Quantum Molecular Magnetism

DOI: 10.1002/anie.201100818

Molecular (Nano) Magnets as Test Grounds of Quantum Mechanics**

*Andrea Dei and Dante Gatteschi**

magnetic properties · nanostructures · quantum chemistry · spintronics · switchable magnets

Since an early age mankind has learned to use magnetic materials to its benefit, but it is only with the development of quantum mechanics that a true understanding of magnetism could be achieved.[1–3] The last few years have seen the development of nanomagnetism, that is, the investigation of magnetic objects in the 1–100 nm size range, in which quantum and classical effects coexist.[4] Molecular nanomagnets (MNMs), based on tailor-made magnetic molecules that are all identical and individually addressable, have attracted considerable interest since the discovery that some molecules show the coexistence of quantum and classic effects, such as hysteresis and quantum tunneling of the magnetization in single molecule magnets (SMMs).[5–15] $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn12) is the archetype of SMMs in which slow relaxation results from the large ground-state spin combined with a huge Ising-type magnetic anisotropy. The cluster mimics bulk behavior because the magnetization must overcome a large energy barrier to invert its direction. The potentially important impact that such systems, having bistable properties and showing quantum effects, may have on magnetic storage of information has prompted many chemists to design and synthesize molecules displaying these features. However, this approach is not simply a matter of scalability. The exploitation of magnetic molecules requires many problems to be solved, which range from addressing single spins to the so-called measurement and interpretation problem, which has been constantly debated since the birth of quantum theory. In other words, the possibility of encountering Schrödinger cats[16] should be always kept in mind. The reduction in the size of magnets has had a profound effect on our views of condensed matter. In fact, MNMs provide many new opportunities to observe quantum effects, which are the subject of intense investigation in spintronics[14,17–27] and quantum computing.[28–36] The former takes advantage of both the charge and the spin of the electron, whereas the goal of the latter is to exploit quantum mechanics to implement more efficient logical processing. In both fields MNMs can make the difference. The aim of this Essay is to highlight the quantum effects that can be observed in MNMs and to show how these systems provide unique opportunities of measuring the direct response of the quantum system to the questions raised by the observer. We believe that MNMs will make a very important contribution to our understanding of the quantum world and will lead to the discovery of new, intriguing properties of matter. To facilitate the design of systems of ever greater complexity, it is necessary that many traditionally formal concepts, like quantum tunneling, coherence, decoherence, entanglement, and superposition, be understandable in a direct and partially intuitive way, acting as keys to open gates to new science and applications.

[*] Prof. A. Dei, Prof. D. Gatteschi
Dipartimento di Chimica "U. Schiff" and UdR INSTM
Università di Firenze
Via della Lastruccia, 3, 50019 Sesto Fiorentino, Firenze (Italy)
E-mail: dante.gatteschi@unifi.it
Homepage: http://www.unifi.it/lamm/

[**] We are indebted with to (in alphabetic order) Lapo Bogani, Andrea Caneschi, Andrea Cornia, Matteo Mannini, Claudio Sangregorio, Roberta Sessoli, Lorenzo Sorace, and Federico Totti for stimulating discussions. We thank Matteo Mannini for help with the artwork. MOLSPINQIP FP7-ICT-2007-211284 and the PRIN 2008-fzk5ac research program are gratefully acknowledged for financial support.

Quantum Paraphernalia

The spin allows the electron to be considered as an elementary logic bit or quantum of information. Progress in instrumental technology has provided tools allowing the detection of individual spins in solid-state systems. The potential applications involve not only the detection of the objects used but also their manipulation. In the traditional investigation of bulk samples, this manipulation is easily achieved by perturbing the system with external magnetic fields, but here the problem is how to change selectively the spin state of a small number of molecules. The evolution of a quantum system as described by the time-dependent Schrödinger equation in principle affords the state of the system at an arbitrary time, provided that the initial state of the quantum system and the Hamiltonian are known. A simple case is given by the two basis vectors $|\uparrow\rangle$ and $|\downarrow\rangle$ (or $|0\rangle$ and $|1\rangle$ when using the language of bits). The definition is generally valid but is applied here specifically to spins. The spin state $|\psi\rangle$ can represent one of the two basis states, characterizing the components of the spin along an external magnetic field [Eq. (1)]:

$$|\psi\rangle = |\uparrow\rangle \quad \text{and} \quad |\psi\rangle = |\downarrow\rangle \tag{1}$$

Nevertheless, being a quantum object, the system can also be in any one of the infinite states $|\psi\rangle = c_\uparrow|\uparrow\rangle + c_\downarrow|\downarrow\rangle$ where $c_\uparrow$ and $c_\downarrow$ are complex numbers such that $|c_\uparrow|^2 + |c_\downarrow|^2 = 1$. The system is said to be in a superposition of states. The existence of a superposition of states is in contrast with what is perceived in the macroscopic world, where in practice only one of the possible alternatives is detected by the measurements, yielding always the same result. The evolution of the states is described by Equation (2):

$$c_\uparrow = e^{-i\phi/2}\cos(\theta/2) \qquad \text{and} \qquad c_\downarrow = e^{i\phi/2}\sin(\theta/2) \tag{2}$$

where θ and ϕ are spherical coordinates.

