* or *white*. One *cell* interacts with the neighbours, typically just the nearest (NN) or the next-nearest (NNN) neighbours, usually only through short-range interactions. The input is defined by an initial configuration of the whole system. Typically one defines a subset of *cells* that can be initially changed and lets the system evolve step by step at finite time intervals. A popular example in 2D is the game of *Life* (Fig. 5) for which different initial configurations give extremely different time evolutions of the system. So, the output itself is the configuration of the system at a given time and in this respect cellular automata are extremely powerful to simulate complex systems.

Considering the essential features of cellular automata as depicted above, it is very tempting to look at molecular arrays as cellular automata. Dr M. Ruben and co-workers have indeed proposed a grid type metal ion architecture to be used as cellular automata.[47] Cells are composed of a small number of differently charged redox centers, interacting by purely electrostatic forces. Prof. L. Cronin at Glasgow University has recently proposed 3D crystals of polyoxometallates (POM) as cellular solids for encoding classical information.[48] His group has actually demonstrated that the basic POM units undergo reversible red–ox transition that can be controlled by redox agents throughout a bulk crystal.[49] Key questions have not been considered yet. For instance, protocols to set the initial configuration (input) and to read the final one (output) have not been figured out.

There are also quantum versions of cellular automata in which two level cells are made of quantum units and it was shown that quantum cellular automata may play as universal machines for quantum computation.[50]
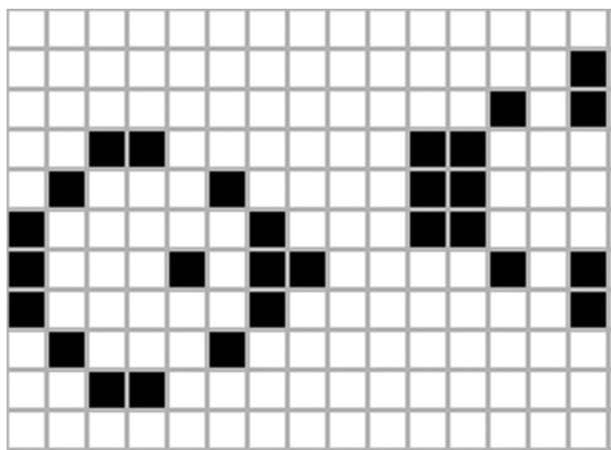
Fig. 5 2D example of cellular automata, more popular as the game of Life.

Cellular automata made of a few elements can be used to perform specific logic gates like AND and OR. These have been recently implemented by means of quantum dots[51] or magnetic dots.[52,53] The scheme depicted in Fig. 6 shows the essential functioning of the gate.

Molecular spins S, either single ions or clusters, embedded in an ordered crystal or arranged on a surface, may thus be considered as discrete cells with a well-defined *up* or *down* magnetic state, such as for instance, the ground molecular (or single ion) $\pm M_z$ state. Each state should be metastable and in this respect the presence of a magnetic anisotropy barrier (for instance of uniaxial type) is useful for keeping the magnetic cell in its initial state and it introduces the need for a specific interaction to flip the spin. (Super-)exchange interactions JS_iS_j respond very well to the requirement of the cellular automata model and provide a broad variety of cases including interactions to nearest-neighbours or to next-nearest-neighbours, Heisenberg, XY or Ising cases as well as ferro- or antiferro-magnetic coupling.

Some grid shaped molecular magnets of Prof. L.K. Thompson look, at first glance, pretty close to a spin version of 2D cellular automata[54,55] considering that many ingredients (local magnetic anisotropy, short range interaction, planar arrangement of spin centres *etc.*) are naturally present in these systems. The reticular map of the atoms observed by STM within such a molecule deposited on graphite is also very
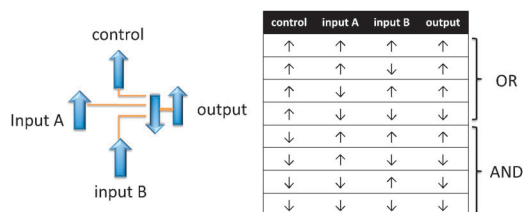

Fig. 6 Classical representation of a possible spin version of a majority gate, analogous to what was proposed and realized with quantum dots[51] and magnetic dots.[52,53] The control input enables to switch the functioning between AND and OR gates as summarised in the truth table. Magnetic interactions are represented by lines connecting arrows (spins).

suggestive[56] but this also leads to still open questions: how can we set inputs? How can we read out the output? Although these look like impossible tasks for now, some recent achievements provide interesting hints. For instance, spin manipulation in an engineered array of Mn atoms by STM combined with inelastic electron tunneling spectroscopy technique[57] have demonstrated that some basic tasks are feasible.

