

## IMANES DE MOLÉCULA ÚNICA: HACIA APLICACIONES TECNOLÓGICAS

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**Resumen:** La utilización de los efectos cuánticos puede influir en gran medida en el funcionamiento de los dispositivos tecnológicos. Hasta la fecha, los conocimientos adquiridos sobre la naturaleza cuántica de varios sistemas han impulsado la propuesta de varias aplicaciones tecnológicas futuristas, como sensores cuánticos, la simulación y la computación cuánticas. Los imanes de molécula única (SMM, por sus siglas en inglés) representan una clase de objetos cuánticos con propiedades prometedoras para ser explotados en las tecnologías cuánticas. Hoy en día, se ha demostrado que los SMMs poseen efectos cuánticos desconcertantes, como la tunelización cuántica de la magnetización (QTM, por sus siglas en inglés), la cuantización de los estados de energía, coherencia, efectos de paridad de espín y el entrelazamiento, entre otros. Además, se han integrado con éxito en dispositivos espintrónicos híbridos de una sola molécula, como los transistores y las válvulas de espín, lo que ha propiciado una amplia investigación de aplicaciones tecnológicas. En este artículo de revisión, se describen algunos aspectos cuánticos clave que hacen de los SMMs sistemas prometedores para propuestas tecnológicas. Además, se describen los dispositivos de una sola molécula, en los que los SMMs se han integrado como dispositivos híbridos, así como las aplicaciones tecnológicas, como sensores cuánticos, la simulación y la computación cuánticas.

**Palabras clave:** Sensores cuánticos, simulaciones cuánticas, computación cuántica, transistor de espín, válvula de espín, bit cuántico, corrección cuántica de errores, tunelamiento cuántico de la magnetización.

**Abstract:** The utilisation of quantum properties can largely impact how technological devices work. Up to date, the acquired knowledge of the quantum nature of several systems inspired the proposal of several novel technologies such as quantum sensing, quantum simulation and quantum computing. Single Molecule Magnets (SMMs) represent a class of quantum objects with promising properties to be exploited in quantum technologies. As of today, SMMs have been shown to possess bewildering quantum effects such as Quantum Tunnelling of the Magnetisation (QTM), quantisation of the energy manifold, coherence, spin parity effects and entanglement, among others. Furthermore, they have been successfully integrated into hybrid single molecule

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spintronic devices, such as spin transistors and spin valves, hence, propitiating extensive investigation of technological applications. In this **Review Article**, some key quantum aspects, which make SMMs promising systems for technological proposals, are revised. Moreover, single-molecule devices, in which SMMs have been integrated in hybrid devices, as well as the technological applications such as quantum sensing, quantum simulation and quantum computing are described. Quantum sensors, quantum simulations, quantum computation, spin transistor, spin valve, quantum bit, quantum error correction, quantum tunneling of magnetisation.

**Keywords:** Quantum sensors, quantum simulations, quantum computation, spin transistor, spin valve, quantum bit, quantum error correction, quantum tunneling of magnetisation.

## INTRODUCTION

When considering the format in which funding agencies provide grants for scientific research, i.e., directed to tackle specific challenges with little or no room to explore adjacent problems, it is important to remember that many great scientific discoveries have been obtained by serendipity. In many cases, by accident, research designed to solve a scientific problem leads to a discovery in a somewhat different field (Bruce, O'hare, & Walton, 2010). The field of molecular magnetism is a clear example of serendipity. This field was discovered by chance when trying to understand the oxygen-evolving complex in Photosystem II (Christou, 1993). To describe the highest oxidation of state of this complex, in the early 1990s, a manganese complex with formula  $[\text{Mn}_{12}(\mu_3\text{-O}_{12})(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \times 2\text{CH}_3\text{COOH} \times 2\text{H}_2\text{O}$  (or Mn12) was

studied with a range of techniques leading to the discovery of a large spin ground state,  $S = 10$ . Remarkably, the ground state of this complex was found to be highly anisotropic, leading to the observation for the first time of an energy barrier to the relaxation at the molecular level (Sessoli, 1993). Conversely to classical magnetism, in which the coupled magnetic moments (3D) give rise to a net magnetisation, the magnetic anisotropy in Mn12 arises from the individual units (0D). Molecules possessing such behaviour were coined SMMs, due to their single-molecule properties. This rather fortuitous discovery propitiated a great deal of interest in both chemists, trying to synthesise SMMs with enhanced properties, and physicists, fascinated by the wealth of properties exhibited by these systems. SMMs were expected to outclass conventional materials in data-storage abilities. To put it into context, if a conventional ninety-minute tape was made of Mn12, the Mn12 tape would be able to store one hundred and fifty years of music. During the first ten years of the SMM field, the complexes were all based in polynuclear transition metal ions. In 2003 the renaissance of SMMs began when it was found that monometallic lanthanide-based complexes could also show an energy barrier to the relaxation, eluding the necessity of polynuclear systems (Ishikawa et al., 2003a). Ever since, SMMs have been shown to exhibit several quantum effects such as Quantisation (Ishikawa et al., 2003b; Sessoli et al., 1993), Quantum Tunnelling of the Magnetisation (QTM) (Chen et al., 2016; Ishikawa et al., 2005; Sangregorio et al., Ohm, Paulsen, 1997; Thomas et al., 1996), Quantum

Coherence (Hill, 2003; Vincent et al., 2012), Berry Phase (Wernsdorfer et al., 2002), Quantum Oscillations (Barco et al., 2000; Bertaina et al., 2008; Carretta et al., 2007; Yang et al., 2012) up to entanglement in ensembles (Candini et al., 2010; Garlatti et al., 2017; Lorusso et al., 2011; Troiani et al., 2013). These characteristics, along with the continuous miniaturisation of devices heading towards molecular levels and atomic levels, led to the proposal of SMMs in several technological applications such as high-density data storage, Quantum Sensing, Quantum Simulation, and ultimately Quantum Computing.

Technologically, we have witnessed the miniaturisation of devices, moving from extremely large computers like the ENIAC, down to powerful computers that can even fit on our pockets. Large interest has been devoted to zero-dimensional as well as 2D materials such as graphene (Novoselov et al., 2004) and graphene-like systems (Chen et al., 2017), due to their remarkable chemical, mechanical and physical properties (Xiang et al., 2015), boosting the investigation of their syntheses (Molina-Jirón et al., 2019; Zhang et al., 2013) and their implementation in spintronic devices (Bogani & Wernsdorfer, 2008; Novoselov et al., 2004; Sun & Rogers, 2007). However, a problem associated to the continuous miniaturisation of computers and its components is the quantum nature taking over at the molecular and atomic scale. The former, also known as Moore's law, acts as driving force for understanding and implementing quantum effects in technological applications. Towards this goal, the first quantum revolution, period in which researchers gained an understanding of quantum effects of physical systems, led to inventions such as the laser and transistors. As follow up step, in the second quantum revolution scientists attempt to employ the acquired quantum mechanical knowledge to engineering quantum systems and implement them in technological applications (Atzori & Sessoli, 2019; Dowling & Milburn, 2003). In this sense, the striking and unique characteristics of SMMs, have motivated intensive investigation of their properties for their integration in several technological applications. The quantum nature exhibited by SMMs could allow the long-sought control of quantum effects and their implementation of practical applications; a goal in the mind of scientists since the quantum mechanical description by Erwin Schrödinger (Schrödinger, 1926).

Numerous are the predicted advantages offered by the implementation of the quantum effects in technological applications. For example, small fluctuations of physical and biological systems could be sensed by exploiting the quantum coherence and entanglement of electronic states, surpassing classical sensing devices (Barry et al., 2016; Boss et al., 2017; Dovzhenko et al., 2018; Jenkins et al., 2019; Lawrie et al., 2019; Lee-Wong et al., 2020; Lovchinsky et al., 2016; Radu et al., 2020; Shi et al., 2015). Simulation of precise quantum mechanical problems, as suggested by Feynman (Feynman, 1982) and Lloyd (Lloyd, 1993) would be possible. Furthermore, arguably the most attractive implementation is the development of a quantum computer. A quantum computer would enable the realisation of particularly difficult and even unachievable tasks, such fast computation of extremely large problems, factorisation of large numbers, to the true universal simulation of large quantum mechanical problems. Remarkably, the possibility of developing a mature quantum computer attracted the attention of not just the scientific community, but also triggered the investment of several companies and consortiums resulting in a 16-qubit processor by the IBM Q-experience (García-Pérez et al., 2020), a 72-qubit quantum chip by Google (Kelly et al., 2015), a 19-qubits computer by Rigetti (Otterbach et al., 2017), a silicon spin-based 2-qubits processor by QuTech (Watson et al., 2018) and ultimately a NASA-Google partnership claiming quantum supremacy (Arute et al., 2019).

Currently, amongst the several systems explored for technological applications, SMMs are very attractive due to their quantum characteristics, tailored control over not just the structural aspects of the systems, but also the control over their electronic and nuclear characteristics. In this Review Article, some key aspects of SMMs for the integration in novel technological applications such as data storage devices, quantum simulators, quantum sensors and quantum computers will be discussed.

## Manifestation of Quantum Effects in SMMs

The quantum characteristics observed in SMMs triggered several proposals in technological applications (Dowling & Milburn, 2003). However, to integrate SMMs into such technologies, certain quantum characteristics must be gathered. This section describes a brief description of certain key quantum characteristics of SMMs, which

makes the candidates to be considered in these novel technologies.

## Quantisation of the Energy manifold

The archetypal  $[\text{Mn}_{12}(\mu_3\text{-O})_2(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \times 2\text{CH}_3\text{COOH} \times 2\text{H}_2\text{O}$

(or  $\text{Mn}_{12}$ ) complex was the first system to show quantisation of the energy manifold (Sessoli et al., 1993). Below a certain temperature, the magnetic ground state of  $\text{Mn}_{12}$  is  $S = 10$ , resulting from the strong interaction of the inner tetrahedron of  $\text{Mn}^{+4}$  and the external  $\text{Mn}^{+3}$  octagon. Although small in magnitude, the Spin-Orbit Coupling (SOC) is of paramount importance in transition metal SMMs since it induces anisotropy.

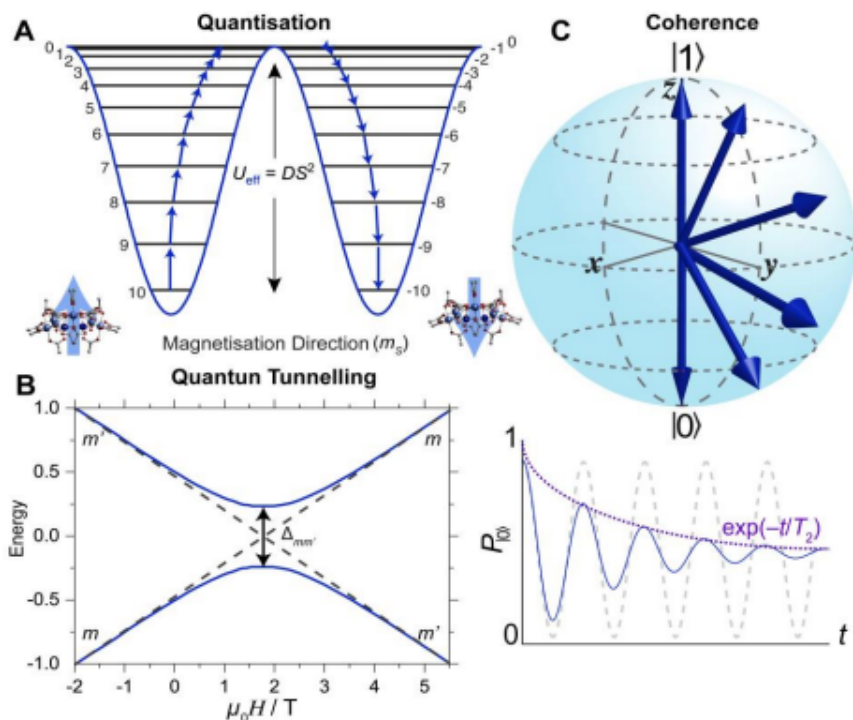


FIGURE 1.