Two processes can change our quantum state: variation of θ changes the spin, while variation of ϕ only changes the phase of the wavefunction. A system can start in an intermediate spin state that is neither $|\psi\rangle = |\uparrow\rangle$ nor $|\psi\rangle = |\downarrow\rangle$ and can continue to move along the sphere just changing its azimuth angle ϕ, without changing its elevation angle θ. If movement along θ is slow, then we can use the system as a classical bit. If all spins in the sample have the same speed of evolution, then the system is evolving coherently, and we can try to use it as a quantum information unit (or qubit).

In principle, the system can continue to rotate in what is called a coherent state, but interaction with the environment will destroy coherence.[37–39] Decoherence is a measure of the instability of the state that can be monitored by τ_d, the characteristic time in which a quantum object loses its phase owing to interaction with the environment. Coherence and decoherence are two fundamental aspects of quantum systems. The former corresponds to correlation between the two states, while the latter corresponds to the destruction of the correlation and the collapse of the superposed states into one. In other words, coherence corresponds to a given superposition state which, owing to interaction with the environment, decays to a nonquantum state.

In many possible applications, the coherence time must be long. This can be achieved in several ways, the first step being the choice of the type of system. It is apparent that a system based on electron spins has an intrinsically shorter decoherence time than a system based on nuclear spins. Molecular magnetism often deals with systems in which unpaired electrons are spatially confined, so that their energy levels can be described as following the features of a quantum object. Imagine a set of paramagnetic metal ions that are never isolated owing to interaction with their environment, which is the host containing the paramagnetic molecule as a guest. A fundamental mechanism of decoherence occurs through the interactions with phonons. This interaction defines the spin-lattice relaxation time T_1. The coupling of the electron spin with a nuclear spin induces a phase shift and intensity decay, with the resulting component oriented in the transverse phase plane. This process is the most effective in determining the decoherence of the quantum state. Its time scale is defined by the transverse relaxation time T_2, the time required for the magnetization in the perpendicular plane to fan out until the net magnetization is zero.

So far we have considered single quantum objects interacting with the environment. Now take two independent quantum objects and, at some point, switch on an interaction between them. If the resulting composite state is such that it cannot be written as a product of individual states, the system is said to be entangled.[40] If the system is coherent and we switch the interaction off again, the correlation will persist, irrespective of time and distance. A general state for two spins is given in Equation (3):

$$|\Psi\rangle = c_{\uparrow\uparrow}|\uparrow\uparrow\rangle + c_{\uparrow\downarrow}|\uparrow\downarrow\rangle + c_{\downarrow\uparrow}|\downarrow\uparrow\rangle + c_{\downarrow\downarrow}|\downarrow\downarrow\rangle \tag{3}$$

where all the coefficients c are complex numbers. If all the coefficients c are given by the product of the corresponding single-spin $c_\uparrow$ and $c_\downarrow$, the composed states can be expressed as products of the initial states $|\Psi\rangle = |\psi\rangle_1|\psi\rangle_2$. There are, however, states in which this does not hold true, for example, the maximally entangled states [Eq. (4)]:

$$|\Psi_\pm\rangle = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle \pm |\downarrow\uparrow\rangle]; \; |\Phi_\pm\rangle = \frac{1}{\sqrt{2}}[|\uparrow\uparrow\rangle \pm |\downarrow\downarrow\rangle] \tag{4}$$

If one state is projected on one of its eigenstates, the projection on the other one is also known.

The entanglement concept provides an opportunity to explain how the classical features of the macroscopic world may originate from the quantum mechanical description of the microscopic world. In fact, it is not straightforward to explain why the investigation of a quantum system which, according to superposition, should yield a multiplicity of answers, actually provides only a restricted and defined range of results

The original answer of the Copenhagen school[41] assumes a separation between the quantum and the classical world and the fact that a classical apparatus is always necessary for performing a measurement. This should justify the fact that all

Andrea Dei was born in 1943 and has been Professor of Inorganic Chemistry at the University of Florence since 1981. His research is devoted to the synthesis of metal complexes acting as potential building blocks for molecular magnetic materials and to the synthesis of electronic bistable molecules showing redox isomerism and photomagnetic activity. He is also interested in the philosophy of science.