7. Quantum communications

The purpose of quantum communication is that of transferring a quantum state from one part to the other of a physical system.[58] A prototypical system for performing such transfer is represented by a linear chain of interacting (pseudo)spins. A quantum-communication protocol essentially consists of the following steps:

(i) the spin chain is initialized in a given (*i.e.* pure) quantum state;

(ii) at time $t = 0$ the first spin in the chain is then rotated into the quantum state $|\phi(0)\rangle_1$ to be transferred;

(iii) the spin chain is left to evolve freely for a given time T;

(iv) at time $t = T$ the final spin in the chain is in a state $|\phi(T)\rangle_N$ that ideally coincides with $|\phi(0)\rangle_1$.

The performance of such a transfer is quantified by the so-called *fidelity*, corresponding to the overlap between $|\phi(T)\rangle_N$ and $|\phi(0)\rangle_1$, minimized over all possible initial states $|\phi(0)\rangle_1$. The fidelity of the transfer process can be in principle enhanced by following different strategies. A comprehensive discussion of these aspects is beyond the scope of the present review: the interested reader is referred to the recent review by Bose.[58]

Hereafter, we focus on those aspects that are of specific interest to the implementation of quantum state transfer with molecular nanomagnets. To this aim, we discuss the specific implications related to the four steps outlined above. We shall refer to a nanomagnet consisting of N exchange-coupled spins, with a Hamiltonian $H_0 = \sum_i J_{i,i+1} \, s_i \cdot s_{i+1} + \mu_B \sum_i g_i \, s_i \cdot B$. For the sake of simplicity, we shall assume that $s_1 = s_N = 1/2$, and that the $N - 2$ intermediate spins are all identical, but not necessarily 1/2 spins. The first requirement essentially translates into the ability of initializing the system into its ground state. In other words, the working temperature should be lower than the energy difference between the ground and first excited state (Δ_{10}). The second requirement implies the capability of modifying the state of the first spin without affecting the rest of chain. Ideally, this might be achieved by turning off the coupling between s_1 and s_2, while manipulating the former one by means of external fields. While different strategies for the dynamical control of the exchange couplings between spins have been envisaged, such requirement might be extremely demanding, especially for individual magnetic ions within a single nanomagnet. A weaker requirement consists of the capability of manipulating the first spin on a timescale that is short compared to the coupling between s_1 and the rest of the chain: $\tau_{in} < \hbar/J_{12}$. Besides, if the spin manipulation is performed through external fields that are homogeneous on the length scale of the nanomagnet size, s_1 has to be spectrally resolved from the remaining spins. In the case of a manipulation through EPR pulses, spectral resolution implies a g factor

that is significantly different from that of the remaining spins: $\Delta g \equiv g_1 - g_{k>1}$. The initial manipulation of s_1 will therefore take a time $\tau_{\text{in}} \sim \Delta g \, B_1$, where B_1 is the maximum intensity of the pulsed field. In the simplest case, the quantum state transfer is based on the free evolution of the chain state. Such free dynamics needs to be coherent. In other words, the time T is limited by the decoherence time, that in nanomagnets typically ranges from 10^2 ns to 10 μs. Quite generally, the waiting time T depends on the desired fidelity; T is bounded from below by the number of spins through which the quantum state has to propagate and by the strength of the spin–spin coupling J (with $J \equiv J_{i,i+1}$ for $N - 2 > i > 1$) that allows such propagation. Finally, the state of the N-th spin at time T needs to be read out. A full characterization of a spin 1/2 density matrix can be performed by measuring the expectation values of the three orthogonal components (quantum tomography). As for the initialization of s_1, also the selective measurement of s_N might require the capability of spectrally resolving such spin from the remaining ones, and of performing the measurements on a timescale smaller than that related to the coupling between s_N and the rest of the chain $\tau_{\text{out}} < \hbar / J_{N-1} J_N$. In recent years, local probes have been successfully used in order to characterize the statical properties of spin rings. These include NMR[59] and X-ray magnetic circular dichroism.[60,61] In fact both these techniques are sensitive to the chemical element. However, in order to probe the coherent dynamics, time resolution is also required.

Conclusions

Results achieved in the last few years and briefly reviewed in the previous sections show that molecular nanomagnets can be considered as mesoscopic solid state systems of interest for quantum computation. Molecular nanomagnets have specific features that make them paradigmatic cases to test models and with which we may build novel quantum architectures. The perspective for long term applications, however, can be in some sense misleading since it may obscure the underlying fascinating science that we can make with these molecular systems and that is currently in progress. For instance, the control achieved at a synthetic level by supramolecular chemistry is extremely powerful and simply beautiful on its own; spectacular results on the manipulation of electronic spins have been obtained and these pose intriguing questions on how to control coherence and entanglement in mesoscopic spin systems. Under technological inputs, molecular magnetism is now moving more and more towards surface science with implications for the use of new experimental techniques and with the development of new synthetic approaches. So the impact of these new ideas is immediate and tangible.

Acknowledgements

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