Quantum Effects in Single-Molecule Magnets: (A) Schematic representation of quantisation of the electronic energy level of  $\text{Mn}_{12}$  with  $S = 10$  and  $U_{\text{eff}} = DS^2$ . The reversal of the magnetisation follows through the  $mS$  states (blue arrows) via phonon absorption (excitation of the spin system to the top of the barrier) and emission (de-excitation to the bottom of the other side of the barrier).

(B) Reversal can likewise occur via QTM through the barrier when the states are in resonance.

(C) Schematic view of Qubit, highlighting the possible states generated by superposition. In a Qubit the coherence sufficiently long to allow the manipulation, operation and read-out vanishes.

The SOC is defined by a spin Hamiltonian of the form:

$$\mathcal{H} = DS_z^2 +$$

$$E(S_x^2 + S_y^2),$$

with  $D$  being the zero-field splitting, and  $E$  the rhombic parameters.

$$DS_z^2,$$

defines the quantisation of the S states as  $m_S = -S \dots S$  is doubly degenerated:

$$E(\pm m_S) = -|D|m_S^2,$$

hence, following a parabola with an energy barrier to the relaxation

$$U_{eff} = -|D|m_S^2$$

(Fig. 1A). Each side corresponds to an opposed orientation of the magnetic moment in the parabola; hence D provides the barrier for the spin to flip its orientation. Due to the spin dependence of the energy barrier, a large spin multiplicity was aimed when synthesising transition metal SMMs.

The synthetic targets of the early development of the field were entirely based on transition metal ions. However, in 2003 a striking result was obtained when Ishikawa determined an energy barrier to the relaxation of single metallic-ion lanthanide-based SMMs (Ishikawa, et al., 2003a). The complex comprised a Tb<sup>3+</sup> ion sandwiched between two phthalocyaninato (Pc) anionic ligands charged balanced by a tetrabutylammonium cation (TBA), namely TBA[TbPc<sub>2</sub>]. Conversely to transition metal SMMs, where polynuclearity was required, the anisotropic property of the lanthanide-SMMs results from the strong intrinsic SOC due to the unquenched orbital momentum and large nuclear charge. The Russell-Saunders (RS) coupling scheme describes the electronic properties of 4f-SMMs ( $\# = |\# - \#| \leq \# \leq \# + \#$ ), given that not S nor L are good quantum numbers. For [TbPc<sub>2</sub>]<sup>-</sup> S = 3 and L = 3, henceforth, J = L + S = 6. Due to the large separation between the J = 6 and J = 5 (ca. 2900 K), solely the J = 6 multiplet is populated at standard conditions. For D<sub>4h</sub> symmetry the Tb<sup>3+</sup> ion sandwiched between the Pc ligands possesses a ligand field of the form (Ishikawa, Sugita, Okubo, et al., 2003b):

$$\mathcal{H}_{lf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \quad (1)$$

being

$$B_q^k$$

experimental parameters. The degeneracy of the 2J+1 states of the J = 6 multiplet is lifted by the ligand field leading to a mJ = ±6 ground doublet with a separation of ca. 600 K from the mJ = ±5 first excited state. As a result, the quantisation axis for the mJ = ±6 ground

state is perpendicular to the Pc plane; this remains frozen under the threshold temperature, generated by the ligand field acting upon the Tb<sup>3+</sup>.

Another surprising aspect of 4f-SMMs is their strong hyperfine coupling, of paramount significance for the observation of other quantum effects as well as their implementation in quantum computing applications (Godfrin et al., 2017). The strong interaction couples the electronic spin strongly to the nuclear spin I = 3/2 of Tb<sup>3+</sup> via the hyperfine and the quadrupolar interaction. While the hyperfine interaction splits the mJ = 6 state in 2I+1 levels, i.e., mI = +3/2, +1/2, -1/2 and -3/2, the quadrupolar term couples the electric field gradient of the magnetic moment, causing an uneven separation between mI states. A spin Hamiltonian of the form (2) describes the system (Ishikawa et al., 2005; Taran et al., 2019):

$$\mathcal{H}_{TbPc_2} = \mathcal{H}_{lf} + \mu_B \mu_0 H \hat{g} J + A_{hyp} I \cdot J + I \hat{P}_{quad} I \quad (2)$$

In (2) the second term is the Zeeman interaction, and the third and fourth terms are the hyperfine and quadrupolar interactions, correspondingly.



## *Coherence and Spin Relaxation*

For the integration of SMMs in devices, working under quantum mechanical laws, an important aspect is to perform logical operations without losing the information during the computational time. Two parameters characterise the performance of the system: the spin-lattice relaxation time,  $T_1$ , and the spin-spin relaxation time,  $T_2$ .  $T_1$  describes the time the magnetisation takes to return to the thermal equilibrium along the z-axis after being tipped  $90^\circ$ .  $T_2$ , or coherence time, describes the superposition lifetime, i.e., the operational time. Physically,  $T_2$  is determined by tipping the magnetisation  $90^\circ$  to the xy-plane from its thermal equilibrium position.  $T_1$  and  $T_2$  are interwoven, as the coherence time is limited by  $T_1$ , as  $2T_1 \geq T_2$ , especially at high temperatures. Similar or even better relaxation times have been observed in SMMs, hence, making SMMs plausible basic units for quantum computers, i.e., the quantum bit or Qubit (Fig. 1C).

The electronic ground state in SMMs is expected to remain frozen below

a certain threshold temperature; nevertheless, temperature-dependent relaxation mechanisms become important when the thermal energy is comparable to the barrier. Hence, the system can relax via various thermally activated mechanisms. Phonon-assisted or Spin-lattice relaxation mechanisms contribute to the relaxation of the magnetisation significantly by modulating the ligand field through vibrations, triggering modulation on the crystal field henceforth prompting transitions between the different spin states. The relaxation channels arise via absorption and/or emission of one or two phonons. These processes are contingent upon the nature of the ion involved, i.e., Kramers or non-Kramers ions. For a Kramers ion, a minimum degeneracy of two is retained, while for non-Kramers ions the degeneracy can be completely removed. Generally, three processes are predominantly involved in the relaxation dynamics of f-SMMs: (i) direct, (ii) Raman and (iii) Orbach process (Fig. 2). In the direct mechanism, the relaxation takes place through the emission of one phonon of energy. Nonetheless, in Orbach and Raman, the relaxation comprises the absorption and reemission of phonons. Whilst the relaxation in the Orbach process goes through a real excited state, the Raman relaxes via a virtual excited state. The understanding of the relaxation mechanisms (Albino et al., 2019; Briganti et al., 2021; Ganzhorn et al., 2016; Kragoskow et al., 2022; Mirzoyan & Hadt, 2020; Santanni et al., 2021) has permitted the synthesis of SMMs with remarkably improved properties (Goodwin et al., 2017; Gould et al., 2022; Guo et al., 2018).

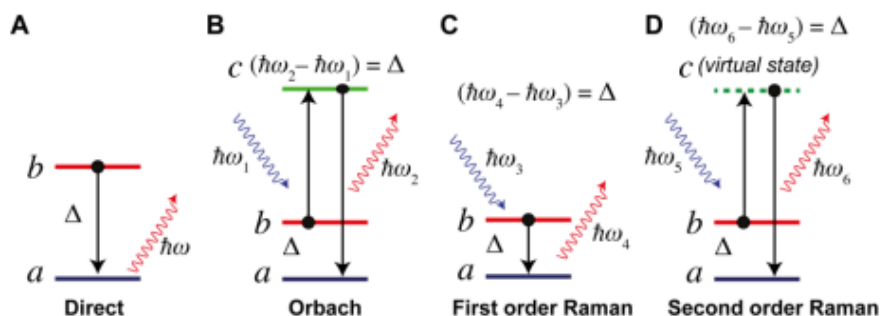


FIGURE 2.

Spin-lattice relaxation processes in SMMs. (A) Direct relaxation process: a phonon with the energy difference between states a and b is absorbed/emitted causing a transition between the states. (B) Orbach process: the absorption of a phonon excites the spin to a low-lying excited state, followed by de-excitation to state and emission of a photon of energy corresponding to the difference in energy of the low-lying excited state and the ground state. (C) First order Raman process: the difference in energy of the scattered phonon causes a de-excitation from state b to a. (D) Second order Raman process: the difference in energy of the scattered phonon is absorbed by the spin. The spin system is excited to a virtual excited state, followed by de-excitation to the ground state.

### *Quantum Tunnelling of the Magnetisation*

The observation of quantum effects has been in the mind of scientist since the early days of the quantum theory. Quantum Tunnelling of the Magnetisation (QTM) is one clear example. The quest of QTM dates to the early 70s in nanoparticles, however, due to inhomogeneities in the size of the particles, the observation stayed elusive until the early 1990s. The advent of the field of molecular magnetism was key for the first observation of QTM in the archetypal Mn12. QTM acts as a non-thermally activated relaxation, providing an alternative route for the relaxation (Gatteschi & Sessoli, 2003). QTM also allows spin reversal under barrier if superposition of the  $\pm m_J$  states exist. In the presence of transverse fields, the degeneracy at the crossing is converted into an avoided level crossing, with a separation  $\Delta E_{\#,\#'}$  (Fig. 1B). The eigenvectors of the Hamiltonian at the avoided crossing are a linear admixture of the positive and negative spin projections, comprising a finite probability of the spin at both sides of the barrier. Hence, spin tunnelling denotes the resonance of the spin at both orientations. The Landau-Zener-Stückelberg (LZS) model describes the tunnelling probability,  $P_{LZ}$ , between states m and m' when sweeping the magnetic field at a rate,  $\dot{H}$ , through the resonance (3):

$$P_{LZ} = 1 - \exp\left(-\pi \omega_T \frac{\Delta E_{\#,\#'}}{\alpha}\right) \quad (3)$$

where  $\omega_T$  is the angular frequency of oscillation between states m and m',  $\Delta E_{\#,\#'}$  is the tunnel splitting by  $\Delta E_{\#,\#'} = 2E_{\#,\#'}$ . The bare tunnel width, field interval where tunnelling is predicted to occur is given by

$$\delta H_0 = \frac{\Delta_{m,m'}}{g\mu_B\mu_0|m-m'|}.$$

It is to be noted that although QTM acts as temperature independent relaxation mechanism, undesired for high-density data storage applications, it plays an significant role in the initialisation, manipulation and read-out of nuclear spins in the TbPc2 complex, which

ultimately lead to the realisation of the Grover's quantum algorithm (Godfrin et al., 2017; Grover, 1997). QTM has also allowed the read- out of the hyperfine-coupled nuclear spin states of a Tb2Pc3 SMM in a single crystal (Moreno-Pineda et al., 2018) and in a spin transistor configuration (Biard et al., 2021).

### *SMMs as Quantum Bits (Qubits) and Multilevel Quantum Bits (Qudits)*

SMMs can act as quantum bits or qubits. Contrasting the classical bit, the qubit can exist as superposition of the  $|1\rangle$  or  $|0\rangle$  states, i.e.

$|\psi\rangle = a_0|0\rangle + a_1|1\rangle$  where the squares of  $a_0$  and  $a_1$  are the amplitude of the probability following  $|a_0|^2 + |a_1|^2 = 1$  (Fig. 1C and 3A). The advantage of qubits to perform immensely large and complex operations resides in the non-orthogonal configurations providing  $2^N$  states, with  $N$  being the number of qubits.

Physical systems to be considered as qubits have to meet certain pre- requisite better known as DiVincenzo criteria (DiVincenzo, 2000): (i) well-defined scalable levels; (ii) long coherence times to perform the computational operation; (iii) initialisation of the well-defined states;

(iv) ability to carry out universal quantum gates via entanglement and/or superposition of states; (v) read-out of the states after the operation. Two other factors are important for quantum communication (DiVincenzo, 2000): (vi) interconversion between dynamic and stationary qubits and

(vii) precise transmission of dynamic qubits. These two are indispensable for the efficient transmission of information when employing photons and for non-local qubits (Milburn, 2009).