Dante Gatteschi has been professor of chemistry at the University of Florence since 1980. His research interests, initially focused on the investigation of coordination compounds, have subsequently been largely centered on the development of molecular magnetism, in which he has been one of the pioneers, obtaining important results.

the measurements yield only a restricted range of results. This assumes a separation between the quantum and the classical world, which is rather difficult to accept.[42] There seems to be a consensus that quantum systems are never isolated from their environments (i.e., they are open systems and not the closed ones described by the Schrödinger equation).[43,44] In the entanglement between the quantum system and the environment, the interference terms in practice disappear, and the possibility of observing the superposition of quantum states vanishes. Zurek[45,46] proposed that the environment-induced decoherence gives rise to a superselection, so that in a measurement only one result is observed among all those arising from the superposition. It is obvious that this feature is essential for understanding quantum information, which is related to the physical information intrinsic to a quantum state.

Single-Molecule Magnets

We have briefly recalled the main features of SMMs, whose impact on quantum effects in mesoscopic matter has been widely discussed. Other milestones have been the observation of quantum interference analogous to the Berry phase in an Fe8 cluster and spin pairing dependent on the tunneling of the magnetization.[47,48]

SMMs have been produced in large numbers, but no substantial improvement has been made compared to the archetypal Mn12 compound in the properties relevant to potential applications, in particular the blocking temperature, that is, the temperature at which the SMM behaviour can be observed.[10,15,49] The goal of increasing the blocking temperature has been pursued by trying to increase the spin S of the ground state and the magnetic anisotropy barrier. It must be stressed that the Arrhenius law [Eq. (5)]:

$$\tau = \tau_0 \exp(\Delta/T) \tag{5}$$

is valid for low temperatures. Furthermore, at high temperature τ_0 is the key parameter in determining the relaxation properties of the system. Rather surprisingly, no attempt to obtain structural correlations for this parameter has been reported.

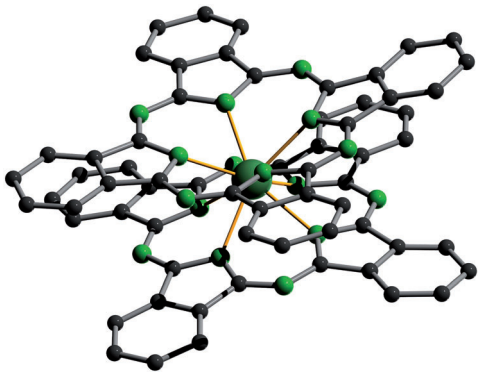

Figure 1. Crystal structure of the [$TbPc_2$] complex. Tb large green sphere, N small green spheres, C black.

The simplest example of a SMM is that of flat molecules like the 4f-metal derivatives with phthalocyaninate (Pc), whose structure is shown in Figure 1. The magnetization of the terbium(III) derivative was found to undergo slower relaxation at higher temperatures compared to the transition-metal-based polynuclear SMMs.[50] At low temperature the interaction of the electron and nuclear spins was clearly observed.

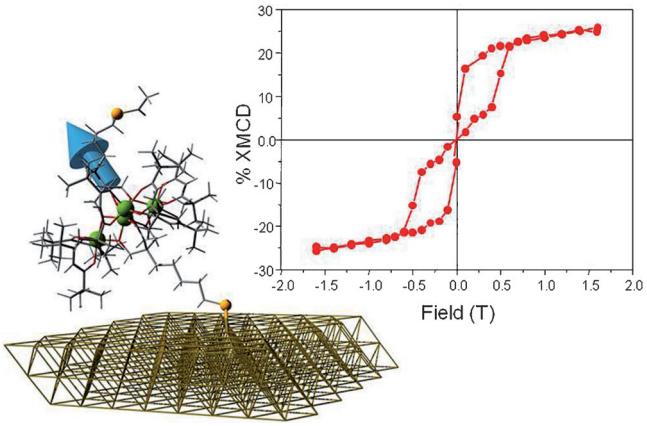

Figure 2. DFT-optimized structure of the Fe4 cluster on a gold surface (left) and its X-ray magnetic circular dichroism (XMCD)-detected magnetic behavior (right). Original data from Ref. [27].

The potential application of these systems as quantum devices requires their characterization in dilute states when organized on suitable substrates. Recently, a sub-monolayer of the SMM Fe4 on gold was found to show magnetic hysteresis below 1 K (Figure 2).[51] This result demonstrates that after grafting the system onto a metallic surface, it retains the original SMM properties.

Molecular Spintronics

MNMs are expected to be increasingly investigated over the coming years within the framework of molecular spintronics, that is, in the utilization of the interaction between the electron spin of a magnetic molecule and the charge flowing through a conductor or a semiconductor. This may allow the achievement of two goals: polarization of charge flow by magnetic effects and spin reversal by polarized charge flows. In the latter case it will be possible to encode and store magnetic information.

Any MNM worthy of consideration must be able to act as a spacer between source and drain electrodes, while maintaining its magnetic properties. Under these conditions, the charge transport is controlled by the spin of the molecule and by its coupling with the metallic junctions.[14,52] If this coupling is weak, charge transport may occur through electron tunneling between the metal and MNM molecular orbitals. In this case, the resonance conditions may be reached by shifting the energy levels by application of an external bias. If

the coupling is strong, both resonant (exchange-coupled) and Kondo tunneling are operative.

To date, by using spin-polarized STM spectroscopy, it is possible to both read and control the spin state of a paramagnetic molecule.[53,54] Molecular spin valves, molecular spin transistors, spin filters and rectifiers, and nano-SQUIDs are currently the subject of extensive research. The description of the magnetic properties of these molecules, when they are involved in a current flow between source and drain electrodes, is problematic because this situation corresponds to a non-equilibrium state,[55] thus precluding the use of variational methods. However, all known SMMs are expected to experience a weak coupling with the metallic surfaces owing to their intrinsic nature. A nice example of the use of magnetic control of electron flow has been reported by Wende,[56] who observed a magnetic interaction between iron porphyrins deposited on an iron and nickel ferromagnetic substrate.

In principle, technology provides the possibility of reading and controlling the spin properties of these systems. Spin-polarized STM spectroscopy or break-junction techniques are reaching a high level of sophistication in this respect. However, the severe conditions of high vacuum and strong magnetic fields required by these techniques cannot yet be tolerated by SMMs. In a similar way, the switching between the two bistable magnetic states (i.e., spin reversal) by means of a spin-polarized electronic flow has been theoretically predicted but not verified experimentally. It is believed that interconversion between spin states may occur through exchange coupling between the polarized electron spin in the lowest unoccupied molecular orbital (LUMO) level and the SMM spin *S*. The recent results obtained in our laboratory, where isolated SMMs on gold have been prepared and characterized by means of X-ray photoelectron spectroscopy (XPS) and XMCD techniques, illustrate the current state-of-the-art in the field.[50,51] Although these techniques provide only averaged information about the magnetic properties of a set of grafted molecules, such studies are believed to offer a good starting point for the description of an SMM system at the nanostructural level. Clearly, a more intriguing description by using a spin-polarized STM technique is highly desired.[53]

Switchable Magnets

In addition to slow relaxation, ideal magnets should have magnetic properties that can be easily tuned under the influence of an external parameter such as temperature, pressure, or electromagnetic radiation.[13] The most extensively investigated switchable magnets are spin-crossover,[57–60] polycyanometallate,[61–63] and metal dioxolene complexes showing redox isomerism.[64–68] The appealing features of these systems are the optical interconversion between different magnetic states, having different conductance, and the possibility to exploit the Stark effect.[17]

Cobalt dioxolene complexes undergo redox isomerism through an intramolecular electron transfer between the ligand and the metal ion (Figure 3). These systems are

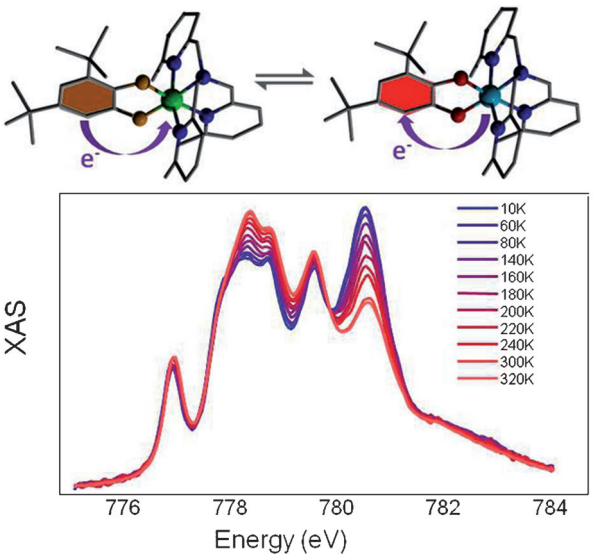

Figure 3. Temperature-dependent Co $L_{2,3}$ edge X-ray absorption spectroscopy (XAS) (bottom) of a cobalt dioxolene complex showing the tautomeric interconversion (top). Extracted from Ref. [68].

attractive because the two redox isomers, for example, Co^{III}(cat) and Co^{II}(SQ) (cat and SQ are the catecholato and semiquinonato forms of *o*-quinone), have different optical and magnetic properties. Co^{III}(cat) is diamagnetic whereas Co^{II}(SQ) has a triplet ground state. Since the redox process is reversible, these systems may be used, in the Aviram–Ratner sense,[69] as diodes when placed between two electrodes.