The facile manipulation of the electronic spins in SMMs, makes electron spin qubits suitable systems for quantum technologies, whereby their manipulation is accessible through application of thermal stimuli, magnetic fields or electromagnetic pulses (Balakrishnan, 2014; Kiktenko et al., 2015a; Kiktenko et al., 2015b; Mohammadi et al., 2011; O'Leary et al., 2006; Popov et al., 2016; Rungta et al., 2007). Recently, systems known as qudits (Fig. 3B), where the  $d$  represents its multilevel character, have gained increasing attention due to the possibility to employ their multilevel nature to conduct complex algorithms in a single physical unit (Atzori et al., 2018; Atzori et al., 2016a; Atzori et al., 2017; Atzori et al., 2016b; Balakrishnan, 2014; Biard et al., 2021; Fataftah et al., 2016; Gedik et al., 2015; Kiktenko et al., 2015; Luo & Wang, 2014;

Mohammadi et al., 2011; Moreno-Pineda et al., 2017; Moreno-Pineda et al., 2018; Yu et al., 2016). Qudits offer several advantages over qubits, such as  $d^N$  orthogonal states, tolerating parallelisation in a single unit with lower error rates compared to qubits (Gottesman, 1999; O'Leary et al., 2006; Richart et al., 2012). It has been proposed that the excited energy states in SMMs can be employed for the realisation of complex quantum gates (Biard et al., 2021; Leuenberger & Loss, 2001; Moreno-Pineda et al., 2017; Moreno-Pineda et al., 2018). Some of the advantages of Qudits over qubits are:

- (i) To perform qugates do not require inter-qubit interaction (Balakrishnan, 2014; Gedik et al., 2015; Kiktenko, Fedorov, Strakhov, et al., 2015);
- (ii) reduced number of gates to execute a computational task (Richart et al., 2012);
- (iii) parallelisable information in a smaller number of physical units (O'Leary et al., 2006);
- (iv) simpler quantum simulations with similar Hilbert space (Neeley et al., 2009);
- (v) lower error rates (Gottesman, 1999; Kues et al., 2017);
- (vi) for quantum cryptography entangled qudits are better suited (Richart et al., 2012);



- (vii) implementation of complex gates in a single unit (Balakrishnan, 2014; Luo & Wang, 2014; Mohammadi et al., 2011; Ralph et al., 2007);
- (viii) large number of operational states with a reduced number of processing units (Kues et al., 2017; Neves et al., 2005).

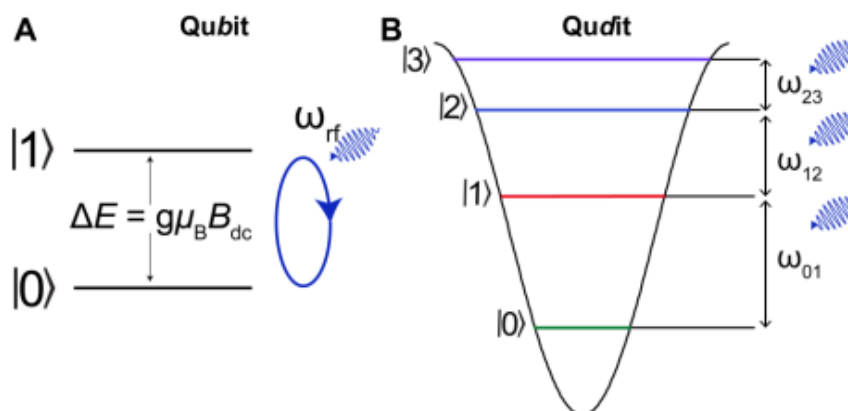


FIGURE 3.

Quantum Computer Building Blocks: (A) Schematic view of the two-level composing the Qubit. Manipulation of these states can be achieved via resonant pulses between the states. (B) Multilevel representation of a Qudit ( $d = 4$ ). The diverse accessible excited states can be exploited to perform quantum gates in a single physical unit.

### *Single Molecule Devices Incorporating SMMs*

SMMs have been integrated in single-molecule devices, leading to unusual results. Taking advantages of the quantum characteristics of SMMs emphasising the possibility to integrate these systems in novel technological devices. Examples of SMMs integrated on devices are spin transistors and spin valves, ultimately enabling the manipulation and read-out of the spin states of the SMM implementation in a quantum algorithm. In the following sections, some key results of SMM integrated in devices and their quantum characteristics will be described.

### *SMM Spin Transistors*

A spin transistor is three-terminal device, where electrons are passed through an SMM, bridging the gap of the junction, from the source to the drain. In this device configuration, it has been possible to manipulate and read-out the electronic states of SMMs. SMMs such as  $\text{Mn}_{12}$  (Heersche et al., 2006),  $\text{Fe}_4$  (Nossa et al., 2013) and  $\text{TbPc}_2$  (Godfrin et al., 2018, 2017; Thiele et al., 2013; Thiele et al., 2014; Vincent et al., 2012) have been integrated into spin transistor devices. However, out of these, the most important results have been accomplished when a  $\text{TbPc}_2$  complex is trapped into gold junctions through electro-migration (Godfrin et al., 2018, 2017; S. Thiele et al., 2013; Thiele et al., 2014; Vincent et al., 2012) (Fig. 4A). The conduction of the electrons through the  $\text{TbPc}_2$  complex results from the exceptionally stable redox state of the  $\text{Tb}^{3+}$  ion, and the  $\pi$ -radical delocalised over the Pc ligands (Godfrin et al., 2018; Godfrin et al., 2017; Thiele et al., 2013; Thiele et al., 2014; Vincent et al., 2012). The read-out of the states is achieved via indirect coupling, while the read-out is achieved due to the strong interaction between the  $\pi$ -radical and the  $\text{Tb}^{3+}$  spins. This allows the observation of change in conductance near zero field. A single charge-degeneracy point with a weak spin  $S = \frac{1}{2}$  Kondo effect, ascribed to the  $\pi$ -radical delocalised over the Pc rings is detected in the differential conductance ( $dI/dV$ ) as a function of drain-source voltage ( $V_{ds}$ ) and gate voltage ( $V_g$ ). Extraordinarily,

due to the ferromagnetic coupling between the  $S = 1/2$  of the  $\pi$  radical to the magnetic moment of the  $Tb^{3+}$  ion, and the hyperfine coupling to the nuclear spin states of the  $Tb^{3+}$  ion, the transport properties reflect the spin cascade i.e.,  $|# = 1/2\#||# = 6\#||# = 3/2\#$ . Close to the charge-degeneracy point, the spin cascade allows the read-out of the nuclear spin states by the spin-dot. Four abrupt jumps in the differential conductance are observed when sweeping the field. The jumps correspond to the reversal of the  $Tb^{3+}$  electron spin through QTM at the nuclear spin crossing (Fig. 4A (lower panel)).

The exceedingly efficient relaxation via QTM at fields between  $\mu_0 H < \pm 50$  mT is of paramount importance for the detection of the spin reversals at these four level crossings (Thiele et al., 2014; Vincent et al., 2012). Furthermore, long  $T_1$  (20  $\mu s$ ) and  $T_2$  (300  $\mu s$ ) 20 and 300 microseconds, have been obtained, leading to their implementation of the Grover's algorithm using the four states of the nuclear spin (Godfrin et al., 2017) (vide infra) and the realisation of an iSWAP quantum gate (Godfrin et al., 2018). More recently, it has been possible to read-out the coupled nuclear spin states – through electronic states of the  $Tb^{3+}$  – in a spin transistor incorporating a  $Tb_2Pc_3$  unit, opening the possibility of the implementation of more complex algorithms (Biard et al., 2021) (Fig. 4B,C).

The integration of SMMs in transistor configuration is also achievable by indirect coupling, in which the molecule is exposed to a weaker back-action. In the indirect coupling arrangement, the spin dot (SMM) is attached to the electrodes by a non-magnetic molecular conductor (read-out dot), in which the gate voltage regulates the coupling between the spin dot and the read-out dot.

### *SMM Spin Valve*

SMMs have also been incorporated into devices in the supramolecular spin valve configuration. (Urdampilleta et al., 2011; Urdampilleta et al., 2013; Urdampilleta et al., 2015) studied this configuration in which a  $TbPc_2$  acts as a spin dot and a carbon nanotube (CNT) acts as a read-out dot. The outstanding structural, electronic, and mechanical characteristics of CNTs make them suitable to act as read-out dot. The

conductance traces are found to be sensitive to charge fluctuations, including the spin reversal process, and are accessible due to the sensible coupling between the SMM and CNT. Owing to the 1D conductor character of the CNT, along with the Kondo effect of the  $TbPc_2$  and the Coulomb blockade exhibited at low temperatures, make the conductance sensitive to charge fluctuations including the spin reversal process. The spin valve CNT- $TbPc_2$  configuration allows the determination of the electronic and nuclear spin characteristic of the  $Tb^{3+}$  ion (Urdampilleta et al., 2011, 2013; Urdampilleta et al., 2015). The read-out was possible through magneto-transport measurements, exploiting the strong interaction between the  $TbPc_2$  molecules suspended on CNTs (Urdampilleta et al., 2013) (Fig. 4D). When the  $TbPc_2$  molecules were aligned in a parallel configuration, a maximum in the conductance is observed (ferromagnetic coupling). In contrast, a minimum conductance was found when the electron spin of the  $TbPc_2$  molecules were aligned antiparallel (antiferromagnetic coupling). Furthermore, the sensitivity of the measurements showcased differently oriented molecules onto the CNT. Additionally, similarly to the spin transistor, the nuclear spin states for each  $TbPc_2$  onto the CNT were sensed by measuring the tunnelling probability as a function of sweep rate (Fig. 4E, F). Between  $\pm 50$  mT four level-crossings are observed, which are associated with the nuclear spin  $I = 3/2$  on  $Tb^{3+}$ . A spin-valve behaviour was observed, acting as a spin polariser-analyser revealing a strong magneto-resistive effect when two  $TbPc_2$  molecules were on the CNT. For the SMM-CNT, working in two working regimes, the fine-tuning and the electronic detection/manipulation of a single magnetic moment were achieved.

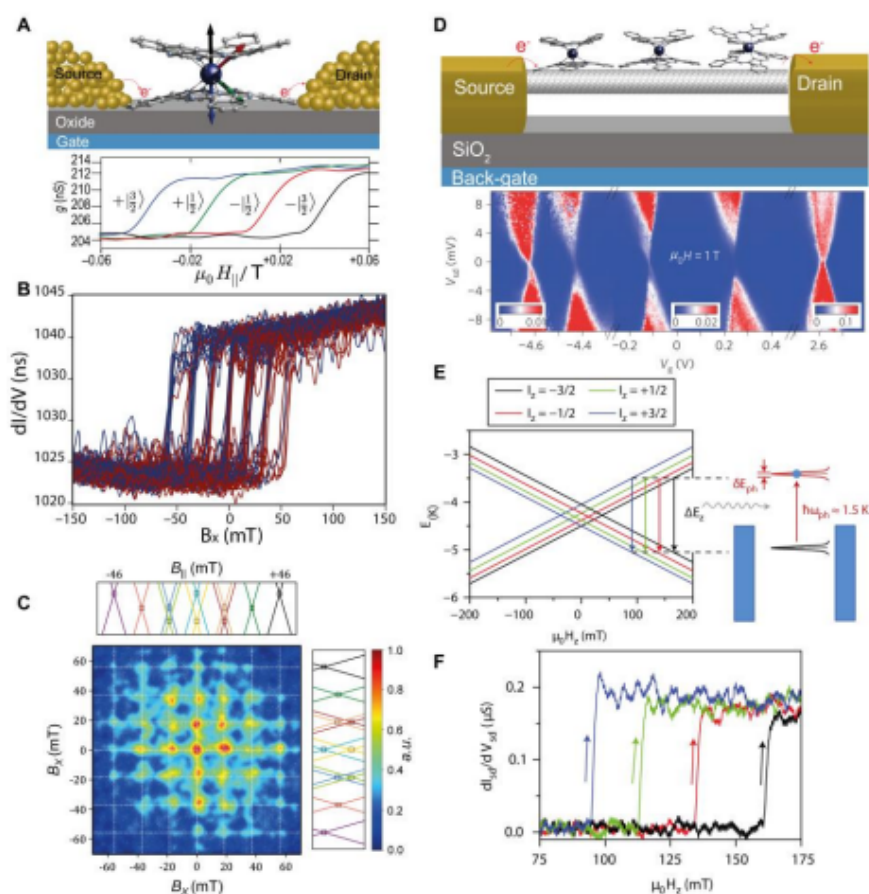


FIGURE 4.

Quantum Spin Transistors and Spin Valves: (A) Pictorial view of a spin transistor with a TbPc<sub>2</sub> molecule bridging the gap between the source and drain (top) and differential conductance studies ( $dI/dV$ ) as a function of drain-source voltage ( $V_{ds}$ ) and gate voltage ( $V_g$ ) (bottom). The conductance jumps correspond to the four-level crossings associated with the nuclear spin  $I = 3/2$  of Tb<sup>3+</sup>. (B)  $dI/dV$  as a function of  $V_{ds}$  and  $V_g$  for a Tb<sub>2</sub>Pc<sub>3</sub> spin transistor device. The conductance jumps correspond to spin reversal at the allowed QTM crossings. (C) Correlation measurement of spins reversals. The x-axis is the conductance jumps during a magnetic field sweep, and the y-axis the conductance jumps during subsequent sweeps. (D) Schematic view of the spin-valve device. A CNT acts as a read-out dot, connecting the drain and source, and the TbPc<sub>2</sub> acts as spin dots. (E) In the spin valve, the magnetisation reversal of the TbPc<sub>2</sub> occurs through a direct transition from the excitation of the electron into a vibrational state in the CNT resonator, revealing the nuclear spin states of the Tb<sup>3+</sup>. (F) Magnetisation reversal of the Tb<sup>3+</sup> is induced by sweeping the magnetic field  $\mu_0 H_2$  resulting in an abrupt increase in the differential conductance through the dot. The switching field is contingent upon the nuclear spin state.

Panel (A) adapted from ref. (Stefan Thiele et al., 2014) and (Moreno-Pineda & Wernsdorfer, 2021) with permission from The American Association for the Advancement of Science (AAAS) and Springer Nature Limited Copyright Ó 2021, respectively. Panels (B) and (C) adapted from ref. (Biard et al., 2021) with permission from Springer Nature Limited Copyright Ó 2021. Panels (E) and (F) adapted from ref. (Ganzhorn et al., 2013) with permission from Springer Nature Limited Copyright Ó 2013.

Below 1 K a magnetoresistance of up to 300% was observed, implying the individual manipulation of a larger number of molecules suspended on the CNT through a local gate. This would grant the implementation of complex quantum computing protocols. Also, it was shown that in the spin valve

configuration, QTM can be suppressed at low temperatures, due to one-dimensional phonons associated with the mechanical motion of the CNT (Ganzhorn et al., 2016). Solely a single mode (direct relaxation), associated with the mechanical motion of the CNT of one-dimensional phonons, correlated with the mechanical motion of CNT, allows relaxation to occur. The so-called quantum Einstein-de Hass effect would allow coherent spin manipulation of the spin states, opening the possibility of coherent manipulation of the spin and entanglement (Ganzhorn et al., 2016).

### *Towards Quantum Technologies Employing SMMs*

The quantum nature displayed by SMMs makes them viable prospects for several technologies, such as quantum sensors, quantum simulators, and quantum computers. The predicted advantages exceed any classical equivalent. Also, as shown in the previous section, SMMs have been successfully incorporated in spin-transistor and spin-valve devices, paving the way to hybrid quantum devices. In the next section a succinct description of the most relevant requirements of SMMs is provided for each technological application in which they have been proposed.

### *Quantum Sensors*

The use of quantum effects in novel technologies tries to exploit these effects to realise certain tasks not achievable with classical analogues. Quantum sensing, or Q-sensing, is an example of the exploitation of quantum effects for developing measuring and sensing protocols with enhanced capabilities. Extremely small fluctuations or perturbations can be sensed by exploiting the sensitivity of quantum states, as confirmed by the detection of gravitational waves employing squeezed states of

light at the Advanced Light Interferometer Gravitational-Wave Observatory (aLIGO) (Aasi et al., 2013).

For the development of Q-sensing, two characteristics are of paramount importance: (i) quantum coherence and (ii) entanglement (Degen et al., 2017; Troiani et al., 2019; Yu et al., 2021). Well-defined levels, initialisation and read-out of their final states must characterise suitable Q-sensing systems. Moreover, the coherent manipulation of the states of the system could be required for certain circumstances. For a successful Q-sensing protocol, the Q-sensor must interact with the system to be measured. This is in stark contrast to the characteristics of the basic unit for quantum computing. The interaction between the Q-sensor and the systems to be sensed triggers changes in the initial properties of the sensor, which can be inferred in the result of the measurement (Fig. 5A, B).

NV centres (Barry et al., 2016; Boss et al., 2017; Cooper et al., 2020; Dovzhenko et al., 2018; Jenkins et al., 2019; Kim et al., 2019; Lee-Wong et al., 2020; Lovchinsky et al., 2016; Radu et al., 2020; Shi et al., 2015), superconducting circuits (Degen et al., 2017), light (Aasi et al., 2013; Lawrie et al., 2019; Panajotov et al., 2004), silicon vacancies (Morley, 2014; Ohshima et al., 2018) and nuclear and electronic spins embedded in magnetic molecules (Troiani et al., 2019; Yu et al., 2021), amongst others, have been considered a plausible candidates for Q-sensors. Nevertheless, the characteristics of single atoms and molecules are better suited to perform sensing at a nanometre scale than any classical sensor, due to their spatial resolution (Troiani et al., 2019; Yu et al., 2021). The chemical control over the synthesis, the engineering of the structural, electronic and nuclear characteristics, make SMMs more appealing candidates for Q-sensing. Furthermore, the noise resilient characteristics of SMMs, preserving the coherence times, is of paramount importance for Q-sensors (Degen et al., 2017; Troiani et al., 2019; Yu et al., 2021). In this regard, the synthetic methodologies for the rational design of SMMs have led to the observation of long coherence times (Coronado, 2020; Gaita-Ariño et al., 2019; Wasielewski et al., 2020) (Fig. 5B). Pulse EPR studies have allowed the observation of

long coherence times in the well-known {Cr7Ni} wheels. Similarly, enhancement of the coherence times of these systems (Wedge et al., 2012), which can remain robust when attached to one (Fernandez

et al., 2015; Ferrando-Soria, et al., 2016; Timco et al., 2009) or more units (Ferrando-Soria et al., 2015), have been achieved, ultimately leading to their proposal for logic gates. Other examples show that through a rational design, in which decoherence sources are eliminated locally, has allowed the detection of long  $T_1$  and  $T_2$  times at room temperature and in bulk crystals (Atzori et al., 2016; Bader et al., 2014). Importantly, coherence times comparable to NV centres (Graham et al., 2017) have been observed in vanadyl-based complexes (Atzori et al., 2018; Atzori et al., 2016a; Atzori et al., 2017; Atzori et al., 2016b; Fataftah et al., 2016; Graham et al., 2014; Shiddiq et al., 2016; Tesi et al., 2016; Yu et al., 2016; Zadrozny et al., 2014).

As an alternative strategy, long coherence times can be obtained by the preparation of magnetic noise resilient systems, eliminating the necessity of magnetic dilution. These are obtained by inducing an interaction that mixes the qubit states, e.g., hyperfine interaction, resulting in an avoided level crossing, termed “clock transitions” (CT). Systems with such characteristics become insensitive to external fluctuations of magnetic fields, leading to long  $T_2$ . An example of magnetic resilient systems is a [Ho(W5O18)2]9– complex (HoW10) with D4d pseudo-axial symmetry (Shiddiq et al., 2016). The combination, hyperfine interactions, of crystal field and Zeeman splitting leads to avoided level crossings between the  $m_J$  levels of the same  $m_I$ . At the CT long  $T_2$  at 5 K is found, offering a complementary strategy to achieve long  $T_2$  values.

Q-sensors incorporating SMMs have been proposed for detecting physical parameters, such as temperature, electrical or magnetic fields, currents, nuclear spins, electronic spins, and magnons to even dark matter (Troiani et al., 2019; Yu et al., 2021) (Fig. 5C,D). An example of a Q-sensing proposal comprising an SMM is given by a single TbPc2 molecule in a transistor configuration, acting as a local thermometer (C. Godfrin et al., 2019). In the transistor, the TbPc2 molecule is coupled to a magnetic field, and it is in equilibrium with the thermal bath, acting as a temperature sensor.



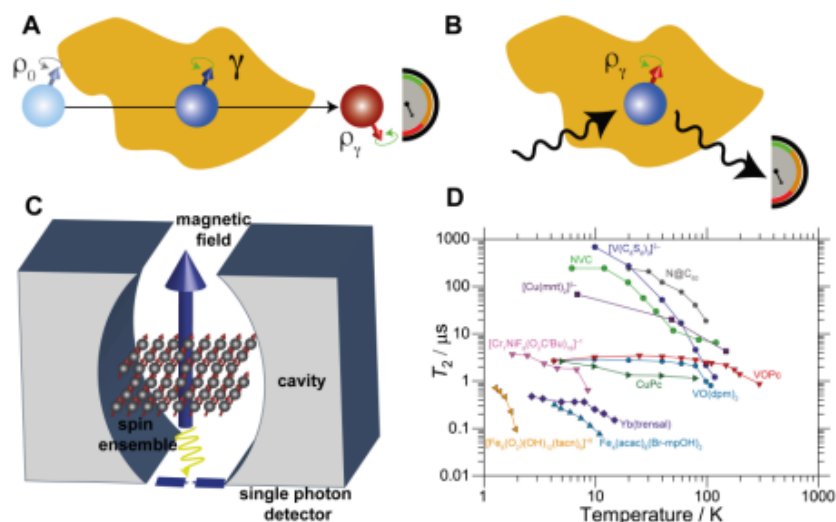


FIGURE 5.

SMMs for Quantum Sensing: (A) The sensor is prepared in an initial state, and it is allowed to interact with the system under investigation. During the interaction, information on the unknown parameter is obtained. Measurements of the final state of the sensor allow the determination of the information of the system under study. (B) In the second configuration, the sensor is embedded in a structure, and its state contains information on the internal parameters of interest. (C) Representation of a spin ensemble in a microwave cavity. The system is driven in the strong coupling, the regime at low temperatures, for the efficient transfer of magnetic excitation to microwave photon. (D) Electron spin-spin relaxation ( $T_2$ ) versus temperature for several molecular qubits. Panel (D) adapted from ref. (Moreno-Pineda, Godfrin, et al., 2018) with permission from The Royal Society of Chemistry.

An exponential law was found through the electrical read-out and monitoring of the spin-flip of the electronic spin after the application of non-resonant microwave pulses, hence acting as a thermometer. Spin-polarised Scanning Tunnelling Microscope (SP-STM) (Wiesendanger et al., 1990; Wiesendanger, 2009), combined with electromagnetic pulses (Troiani et al., 2019), have been also proposed for local sensing. The procedure involves the application of a microwave pulse, which prompts an electronic transition, henceforth, altering the population of the centre which is successively detected by the SP-STM tip (Bae et al., 2018; Moreno-Pineda & Wernsdorfer, 2021; Willke et al., 2018; Willke, Paul, et al., 2018; Willke et al., 2019a; Willke et al., 2019b; Yang et al., 2017, 2019). An analogous protocol has been proposed for the detection of the electronic and nuclear spin properties of a  $TbPc_2$  system. Spin assemblies can in principle also allow the detection of magnetic fields in the strong coupling regime and for the detection of dark matter (Troiani et al., 2019) (Fig. 5C).

### Quantum Simulators

In the early 1980s, Richard Feynman postulated that a computer implementing quantum effects could simulate quantum systems better than any classical analogue, highlighting the limitations of classical computers (Feynman, 1982). A system which exploits quantum effects can be prepared to mimic the dynamics of complex quantum mechanical problems.