At cryogenic temperatures, the Co^{III}(cat) charge distribution is thermodynamically favored, but the metastable Co^{II}(SQ) species can be accessed by photogeneration.[70–72] When irradiation is stopped, the relaxation decay of the metastable species follows two different regimes, one nearly independent of temperature down to 20 K and one with temperature-activated behavior at higher temperatures. Typical lifetimes are in the range 10^4–10^7 s at 10 K and 1–200 ns at room temperature. The observed relaxation behavior can be interpreted within the framework of the nonadiabatic multiphonon relaxation model, as proposed for spin-crossover complexes.[73] This treatment is expected to work in the limit of strong vibronic coupling between two different spin states in different nuclear configurations.[74] The rate constant of the process is tunneling-dependent, as it is determined by the overlap between the vibrational wave functions of the initial and final states. At high temperatures, the excited vibrational levels are populated and the relaxation rate follows the Arrhenius' law, whereas at low temperatures, where only the vibrational ground state of the Co^{II}(SQ) species is populated, a temperature-independent relaxation rate is observed. These considerations can be summarized in terms of quantum coherence between the vibrational states and quantum decoherence with the environment. This model supports the overall picture of the relaxation process as involving two closely coupled coevolving systems. The possibility of inducing the interconversion by means of an electric field is currently being investigated.

Quantum Computers: The Key Ideas

Classical computers exploit the fact that a state is defined by a sequence of binary on–off sub-states, labeled as bits. Quantum computers (QC) substitute such states with a quantum superposition of states, as those described in the introduction. This means that the system exists in a state that is expressed by the linear combinations of the different possible states. Fundamentally, the superposition allows many calculations to be performed at the same time, since the evolution of the system involves the simultaneous evolution of all the states. In other words, although the information that can be obtained by a qubit is always the same as a digital bit, the difference resides in the way the information is processed.

Although the potential and appealing characteristics of the QC have been known since the 1970s,[75,76] there are currently still no working Q-computers. This lack is mostly due to our present difficulties in meeting the DiVincenzo criteria,[77] that is, the fundamental requirements to develop a working Q-computer. Nuclear spins fulfill all of the criteria, and indeed they were exploited in the first attempts for realization of a QC. However, they have the crucial disadvantage that their process times are intrinsically slow, and this drawback severely limits their usefulness. Consequently, all other examples are based on electron-spin Q-bits.

Q-systems are now reasonably well understood;[32,35] but decoherence times are still a matter of debate, as there are some doubts that it will be possible to have really long coherence times at room temperature. While quantum optics systems, such as Rydberg and trapped atoms, have extremely long coherence times, the best electron coherence times in solid-state systems are those obtained for nitrogen-vacancy centers in diamond, reaching micro- to milliseconds at room temperatures.[78,79] Nevertheless, the criterion that requires individual qubits to be organized so as to make them communicate in a known way is the one that proves to be the most problematic. Attempts are presently under way to overcome this difficulty, and they have already given extremely interesting results. In our opinion, this is the point that makes molecular systems special: with a molecular structure the centers are automatically ordered and well-placed, without the need of further structuring.

In order to work correctly, the system of qubits must be coherent. For this reason, efforts have been focused on exploiting systems where charges are localized and that are constituted by identical subunits without impurities. The positive aspects associated with molecular clusters, besides the possibility of having at hand well-characterized identical objects, are the following: 1) the construction of tailor-made molecules by carefully tuning the properties of the system; 2) control of intermolecular interactions through supramolecular chemistry techniques, enabling them to be switched on and off; 3) their intrinsic long coherence time, which can be controlled at the molecular level.[30,35,80]

Designing systems which can be used as qubits also requires that measurement of the entanglement be appropriately carried out. For magnetic resonance, the presence of magnetic nuclei can be an opportunity or be detrimental, depending on the experiment. Mehring and coworkers reported entangled properties of electron and spin nuclei in an EPR/NMR spectroscopy experiments performed on CH malonyl radicals trapped in single crystals of malonic acid.[81] Similar results were obtained in ^{15}N endofullerenes.[82] Much more complex structures incorporating 3d metal ions were used by other groups.[35,83,84] An early attempt to produce an $S = {}^1/_2$ system in a complex way was reported by Ardavan et al.,[28] who noted a reasonably long relaxation time in Cr_7Ni.

Final Remarks

The observation of magnetic properties of single molecules or clusters of a few molecules has been made possible by recent advances in technology. This drastically changes the scenario, as it is now possible to extract new kinds of information and to conceive unprecedented applications. Optical irradiation, spin torque mechanisms, and electrostatic potential can be proposed as appropriate tools to manipulate spins. In this case, MNMs have two main advantages: they are characterized by confined electrons and they provide identical units. The former condition is extremely important because itinerant charges are a dramatic source of decoherence. Furthermore, in principle, it is possible to know the structural parameters of the MNMs, a feature which allows the description of a quantum object using classical observables and is independent of quantum considerations.

There is no doubt that this approach generates new problems. To date the development of MNMs has been determined by the hypothesis that the constituent molecules could be properly described as a quantum box with an inherent set of discrete single or degenerate energy levels. These sophisticated characteristics are partially or totally lost when an electron flows across the molecule. In this case, the properties of the system are determined by the interaction with electrodes and by the properties of the transient excited states. Indeed, it is rather unclear if under these non-equilibrium conditions the quantum-box description continues to be valid. This aspect is extremely important if information storage and data processing are the main goals of these investigations.