SMMs are especially attractive systems given that these show all the requirements to act as qubits (Coronado, 2020; Crippa et al., 2021; Gaita-Ariño et al., 2019; Moreno-Pineda, et al., 2018; Sugisaki et

al., 2019; Wasielewski et al., 2020). Furthermore, SMMs can mimic the evolution of quantum mechanical problems and their structural and electronic properties can be tuned by chemical means. An aspect of paramount importance for the realisation of quantum operation is the possibility of bringing two qubits into proximity to accomplish quantum gates (Aguilà et al., 2014; Aromí et al., 2012; Atzori et al., 2018b; Ferrando-Soria et al., 2016; Luis et al., 2011; Montanaro, 2016; Nakazawa et al., 2012; Timco et al., 2009). Additionally, the multilevel character of SMMs can be exploited, utilising the various two-levels systems as qubit units (Moreno-Pineda et al., 2018; Stepanenko et al., 2008). Likewise, SMMs with a switchable interaction between two units can act as quantum simulators. The {Cr7Ni} dimers represent an example to simulate quantum gates (Chiesa et al., 2016; Chiesa et al., 2014; Ferrando-Soria et al., 2016) (Fig. 6A).

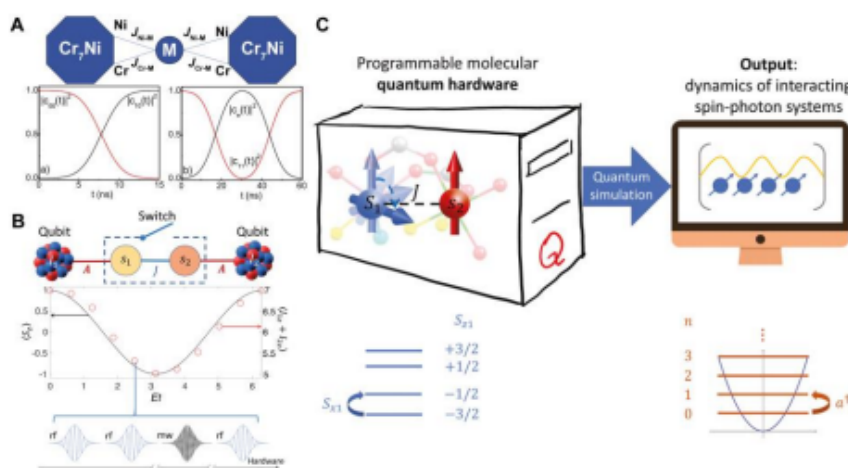


FIGURE 6.

Quantum Simulations with SMMs: (A) Schematic representation of a pair of {Cr7Ni} rings, linked by a Ni<sup>2+</sup> ion (to) and single-qubit rotation and simulation of a two-qubits gate-controlled  $j$  (C-j) (bottom). (B) View of a hybrid nuclear-electronic spin architecture. Quantum simulation of the oscillation of the magnetisation for an  $S = 1$  spin experiencing QTM and sequence of pulses required for the simulation. (C) Schematic view of a multilevel molecular quantum simulator. The system is composed of a qudit spin  $S_1$  coupled by exchange interaction  $J$  to a spin  $s_2 = 1/2$ . Panels (A) adapted from ref. (Alessandro Chiesa et al., 2014) and panel (B) adapted from ref. (Atzori, Chiesa, et al., 2018) and panel (C) adapted from ref. (Tacchino, Chiesa, Sessoli, Tavernelli, & Carretta, 2021) with permission from The Royal Society of Chemistry.

Atzori and co-workers described an important example for the implementation of an SMM for quantum simulations (Atzori et al., 2018b). The experiments were carried out employing a dimeric vanadium (IV) complex with formula  $[\text{PPh}_4]_4[(\text{VO})_2(\text{L}_1)_2]$  ( $\text{L}_1$  = tetraanion of  $\text{C}_6\text{H}_3(\text{OH})_2\text{-CONH-C}_6\text{H}_4\text{-CONH-C}_6\text{H}_3(\text{OH})_2$ ),

utilising both the electronic and nuclear spins. In the vanadyl dimer, the electronic spins are coupled by an exchange interaction, while the electronic and nuclear states are coupled via the hyperfine interaction (Fig. 6B). This interaction allows the rotation of the electronic states, which is contingent upon the nuclei, therefore, the SMM can be implemented in two-qubits gates, where the indirect interaction acts as a switch. The long coherence and the strong hyperfine interaction make the system very appealing (Atzori et al., 2016a; Atzori et al., 2016b; Graham et al., 2017; Yu et al., 2016; Zadrozny et al., 2014; Zadrozny et al., 2015). A controlled shift (Cj) two qubits quantum gate,

which generates entanglement between the qubits adding a phase to one of the states, whilst leaving the remaining three states unaffected, was achieved by exploiting the multilevel character of the system. By

utilising the vanadyl dimer as a quantum simulator, it was possible to simulate the quantum tunnelling of the magnetisation of  $S = 1$ , with high fidelities.

More recently, an SMM acting as qudits unit (Atzori et al., 2018a; Atzori et al., 2016a; Atzori et al., 2017; Atzori et al., 2016b; Balakrishnan, 2014; Biard et al., 2021; Fataftah et al., 2016; Gedik et al., 2015; Kiktenko et al., 2015; Luo & Wang, 2014; Mohammadi et al., 2011; Moreno-Pineda et al., 2017; Moreno-Pineda et al., 2018; Yu et al., 2016), comprising a dimer based on two spins, i.e., an  $S = 1/2$  and  $S = 3/2$  spins, manipulated by microwave pulses, have been proposed as quantum simulator for light-matter interactions (Fig. 6C). The scheme exploits the spin  $S$  ion to encode the photon field facilitating the digital simulation of a broad range of spin-boson models with a higher efficiency than multi-qubit units (Tacchino et al., 2021).

## Quantum Computers

Feynman's proposal for the efficient simulation of quantum systems employing a quantum computer (Feynman, 1982) was backed by Shor (Shor, 1997), Grover (Grover, 1997), Lloyds (Lloyd, 1993), among others when they highlighted that a quantum computer would offer unparalleled advantages over classical computers. Today, the field of quantum computing is an active field and ever-growing field, incorporating several companies and consortiums. These have invested staggering amounts of money in the quest for a functional quantum computer.

Due to the facile manipulation of the electronic spins of SMMs, these have been proposed as electron spin qubits, whereby manipulation is achieved through the application of thermal stimuli, magnetic fields or electromagnetic pulses (Balakrishnan, 2014; Kiktenko et al., 2015a; Kiktenko et al., 2015b; Mohammadi et al., 2011; O'Leary et al., 2006; Popov et al., 2016; Rungta et al., 2007). One important method for manipulation of the electronic spins of SMMs is Electron Paramagnetic Resonance (EPR) pulses, as shown with the {Cr7Ni} antiferromagnetic wheels. A strong antiferromagnetic coupling between the  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  comprising the wheel leads to a well-defined and isolated spin  $S = 1/2$  ground state (Troiani et al., 2005). Besides transition metal-based SMMs, lanthanide-based SMMs have also been proposed as qubits (Aguilà et al., 2014; Pedersen et al., 2016; Shiddiq et al., 2016) owing to their inherent magnetic anisotropy and ground doublet state characteristics. A cNOT gate was proposed employing an asymmetric lanthanide dimer with a small interaction between the  $\text{Ce}^{3+}$  and  $\text{Er}^{3+}$  lanthanide ions. In principle, the electronic states in the dimer can be manipulated by resonance frequencies or fields (Aguilà et al., 2014).

The advantage of the utilisation of qudits was shown in a gadolinium polyoxometalate complex with the formula  $\text{K}_{12}\text{Gd}(\text{H}_2\text{O})\text{P}_5\text{W}_{30}\text{O}_{110} \cdot 27.5\text{H}_2\text{O}$  ( $\text{GdW}_{30}$ ) (Jenkins et al., 2017; Martínez-Pérez et al., 2012). EPR studies show that the eight electronic states, arising from the  $S = 7/2$  state, can be manipulated by EPR pulses. Long coherence values were found,  $T_2$  between 400 and 600 ns and  $T_1$  between 2.3 to 2.6  $\mu\text{s}$  were determined. Due to the accessible states and the ability to manipulate them, it was possible to carry out a controlled-controlled-NOT (cNOT) or Toffoli gate, highlighting the advantages of multilevel systems.

The previous examples demonstrate the importance of the electronic states embedded in SMMs for their implementation in quantum information technologies. Nonetheless, the electron spin is extremely susceptible to fluctuation originating from the spin bath and neighbouring molecules. Moreover, the majority of explored SMMs have been investigated on large assemblies, which in turn, could compromise the initialisation, manipulation, and coherence characteristics due to inhomogeneity effects. Towards the integration of SMMs in hybrid spintronic devices, in which the magnetic molecules would be in direct contact with metallic leads, systems possessing larger robustness are sought (Moreno Pineda et al., 2016). In this context, the  $\text{TbPc}_2$  molecule has been proven to act as a nuclear spin qudit, with the four nuclear states acting as quantum register, ultimately leading to the realisation of a quantum algorithm.

The  $\text{TbPc}_2$  molecule is a remarkably stable system and have been deposited in numerous substrates (Moreno Pineda et al., 2016) and integrated into spin transistors and spin valve configurations (vide supra). When  $\text{TbPc}_2$  has been embedded in a transistor device configuration, the electrical manipulation and read-out of the electronic properties of the molecule have been achieved by injecting electrons through the source –  $\text{TbPc}_2$  – drain, allowing to sense of the charge state of the molecule. The read-out of the nuclear states is then feasible due to the indirect coupling between the electronic spin and nuclear spin via the hyperfine interaction (Godfrin et al., 2017) (vide supra). At sub-kelvin temperatures and low applied fields, initialisation of the four nuclear qudits states, i.e.,  $|m_s = \pm 1/2\rangle$  and  $|m_s = \pm 3/2\rangle$  (Thiele et al., 2013; Thiele et al., 2014), is achieved. Furthermore, the uneven separation of the nuclear states, resulting from the quadrupolar interaction (Thiele et al., 2014), allows the manipulation of these states (Fig. 7A,B). Long  $T_1$  and  $T_2$  values were observed, which along with the ability to read out, initialise and manipulate the nuclear states, allowed the implementation of the Grover's algorithm (Godfrin et al., 2017) (Fig. 7C,D).

An additional aspect of the implementation of SMMs in quantum information technologies is the ability to protect the information from quantum noise and decoherence sources. In this regard, quantum error correction (QEC) is essential for the development of fault-tolerant universal quantum computing. QEC in principle, reduces errors arising from noise, gates operation, faulty initialisation, manipulation, and measurements of the quantum information. QEC schemes work encoding the quantum information into systems possessing more than two energy levels “logical qubits”; these qubits can bring the system into a well-defined state outside the computational subspace, hence, enabling the detection of errors and their correction. For the execution of common QEC protocols, the logical qubits are encoded in several ancillary states and several other physical units (Aguilà et al., 2014; Atzori, Chiesa, et al., 2018; Chiesa et al., 2014; Ferrando-Soria et al., 2016a; Ferrando-Soria et al., 2016b; Luis et al., 2011; Shiddiq et al., 2016; Zadrozny et al., 2015). Due to the requirement of non-local states in distinct objects to carry out QEC and quantum computation, this protocol seems not very viable. Alternatively, to circumvent this problem, the logical qubits can be encoded in a single-multilevel quantum object, or qudit (Atzori, Benci, et al., 2018; Atzori et al., 2016a; Atzori et al., 2017; Atzori et al., 2016b; Biard et al., 2021; Fataftah et al., 2016; Moreno-Pineda et al., 2017; Moreno-Pineda et al., 2018; Yu et al., 2016).

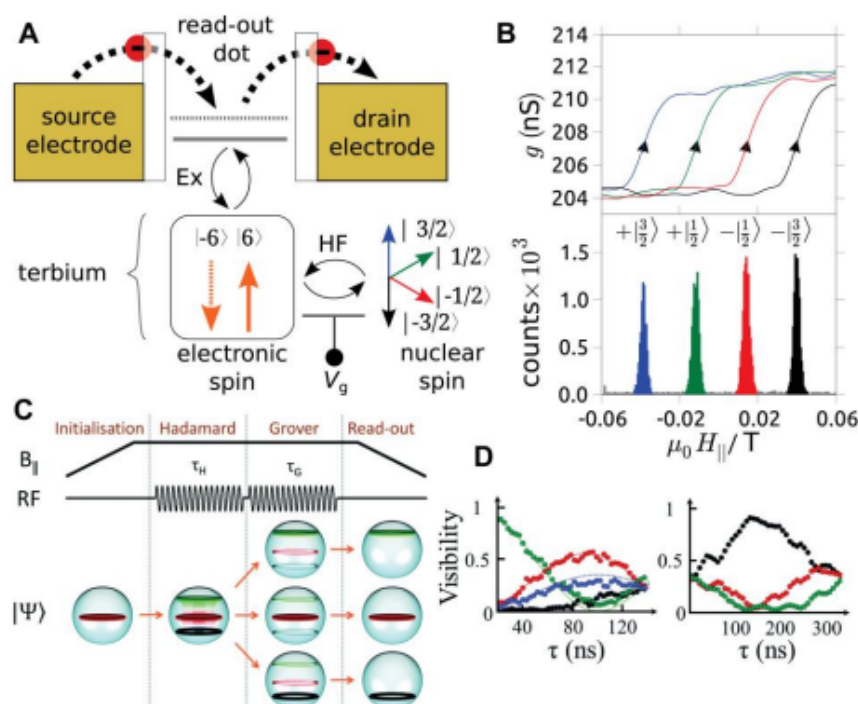


FIGURE 7.

Quantum Computing with SMMs: (A) Schematic view of the read-out cascade occurring in [TbPc2] in the transistor device. (B) (top) hysteresis loops obtained from conductance measurements and (bottom) histograms of the conductance jumps corresponding to the nuclear states in the [TbPc2]. (C) Grover algorithm is implemented using four different steps: initialisation, Hadamard gate, Grover gate and final read-out. (D) (left) Evolution of the population as a function of the Hadamard gate pulse length. (Right) Evolution of the population in the function of the Grover gate pulse length. Starting from a superposed state (obtain by a Hadamard pulse sequence) the system oscillated between this superposed state and the desired state (black points). Panels (A) and (B) adapted from ref. (Stefan Thiele et al., 2014) with permission from The American Association for the Advancement of Science (AAAS). Panels (C) and (D) adapted.



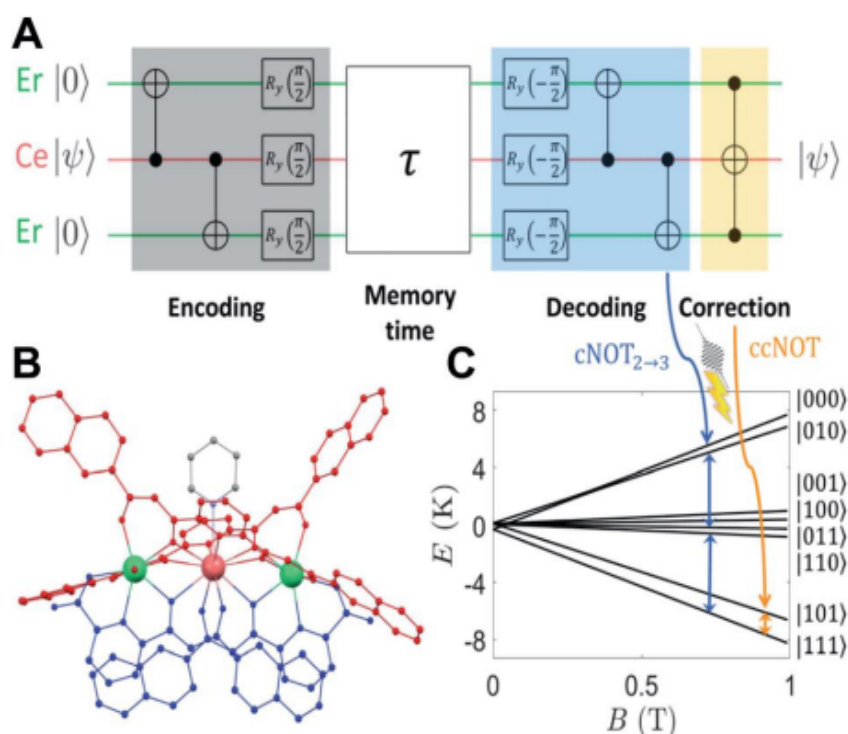


FIGURE 8.

Quantum Computing with SMMs: (A) Three-qubit phase-flip repetition code quantum circuit. The central qubit carries the information, while the remaining act as auxiliary qubits. (B) Molecular structure of f-SMM (Er, green, and Ce, light red) corresponding to the qubits of the circuit depicted in (A). (C) Energy levels as a function of the external field  $B$  applied along  $z$  (the Er–Ce direction). Adapted from ref. (Macaluso et al., 2020) with permission from The Royal Society of Chemistry.

In this context, SMMs seem very appealing due to their multilevel characteristics. An example of such advantages in SMMs for QEC, a heterometallic trinuclear [ErCeEr] trinuclear complex, with an interaction connecting the Er–Ce pair, as determined by SQUID magnetometry, heat capacity and EPR spectroscopy (Fig. 8) (Macaluso et al., 2020), was shown to be suitable for QEC protocols. Numerical simulation showed that the [ErCeEr] complex can be exploited in a three-qubit repetition code to protect qubits from single-bit or phase-flip errors (Fig. 8A) (Nielsen & Chuang, 2012). The correction protocol involves encoding, decoding and correction stages. Two controlled-NOT (cNOT) two-qubit gates inducing a flip on the target qubit, which is protected from error due to entanglement, comprises the encoding

step. A memory time stores the qubit, while the decoding (reverse encoding) is implemented subsequently. A single controlled-controlled-NOT (ccNOT) gate applied to the qubit acts as a correction step. As determined by numerical simulations, the SMMs can efficiently shield the encoded information in the qubit from decoherence. A {Cr7Ni}-Cu system, in which the electronic state of the {Cr7Ni} and the nuclear state embedded in the Cu ion can also be exploited for error correction (Lockyer et al., 2021). Execution of complex quantum algorithms required idle times, between sets of quantum operations for long times. The nuclear spins embedded in the  $\text{Cu}^{2+}$ , are employed as quantum memory to store information during idle times. By exploiting the nuclear states in the  $\text{Cu}^{2+}$ , acting as storage states with quantum error correction, it was shown that information can be protected for times much longer than the processor coherence. Unquestionably, these examples paved the way for SMMs for universal fault-tolerant quantum computer architectures (Chiesa et al., 2020).

## CONCLUSIONS

SMMs have been in the heart of many studies since their discovery in the early 1990s, leading to the observation of intriguing quantum effects. After more than 30 years of intensive research of SMMs, the acquired knowledge of these systems placed them as a promising candidate for new technological applications. Today, it is possible to observe energy barriers to the relaxation well above liquid nitrogen temperatures

(Goodwin et al., 2017; Gould et al., 2022; Guo et al., 2018), systems having extraordinary long coherence times (Coronado, 2020; Gaita-Ariño et al., 2019; Wasielewski et al., 2020) the manipulation of their quantum states to their integration of hybrid spin architectures (Biard et al., 2021; Godfrin et al., 2018, 2017; S. Thiele et al., 2013; Stefan Thiele et al., 2014; Urdampilleta et al., 2011, 2013; Urdampilleta et al., 2015; Vincent et al., 2012), eventually, permitting the execution of the quantum Grover's algorithm (C. Godfrin et al., 2017). The achievements reached up to this point, acting as first quantum revolution, can be considered as the scaffolding for developing novel technologies. Towards the utilisation of quantum properties in technological applications, the second quantum revolution endeavours to engineer and

implement these in hybrid devices. Due to the remarkable control gained of SMMs till today, over their structural, electronic, and nuclear characteristics, these molecules close of being part of novel technologies. The coherence and spatial resolution, make these systems plausible quantum sensors. Moreover, they have been shown to viable to act as quantum simulators and fault-resilient quantum computers.

While we did not intend to comprehensively compile the results obtained in the very active and promising field of SMMs, we hope to have provided here an interesting overview of actions, which evidence the manifestation of quantum mechanical effects through prospects of systems and devices integrated by SMMs for state-of-the-art technological applications. Applications such as these are likely to play a leading role in the future development of SMMs, changing the paradigm, just as nanoscience did.

## REFERENCES

- Aasi, J., Abadie, J., Abbott, B. P., Abbott, R., Abbott, T. D., Abernathy, M. R., ... Zweizig, J. (2013). Enhanced sensitivity of the LIGO gravitational wave detector by using squeezed states of light. *Nature Photonics*, 7(8), 613–619. <https://doi.org/10.1038/nphoton.2013.177>
- Aguilà, D., Barrios, L. A., Velasco, V., Roubeau, O., Repollés, A., Alonso, P. J., ... Aromí, G. (2014). Heterodimetallic [LnLn'] lanthanide complexes: Toward a chemical design of two-qubit molecular spin quantum gates. *Journal of the American Chemical Society*, 136(40), 14215–14222. <https://doi.org/10.1021/ja507809w>
- Albino, A., Benci, S., Tesi, L., Atzori, M., Torre, R., Sanvito, S., ... Lunghi, A. (2019). First-Principles Investigation of Spin-Phonon Coupling in Vanadium-Based Molecular Spin Quantum Bits. *Inorganic Chemistry*, 58(15), 10260–10268. <https://doi.org/10.1021/acs.inorgchem.9b01407>
- Aromí, G., Aguilà, D., Gamez, P., Luis, F., & Roubeau, O. (2012). Design of magnetic coordination complexes for quantum computing. *Chemical Society Reviews*, 41(2), 537–546. <https://doi.org/10.1039/c1cs15115k>
- Arute, F., Arya, K., Babbush, R., Bacon, D., Bardin, J. C., Barends, R., ... Martinis, J. M. (2019). Quantum supremacy using a programmable superconducting processor. *Nature*, 574(7779), 505–510. <https://doi.org/10.1038/s41586-019-1666-5>
- Atzori, M., Benci, S., Morra, E., Tesi, L., Chiesa, M., Torre, R., ... Sessoli, R. (2018a). Structural Effects on the Spin Dynamics of Potential Molecular Qubits. *Inorganic Chemistry*, 57(2), 731–740. <https://doi.org/10.1021/acs.inorgchem.7b02616>
- Atzori, M., Chiesa, A., Morra, E., Chiesa, M., Sorace, L., Carretta, S., ... Sessoli, R. (2018b). A two-qubit molecular architecture for electron-mediated nuclear quantum simulation. *Chemical Science*, 9(29), 6183–6192. <https://doi.org/10.1039/c8sc01695j>