The problem of quantum measurement, whose essence has been debated in theoretical physics for eighty years, is also important. The approach now predicts that the Galilean concept of reproducibility of observations, which is fundamental to physics, does not hold and must be substituted by the reproducibility of statistical experiments, which is fundamentally different. Moreover, we must accept that the result of a measurement is well-defined and in open contrast with the superposition of results we should expect from the theory. In other words, we assume for the quantum object a description that does not hold when we look at the object itself. Two considerations are necessary. The first is that no phenomenon can be considered a phenomenon if it is not observed. The second is that a cognitive act cannot disregard the relativity and the objectivity of the relationship between the object and the observer. In this sense, we must accept that we can obtain information on the quantum object only in an

indirect way. The measurement we conduct in our laboratories is controlled by the way in which the quantum object communicates with the surrounding environment. Hence, we retrieve the information conveyed by the quantum object to the environment, which is entangled with it. For this reason the consideration of environment-induced decoherence, where the environment itself acts as observer and destroys superpositions, is essential. It is obvious that the same considerations hold if we consider, according to the Copenhagen scool, the interaction between the quantum object and the apparatus: the result is the same, even if independent of the observer. However, it should be stressed that this is only one possible way of conceiving how quantum information can be transformed into classical information.

We conclude that the approach used so far in molecular magnetism has many limitations once applied to single molecular objects. Indeed, this approach obeyed the concept of a science based on experiments, where in principle it is possible to know a value of a property of a discrete molecular system. In this case it is mandatory to plan a measurement in the simplest conditions, trying to exclude any perturbing factor. We must realize that the experiment is only a tool and is not the essence of all our possible knowledge. Quantum phenomena are characterized by holism or nonseparability, as entanglement shows. This feature distinguishes quantum physics from classical physics, and it determines two different cognitive approaches in reciprocal open contrast. This concept is not new—it is intrinsic in the formulation of the Schrödinger equation—but surprisingly, it has been ignored by most of the scientific community. Entanglement is synonymous with nonseparability and simply means in its essence that when two states are entangled it is not possible to separately determine the properties of the two constituent states. This feature is common in the microscopic world. Therefore, it is key to the description of all the aspects of the interactions of the molecule as a quantum object with itself and with the environment, the measurement apparatus, and the observer. Accordingly, it rules the physical world we investigate and necessitates its adoption as an epistemic methodology. This is the important timely lesson we can learn from the future developments of molecular magnetism.

Received: February 1, 2011
Revised: June 14, 2011
Published online: November 7, 2011