- Atzori, M., Morra, E., Tesi, L., Albino, A., Chiesa, M., Sorace, L., & Sessoli, R. (2016a). Quantum Coherence Times Enhancement in Vanadium(IV)-based Potential Molecular Qubits: The Key Role of the Vanadyl Moiety. *Journal of the American Chemical Society*, 138(35), 11234–11244. <https://doi.org/10.1021/jacs.6b05574>
- Atzori, M., & Sessoli, R. (2019). The Second Quantum Revolution: Role and Challenges of Molecular Chemistry. *Journal of the American Chemical Society*, 141(29), 11339–11352. <https://doi.org/10.1021/jacs.9b00984>
- Atzori, M., Tesi, L., Benci, S., Lunghi, A., Righini, R., Taschin, A., ... Sessoli, R. (2017). Spin Dynamics and Low Energy Vibrations: Insights from Vanadyl-Based Potential Molecular Qubits. *Journal of the American Chemical Society*, 139(12), 4338–4341. <https://doi.org/10.1021/jacs.7b01266>
- Atzori, M., Tesi, L., Morra, E., Chiesa, M., Sorace, L., & Sessoli, R. (2016b). Room-Temperature Quantum Coherence and Rabi Oscillations in Vanadyl Phthalocyanine: Toward Multifunctional Molecular Spin Qubits. *Journal of the American Chemical Society*, 138(7), 2154–2157. <https://doi.org/10.1021/jacs.5b13408>
- Bader, K., Dengler, D., Lenz, S., Endeward, B., Jiang, S. Da, Neugebauer, P., & Van Slageren, J. (2014). Room temperature quantum coherence in a potential molecular qubit. *Nature Communications*, 5(1), 5304. <https://doi.org/10.1038/ncomms6304>
- Bae, Y., Yang, K., Willke, P., Choi, T., Heinrich, A. J., & Lutz, C. P. (2018). Enhanced quantum coherence in exchange coupled spins via singlet-triplet transitions. *Science Advances*, 4(11), eaau4159. <https://doi.org/10.1126/sciadv.aau4159>
- Balakrishnan, S. (2014). Various Constructions of Qudit SWAP Gate. *Physics Research International*, 2014, 1–5. <https://doi.org/10.1155/2014/479320>
- Barco, E. del, Hernandez, J., Tejada, J., Biskup, N., Achey, R., Rutel, I., ... Brooks, J. (2000). High-frequency resonant experiments in molecular clusters. *Physical Review B - Condensed Matter and Materials Physics*, 62(5), 3018–3021. <https://doi.org/10.1103/PhysRevB.62.3018>
- Barry, J. F., Turner, M. J., Schloss, J. M., Glenn, D. R., Song, Y., Lukin, M. D., ... Walsworth, R. L. (2016). Optical magnetic detection of single- neuron action potentials using quantum defects in diamond. *PNAS*, 113(49), 14133–14138. <https://doi.org/10.1073/pnas.1601513113>
- Bertaina, S., Gambarelli, S., Mitra, T., Tsukerblat, B., Müller, A., & Barbara, B. (2008). Quantum oscillations in a molecular magnet. *Nature*, 453(7192), 203–206. <https://doi.org/10.1038/nature06962>
- Biard, H., Moreno-Pineda, E., Ruben, M., Bonet, E., Wernsdorfer, W., & Balestro, F. (2021). Increasing the Hilbert space dimension using a single coupled molecular spin. *Nature Communications*, 12(1), 4443. <https://doi.org/10.1038/s41467-021-24693-6>
- Bogani, L., & Wernsdorfer, W. (2008). Molecular spintronics using single-molecule magnets. *Nature Materials*, 7(3), 179–186. <https://doi.org/10.1038/nmat2133>
- Boss, J. M., Cujia, K. S., Zopes, J., & Degen, C. L. (2017). Quantum sensing with arbitrary frequency resolution. *Science*, 356(6340), 837–840. <https://doi.org/10.1126/science.aam7009>
- Briganti, M., Santanni, F., Tesi, L., Totti, F., Sessoli, R., & Lunghi, A. (2021). A Complete Ab Initio View of Orbach and Raman Spin–Lattice Relaxation in a Dysprosium Coordination Compound. *Journal of the American Chemical Society*, 143(34), 13633–13645. <https://doi.org/10.1021/jacs.1c05068>
- Bruce, D. W., O'hare, D., & Walton, R. I. (n.d.). *Molecular Materials (Inorganic Materials Series)*. Candini, A., Lorusso, G., Troiani, F., Ghirri, A., Carretta, S., Santini, P., ... Affronte, M. (2010). Entanglement in supramolecular spin systems of two weakly coupled antiferromagnetic rings (purple-Cr7Ni). *Physical Review Letters*, 104(3), 037203. <https://doi.org/10.1103/PhysRevLett.104.037203>
- Carretta, S., Santini, P., Amoretti, G., Guidi, T., Copley, J. R. D., Qiu, Y., ... Winpenny, R. E. P. (2007). Quantum oscillations of the total spin in a heterometallic antiferromagnetic ring: Evidence from neutron spectroscopy. *Physical Review Letters*, 98(16), 167401. <https://doi.org/10.1103/PhysRevLett.98.167401>
- Chen, Y. C., Liu, J. L., Ungur, L., Liu, J., Li, Q. W., Wang, L. F., ... Tong, M. L. (2016). Symmetry-Supported Magnetic Blocking at 20 K in Pentagonal Bipyramidal Dy(III) Single-Ion Magnets. *Journal of the American Chemical Society*, 138(8), 2829–2837. <https://doi.org/10.1021/jacs.5b13584>

- Chen, Z., Molina-Jirón, C., Klyatskaya, S., Klappenberger, F., & Ruben, M. (2017). 1D and 2D Graphdiynes: Recent Advances on the Synthesis at Interfaces and Potential Nanotechnological Applications. *Annalen Der Physik*, 529(11), 1–20. <https://doi.org/10.1002/andp.201700056>
- Chiesa, A., Macaluso, E., Petiziol, F., Wimberger, S., Santini, P., & Carretta, S. (2020). Molecular Nanomagnets as Qubits with Embedded Quantum-Error Correction. *The Journal of Physical Chemistry Letters*, 11(20), 8610–8615. <https://doi.org/10.1021/acs.jpcclett.0c02213>
- Chiesa, Alessandro, Santini, P., & Carretta, S. (2016). Supramolecular Complexes for Quantum Simulation. *Magnetochemistry*, 2(4), 37. <https://doi.org/10.3390/magnetochemistry2040037>
- Chiesa, A., Whitehead, G. F. S., Carretta, S., Carthy, L., Timco, G. A., Teat, S. J., ... Santini, P. (2014). Molecular nanomagnets with switchable coupling for quantum simulation. *Scientific Reports*, 4(1), 7423. <https://doi.org/10.1038/srep07423>
- Christou, G. (1993). Manganese carboxylate aggregates of biological relevance. *Journal of Inorganic Biochemistry*, 51(1–2), 445. [https://doi.org/10.1016/0162-0134\(93\)85473-L](https://doi.org/10.1016/0162-0134(93)85473-L)
- Cooper, A., Sun, W. K. C., Jaskula, J. C., & Cappellaro, P. (2020). Identification and Control of Electron-Nuclear Spin Defects in Diamond. *Physical Review Letters*, 124(8), 83602. <https://doi.org/10.1103/PhysRevLett.124.083602>
- Coronado, E. (2020). Molecular magnetism: from chemical design to spin control in molecules, materials and devices. *Nature Reviews Materials*, 5(2), 87–104. <https://doi.org/10.1038/s41578-019-0146-8>
- Crippa, L., Tacchino, F., Chizzini, M., Aita, A., Grossi, M., Chiesa, A., ... Carretta, S. (2021). Simulating Static and Dynamic Properties of Magnetic Molecules with Prototype Quantum Computers. *Magnetochemistry*, 7(8), 117. <https://doi.org/10.3390/magnetochemistry7080117>
- Degen, C. L., Reinhard, F., & Cappellaro, P. (2017). Quantum sensing. *Reviews of Modern Physics*, 89(3), 035002. <https://doi.org/10.1103/RevModPhys.89.035002>
- DiVincenzo, D. P. (2000). The physical implementation of quantum computation. *Fortschritte Der Physik*, 48(9–11), 771–783. [https://doi.org/10.1002/1521-3978\(200009\)48:9/11<771::AID-ROP771>3.0.CO;2-E](https://doi.org/10.1002/1521-3978(200009)48:9/11<771::AID-ROP771>3.0.CO;2-E)
- Dovzhenko, Y., Casola, F., Schlotter, S., Zhou, T. X., Büttner, F., Walsworth, R. L., ... Yacoby, A. (2018). Magnetostatic twists in room- temperature skyrmions explored by nitrogen-vacancy center spin texture reconstruction. *Nature Communications*, 9(1), 2712. <https://doi.org/10.1038/s41467-018-05158-9>
- Dowling, J. P., & Milburn, G. J. (2003). Quantum technology: The second quantum revolution. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 361(1809), 1655–1674. <https://doi.org/10.1098/rsta.2003.1227>
- Fataftah, M. S., Zadrozny, J. M., Coste, S. C., Graham, M. J., Rogers, D. M., & Freedman, D. E. (2016). Employing Forbidden Transitions as Qubits in a Nuclear Spin-Free Chromium Complex. *Journal of the American Chemical Society*, 138(4), 1344–1348. <https://doi.org/10.1021/jacs.5b11802>
- Fernandez, A., Moreno Pineda, E., Muryn, C. A., Sproules, S., Moro, F., Timco, G. A., ... Winpenny, R. E. P. (2015). G-Engineering in Hybrid Rotaxanes to Create AB and AB<sub>2</sub> Electron Spin Systems: EPR Spectroscopic Studies of Weak Interactions between Dissimilar Electron Spin Qubits. *Angewandte Chemie - International Edition*, 54(37), 10858–10861. <https://doi.org/10.1002/anie.201504487>
- Ferrando-Soria, J., Fernandez, A., Moreno Pineda, E., Varey, S. A., Adams, R. W., Vitorica-Yrezabal, I. J., ... Winpenny, R. E. P. (2015). Controlled Synthesis of Nanoscopic Metal Cages. *Journal of the American Chemical Society*, 137(24), 7644–7647. <https://doi.org/10.1021/jacs.5b04664>
- Ferrando-Soria, J., Magee, S. A., Chiesa, A., Carretta, S., Santini, P., Vitorica-Yrezabal, I. J., ... Winpenny, R. E. P. (2016a). Switchable Interaction in Molecular Double Qubits. *Chem*, 1(5), 727–752. <https://doi.org/10.1016/j.chempr.2016.10.001>
- Ferrando-Soria, J., Moreno Pineda, E., Chiesa, A., Fernandez, A., Magee, S. A., Carretta, S., ... Winpenny, R. E. P. (2016b). A modular design of molecular qubits to implement universal quantum gates. *Nature Communications*, 7, 11377. <https://doi.org/10.1038/ncomms11377>