[1] W. Heisenberg, *Z. Phys.* **1926**, *38*, 411.
[2] P. A. M. Dirac, *Proc. R. Soc. London Ser. A* **1929**, *123*, 714.
[3] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibility*, Oxford University Press, Oxford, **1932**.
[4] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, **2006**.
[5] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
[6] L. Gunther, B. Barbara, *Quantum Tunneling of Magnetization, QTM '94*, Kluwer, Dordrecht, **1995**.
[7] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, *383*, 145.
[8] H. J. Eppley, S. M. J. Aubin, M. W. Wemple, D. M. Adams, H. L. Tsai, V. A. Grillo, S. L. Castro, Z. M. Sun, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1997**, *305*, 167.
[9] W. Wernsdorfer, N. Aliaga-Alcade, D. N. Hendrickson, G. Cristou, *Nature* **2002**, *416*, 406.
[10] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268.
[11] E. Coronado, A. Forment-Aliaga, A. Gaita-Ariño, C. Giménez-Saiz, F. M. Romero, W. Wernsdorfer, *Angew. Chem.* **2004**, *116*, 6278; *Angew. Chem. Int. Ed.* **2004**, *43*, 6152.
[12] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2007**, *129*, 8139.
[13] O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem.* **2007**, *119*, 2200; *Angew. Chem. Int. Ed.* **2007**, *46*, 2152.
[14] L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179.
[15] B. Barbara, *Inorg. Chim. Acta* **2008**, *361*, 3371.
[16] E. Schrödinger, *Naturwissenschaften* **1935**, *23*, 807; E. Schrödinger, *Naturwissenschaften* **1935**, *23*, 824; E. Schrödinger, *Naturwissenschaften* **1935**, *23*, 844.
[17] S. Sanvito, *J. Mater. Chem.* **2007**, *17*, 4455.
[18] F. Meier, V. Cerletti, O. Gywal, D. Loss, D. D. Awschalom, *Phys. Rev. B* **2004**, *69*, 195315.
[19] A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito, *Nat. Mater.* **2005**, *4*, 335.
[20] A. Fert, *Angew. Chem.* **2008**, *120*, 6042; *Angew. Chem. Int. Ed.* **2008**, *47*, 5956.
[21] M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. M. Talarico, M.-A. Arrio, A. Cornia, D. Gatteschi, R. Sessoli, *Nat. Mater.* **2009**, *8*, 194.
[22] V. A. Dediu, L. E. Hueso, I. Bergenti, C. Taliani, *Nat. Mater.* **2009**, *8*, 707.
[23] L. Catala, D. Brinzei, Y. Prado, A. Gloter, O. Stephan, G. Rogez, T. Mallah, *Angew. Chem.* **2009**, *121*, 189; *Angew. Chem. Int. Ed.* **2009**, *48*, 183.
[24] J. J. Parks, A. R. Champagne, G. R. Hutchison, S. Flores-Torres, H. D. Abruña, D. C. Ralph, *Phys. Rev. Lett.* **2007**, *99*, 026601.
[25] S. Lothl, M. Etzkorn, C. P. Lutz, D. M. Eigler, A. J. Heinrich, *Science* **2010**, *329*, 1628.
[26] S. Loth, K. von Bergmann, M. Ternes, A. F. Otte, C. P. Lutz, A. J. Heinrich, *Nat. Phys.* **2010**, *6*, 340.
[27] M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, *Nature* **2010**, *468*, 417.
[28] A. Ardavan, O. Rival, J. J. Morton, S. J. Blundell, A. M. Tyryshkin, G. A. Timco, R. E. P. Winpenny, *Phys. Rev. Lett.* **2007**, *98*, 057201.
[29] N. Baadji, M. Piacenza, T. Tugsuz, F. Della Sala, G. Maruccio, S. Sanvito, *Nat. Mater.* **2009**, *8*, 813.
[30] M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789.
[31] F. Troiani, A. Ghiri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco, R. E. P. Winpenny, *Phys. Rev. Lett.* **2005**, *94*, 207208.
[32] J. Lehmann, A. Gaita-Ariño, E. Coronado, D. Loss, *Nat. Nanotechnol.* **2007**, *2*, 312.
[33] J. Lehmann, A. Gaita-Ariño, E. Coronado, D. Loss, *J. Mater. Chem.* **2009**, *19*, 1672.
[34] A. Ardavan, S. J. Blundell, *J. Mater. Chem.* **2009**, *19*, 1754.
[35] P. C. E. Stamp, A. Gaita-Ariño, *J. Mater. Chem.* **2009**, *19*, 1718.
[36] G. A. Timco, S. Carretta, F. Troiani, F. Tuna, R. J. Pritchard, C. A. Muryn, E. J. L. McInnes, A. Ghirri, A. Candini, P. Santini, G. Amoretti, M. Affronte, R. E. P. Winpenny, *Nat. Nanotechnol.* **2009**, *4*, 173.
[37] E. Schrödinger, *Naturwissenschaften* **1926**, *14*, 664.
[38] J. R. Klauder, B. Skagerstam, *Coherent States*, World Scientific, Singapore, **1985**, p. 33.
[39] P. C. E. Stamp, *Studies His. Phil. Mod. Phys.* **2006**, *37*, 467.
[40] E. Schrödinger, *Proc. Cambridge Philos. Soc.* **1935**, *31*, 555.

[41] J. von Neumann, *Mathematische Grundlagen der Quantenmechanik*, Springer, Berlin, **1932**.
[42] J. S. Bell, *Speakable and Unspeakable in Quantum Mechanics*, Cambridge University Press, Cambridge, **1987**.
[43] H. D. Zeh, *Found. Phys.* **1970**, *1*, 69.
[44] E. Joos, H. D. Zeh, C. Kiefer, D. Giulini, J. Kupsch, I.-O. Stamatescu, *Decoherence and the Appearance of a Classical World in Quantum Theory*, 2nd ed., Springer, New York, **2003**.
[45] W. H. Zurek, *Phys. Today* **1991**, *44*, 36.
[46] W. H. Zurek, *Rev. Mod. Phys.* **2003**, *75*, 715.
[47] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133.
[48] W. Wernsdorfer, S. Bhaduri, C. Boskovic, G. Christou, D. N. Hendrickson, *Phys. Rev. B* **2002**, *65*, 180403.
[49] R. Sessoli, *Inorg. Chim. Acta* **2008**, *361*, 3356.
[50] N. Ishikawa, M. Sugita, W. Wernsdorfer, *Angew. Chem.* **2005**, *117*, 2991; *Angew. Chem. Int. Ed.* **2005**, *44*, 2931.
[51] L. Margheriti, D. Chiappe, M. Mannini, P.-E. Car, P. Sainctavit, M.-A. Arrio, F. B. de Mongeot, J. C. Cezar, F. M. Piras, A. Magnani, E. Otero, A. Caneschi, R. Sessoli, *Adv. Mater.* **2010**, *22*, 5488.
[52] E. A. Osorio, K. Moth-Pulsen, H. S. J. van der Zant, J. Paaske, P. Hedegård, K. Flensberg, J. Bendix, T. Bjornhølm, *Nano Lett.* **2010**, *10*, 105.
[53] a) F. Meier, L. Zhou, J. Wiebe, R. Wiesendanger, *Science* **2008**, *320*, 82; b) R. Wiesendanger, *Curr. Opin. Solid State Mater. Sci.* **2011**, *15*, 1.
[54] C. F. Hirjibehedin, C.-Y. Lin, A. F. Otte, M. Ternes, C. P. Lutz, B. Jones, A. J. Heinrich, *Science* **2007**, *317*, 1199.
[55] M. Stamenova, S. Sanvito, T. Todorov, *Phys. Rev. B* **2005**, *72*, 134407.
[56] H. Wende, M. Bernien, J. Luo, C. Sorg, N. Ponpandian, J. Kurde, J. Miguel, M. Piantek, X. Xu, Ph. Eckhold, W. Kuch, K. Baberschke, P. M. Panchmatia, B. Sanyal, P. M. Oppeneer, O. Eriksson, *Nat. Mater.* **2007**, 6, 516.
[57] P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem.* **1994**, *106*, 2109; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024.
[58] *Top. Curr. Chem.* **2004**, *233–235* (Eds.: P. Gütlich, H. A. Goodwin).
[59] J.-F. Létard, *J. Mater. Chem.* **2006**, *16*, 2550.
[60] M.-L. Boillot, S. Pillet, A. Tissot, E. Rivière, N. Claiser, C. Lecomte, *Inorg. Chem.* **2009**, *48*, 4729.
[61] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704.
[62] A. Bleuzen, C. Lomenech, V. Escax, F. Villain, F. Varret, C. Cartier dit Moulin, M. Verdaguer, *J. Am. Chem. Soc.* **2000**, *122*, 6648.
[63] A. Dei, *Angew. Chem.* **2005**, *117*, 1184; *Angew. Chem. Int. Ed.* **2005**, *44*, 1160.
[64] D. N. Hendrickson, C. G. Pierpont, *Top. Curr. Chem.* **2004**, *234*, 63.
[65] A. Dei, D. Gatteschi, C. Sangregorio, L. Sorace, *Acc. Chem. Res.* **2004**, *37*, 827.
[66] E. Evangelio, D. Ruiz-Molina, *Eur. J. Inorg. Chem.* **2005**, 2957.
[67] C. Carbonera, A. Dei, J. F. Létard, C. Sangregorio, L. Sorace, *Angew. Chem.* **2004**, *116*, 3198; *Angew. Chem. Int. Ed.* **2004**, *43*, 3136.
[68] G. Poneti, M. Mannini, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, J. C. Cezar, A. Dei, *Angew. Chem.* **2010**, *122*, 1998; *Angew. Chem. Int. Ed.* **2010**, *49*, 1954.
[69] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
[70] O. Sato, S. Hayami, Z.-Z. Gu, K. Takahshi, R. Nakjima, A. Fujishima, *Chem. Phys. Lett.* **2002**, *355*, 169.
[71] A. Beni, A. Dei, M. Rizzitano, L. Sorace, *Chem. Commun.* **2007**, 2160.
[72] P. Dapporto, A. Dei, G. Poneti, L. Sorace, *Chem. Eur. J.* **2008**, *14*, 10915.
[73] E. Buhks, G. Navon, M. Bixon, J. Jortner, *J. Am. Chem. Soc.* **1980**, *102*, 2918.
[74] A. Hauser, *Top. Curr. Chem.* **2004**, *235*, 155.
[75] S. Holevo, *Probl. Inf. Transm. (Engl. Transl.)* **1973**, *9*, 177.
[76] P. Poplavskii, *Uspekhi Fizicheskikh Nauk* **1975**, *115*, 465.
[77] D. DiVincenzo, *Phys. Rev. A* **1995**, *51*, 1015.
[78] G. Balasubramanian, P. Neumann, D. Twitchen, M. Markham, R. Kolesov, N. Mizuochi, J. Isoya, J. Achard, J. Beck, J. Tissler, V. Jacques, P. R. Hemmer, F. Jelezko, J. Wrachtrup, *Nature Mater.* **2009**, *8*, 383
[79] J. Wrachtrup, F. Jelezko *J. Phys. Cond. Matt.* **2006**, *18,* S807
[80] M. Affronte, *J. Mater. Chem.* **2009**, *19*, 1731.
[81] M. Mehring, J. Mende, W. Scherer, *Phys. Rev. Lett.* **2003**, 90, 153001.
[82] M. Mehring, W. Scherer, A. Weidinger, *Phys. Rev. Lett.* **2004**, *93*, 206603.
[83] S. Bertaina, S. Gambarelli, T. Mitra, B. Tsukerblat, A. Müller, B. Barbara, *Nature* **2008**, *453*, 203.
[84] G. A. Timco, E. J. L. McInnes, R. J. Pritchard, F. Tuna, R. E. P. Winpenny, *Angew. Chem.* **2008**, *120*, 9827; *Angew. Chem. Int. Ed.* **2008**, *47*, 9681.