- Feynman, R. P. (1982). Simulating physics with computers. *International Journal of Theoretical Physics*, 21(6–7), 467–488. <https://doi.org/10.1007/BF02650179>
- Gaita-Ariño, A., Luis, F., Hill, S., & Coronado, E. (2019). Molecular spins for quantum computation. *Nature Chemistry*, 11(4), 301–309. <https://doi.org/10.1038/s41557-019-0232-y>
- Ganzhorn, M., Klyatskaya, S., Ruben, M., & Wernsdorfer, W. (2013). Strong spin-phonon coupling between a single-molecule magnet and a carbon nanotube nanoelectromechanical system. *Nature Nanotechnology*, 8(3), 165–169. <https://doi.org/10.1038/nnano.2012.258>
- Ganzhorn, M., Klyatskaya, S., Ruben, M., & Wernsdorfer, W. (2016). Quantum Einstein-de Haas effect. *Nature Communications*, 7(1), 11443. <https://doi.org/10.1038/ncomms11443>
- García-Pérez, G., Rossi, M. A. C., & Maniscalco, S. (2020). IBM Q Experience as a versatile experimental testbed for simulating open quantum systems. *Npj Quantum Information*, 6(1), 1. <https://doi.org/10.1038/s41534-019-0235-y>
- Garlatti, E., Guidi, T., Ansbro, S., Santini, P., Amoretti, G., Ollivier, J., ... Carretta, S. (2017). Portraying entanglement between molecular qubits with four-dimensional inelastic neutron scattering. *Nature Communications*, 8(1), 14543. <https://doi.org/10.1038/ncomms14543>
- Gatteschi, D., & Sessoli, R. (2003). Quantum tunneling of magnetization and related phenomena in molecular materials. *Angewandte Chemie - International Edition*, 42(3), 268–297. <https://doi.org/10.1002/anie.200390099>
- Gedik, Z., Silva, I. A., Çakmak, B., Karpas, G., Vidoto, E. L. G., Soares-Pinto, D. O., ... Fanchini, F. F. (2015). Computational speed-up with a single qudit. *Scientific Reports*, 5(1), 14671.
- Godfrin, C., Ferhat, A., Ballou, R., Klyatskaya, S., Ruben, M., Wernsdorfer, W., & Balestro, F. (2017). Operating Quantum States in Single Magnetic Molecules: Implementation of Grover's Quantum Algorithm. *Physical Review Letters*, 119(18), 187702.
- Godfrin, C., Lumetti, S., Biard, H., Bonet, E., Klyatskaya, S., Ruben, M., ... Balestro, F. (2019). Microwave-assisted reversal of a single electron spin. *Journal of Applied Physics*, 125(14). <https://doi.org/10.1063/1.5064593>
- Godfrin, Clément, Ballou, R., Bonet, E., Ruben, M., Klyatskaya, S., Wernsdorfer, W., & Balestro, F. (2018). Generalized Ramsey interferometry explored with a single nuclear spin qudit. *Npj Quantum Information*, 4(1), 53. <https://doi.org/10.1038/s41534-018-0101-3>
- Godfrin, Clément, Thiele, S., Ferhat, A., Klyatskaya, S., Ruben, M., Wernsdorfer, W., & Balestro, F. (2017). Electrical Read-Out of a Single Spin Using an Exchange-Coupled Quantum Dot. *ACS Nano*, 11(4), 3984–3989. <https://doi.org/10.1021/acsnano.7b00451>
- Goodwin, C. A. P., Ortu, F., Reta, D., Chilton, N. F., & Mills, D. P. (2017). Molecular magnetic hysteresis at 60 kelvin in dysprosocenium. *Nature*, 548(7668), 439–442. <https://doi.org/10.1038/nature23447>
- Gottesman, D. (1999). Fault-tolerant quantum computation with higher-dimensional systems. In *Lecture Notes in Computer Science (including subseries Lecture Notes in Artificial Intelligence and Lecture Notes in Bioinformatics)* (Vol. 1509, pp. 302–313). [https://doi.org/10.1007/3-540-49208-9\\_27](https://doi.org/10.1007/3-540-49208-9_27)
- Gould, C. A., McClain, K. R., Reta, D., Kragoskow, J. G. C., Marchiori, D. A., Lachman, E., ... Long, J. R. (2022). Ultrahard magnetism from mixed-valence dilanthanide complexes with metal-metal bonding. *Science*, 375(6577), 198–202. <https://doi.org/10.1126/science.abl5470>
- Graham, M. J., Krzyaniak, M. D., Wasielewski, M. R., & Freedman, D. E. (2017). Probing Nuclear Spin Effects on Electronic Spin Coherence via EPR Measurements of Vanadium(IV) Complexes. *Inorganic Chemistry*, 56(14), 8106–8113. <https://doi.org/10.1021/acs.inorgchem.7b00794>
- Graham, M. J., Zadrozny, J. M., Fataftah, M. S., & Freedman, D. E. (2017). Forging Solid-State Qubit Design Principles in a Molecular Furnace. *Chemistry of Materials*, 29(5), 1885–1897. <https://doi.org/10.1021/acs.chemmater.6b05433>
- Graham, M. J., Zadrozny, J. M., Shiddiq, M., Anderson, J. S., Fataftah, M. S., Hill, S., & Freedman, D. E. (2014). Influence of electronic spin and spin-orbit coupling on decoherence in mononuclear transition metal complexes. *Journal of the American Chemical Society*, 136(21), 7623–7626. <https://doi.org/10.1021/ja5037397>



- Grover, L. K. (1997). Quantum Mechanics Helps in Searching for a Needle in a Haystack. *Physical Review Letters*, 79(2), 325–328. <https://doi.org/10.1103/PhysRevLett.79.325>
- Guo, F. S., Day, B. M., Chen, Y. C., Tong, M. L., Mansikkamäki, A., & Layfield, R. A. (2018). Magnetic hysteresis up to 80 kelvin in a dysprosium metallocene single-molecule magnet. *Science*, 362(6421), 1400–1403. <https://doi.org/10.1126/science.aav0652>
- Heersche, H. B., De Groot, Z., Folk, J. A., Van Der Zant, H. S. J., Romeike, C., Wegewijs, M. R., ... Cornia, A. (2006). Electron transport through single Mn12 molecular magnets. *Physical Review Letters*, 96(20), 206801. <https://doi.org/10.1103/PhysRevLett.96.206801>
- Hill, S. (2003). Quantum Coherence in an Exchange-Coupled Dimer of Single-Molecule Magnets. *Science*, 302(5647), 1015–1018. <https://doi.org/10.1126/science.1090082>
- Ishikawa, N., Sugita, M., Ishikawa, T., Koshihara, S. Y., & Kaizu, Y. (2003a). Lanthanide double-decker complexes functioning as magnets at the single-molecular level. *Journal of the American Chemical Society*, 125(29), 8694–8695. <https://doi.org/10.1021/ja029629n>
- Ishikawa, N., Sugita, M., Okubo, T., Tanaka, N., Iino, T., & Kaizu, Y. (2003b). Determination of ligand-field parameters and f-electronic structures of double-decker bis(phthalocyaninato)lanthanide complexes. *Inorganic Chemistry*, 42(7), 2440–2446. <https://doi.org/10.1021/ic026295u>
- Ishikawa, N., Sugita, M., & Wernsdorfer, W. (2005). Quantum tunneling of magnetization in lanthanide single-molecule magnets: Bis(phthalocyaninato)terbium and bis(phthalocyaninato)dysprosium anions. *Angewandte Chemie - International Edition*, 44(19), 2931–2935. <https://doi.org/10.1002/anie.200462638>
- Jenkins, A., Pelliccione, M., Yu, G., Ma, X., Li, X., Wang, K. L., & Jayich, A. C. B. (2019). Single-spin sensing of domain-wall structure and dynamics in a thin-film skyrmion host. *Physical Review Materials*, 3(8), 83801. <https://doi.org/10.1103/PhysRevMaterials.3.083801>
- Jenkins, M. D., Duan, Y., Diosdado, B., García-Ripoll, J. J., Gaita-Ariño, A., Giménez-Saiz, C., ... Luis, F. (2017). Coherent manipulation of three-qubit states in a molecular single-ion magnet. *Physical Review B*, 95(6), 064423. <https://doi.org/10.1103/PhysRevB.95.064423>
- Kelly, J., Barends, R., Fowler, A. G., Megrant, A., Jeffrey, E., White, T. C., ... Martinis, J. M. (2015). State preservation by repetitive error detection in a superconducting quantum circuit. *Nature*, 519(7541), 66–69. <https://doi.org/10.1038/nature14270>
- Kiktenko, E. O., Fedorov, A. K., Man'ko, O. V., & Man'ko, V. I. (2015a). Multilevel superconducting circuits as two-qubit systems: Operations, state preparation, and entropic inequalities. *Physical Review A*, 91(4), 042312. <https://doi.org/10.1103/PhysRevA.91.042312>
- Kiktenko, E. O., Fedorov, A. K., Strakhov, A. A., & Man'ko, V. I. (2015b). Single qudit realization of the Deutsch algorithm using superconducting many-level quantum circuits. *Physics Letters, Section A: General, Atomic and Solid State Physics*, 379(22–23), 1409–1413. <https://doi.org/10.1016/j.physleta.2015.03.023>
- Kim, D., Ibrahim, M. I., Foy, C., Trusheim, M. E., Han, R., & Englund, D. R. (2019). A CMOS-integrated quantum sensor based on nitrogen–vacancy centres. *Nature Electronics*, 2(7), 284–289. <https://doi.org/10.1038/s41928-019-0275-5>
- Kragoskow, J. G. C., Marbey, J., Buch, C. D., Nehrkorn, J., Ozerov, M., Piligkos, S., ... Chilton, N. F. (2022). Analysis of vibronic coupling in a 4f molecular magnet with FIRMS. *Nature Communications*, 13(1), 825. <https://doi.org/10.1038/s41467-022-28352-2>
- Kues, M., Reimer, C., Roztocki, P., Cortés, L. R., Sciara, S., Wetzel, B., ... Morandotti, R. (2017). On-chip generation of high-dimensional entangled quantum states and their coherent control. *Nature*, 546(7660), 622–626. <https://doi.org/10.1038/nature22986>
- Lawrie, B. J., Lett, P. D., Marino, A. M., & Pooser, R. C. (2019). Quantum Sensing with Squeezed Light. *ACS Photonics*, 6(6), 1307–1318. <https://doi.org/10.1021/acsp Photonics.9b00250>
- Lee-Wong, E., Xue, R., Ye, F., Kreisel, A., Van Der Sar, T., Yacoby, A., & Du, C. R. (2020). Nanoscale detection of magnon excitations with variable wavevectors through a quantum spin sensor. *Nano Letters*, 20(5), 3284–3290. <https://doi.org/10.1021/acs.nanolett.0c00085>

- Leuenberger, M. N., & Loss, D. (2001). Quantum computing in molecular magnets. *Nature*, 410(6830), 789–793. <https://doi.org/10.1038/35071024>
- Lloyd, S. (1993). A potentially realizable quantum computer. *Science*, 261(5128), 1569–1571. <https://doi.org/10.1126/science.261.5128.1569>
- Lockyer, S. J., Chiesa, A., Timco, G. A., McInnes, E. J. L., Bennett, T. S., Vitorica-Yrezabal, I. J., ... Winpenny, R. E. P. (2021). Targeting molecular quantum memory with embedded error correction. *Chemical Science*, 12(26), 9104–9113. <https://doi.org/10.1039/d1sc01506k>
- Lorusso, G., Troiani, F., Bellini, V., Ghirri, A., Candini, A., Carretta, S., ... Affronte, M. (2011). Spin entanglement in supramolecular systems. *Journal of Physics: Conference Series*, 303(1), 012033. <https://doi.org/10.1088/1742-6596/303/1/012033>
- Lovchinsky, I., Sushkov, A. O., Urbach, E., de Leon, N. P., Choi, S., De Greve, K., ... Lukin, M. D. (2016). Nuclear magnetic resonance detection and spectroscopy of single proteins using quantum logic. *Science*, 351(6275), 836–841. <https://doi.org/10.1126/science.1228022>
- Luis, F., Repollés, A., Martínez-Pérez, M. J., Aguilà, D., Roubeau, O., Zueco, D., ... Aromí, G. (2011). Molecular prototypes for spin-based CNOT and SWAP quantum gates. *Physical Review Letters*, 107(11), 117203. <https://doi.org/10.1103/PhysRevLett.107.117203>
- Luo, M., & Wang, X. (2014). Universal quantum computation with qudits. *Science China: Physics, Mechanics and Astronomy*, 57(9), 1712–1717. <https://doi.org/10.1007/s11433-014-5551-9>
- Macaluso, E., Rubín, M., Aguilà, D., Chiesa, A., Barrios, L. A., Martínez, J. I., ... Carretta, S. (2020). A heterometallic [LnLn' Ln] lanthanide complex as a qubit with embedded quantum error correction. *Chemical Science*, 11(38), 10337–10343. <https://doi.org/10.1039/D0SC03107K>
- Martínez-Pérez, M. J., Cardona-Serra, S., Schlegel, C., Moro, F., Alonso, P. J., Prima-García, H., ... Luis, F. (2012). Gd-based single-ion magnets with tunable magnetic anisotropy: Molecular design of spin qubits. *Physical Review Letters*, 108(24), 247213. <https://doi.org/10.1103/PhysRevLett.108.247213>
- Milburn, G. J. (2009). Photons as qubits. *Physica Scripta T*, T137, 014003. <https://doi.org/10.1088/0031-8949/2009/T137/014003>
- Mirzoyan, R., & Hadt, R. G. (2020). The dynamic ligand field of a molecular qubit: Decoherence through spin-phonon coupling. *Physical Chemistry Chemical Physics*, 22(20), 11249–11265. <https://doi.org/10.1039/d0cp00852d>
- Mohammadi, M., Niknafs, A., & Eshghi, M. (2011). Controlled gates for multi-level quantum computation. *Quantum Information Processing*, 10(2), 241–256. <https://doi.org/10.1007/s11128-010-0192-z>
- Molina-Jirón, C., Chellali, M. R., Kumar, C. N. S., Kübel, C., Velasco, L., Hahn, H., ... Ruben, M. (2019). Direct Conversion of CO<sub>2</sub> to Multi-Layer Graphene using Cu–Pd Alloys. *ChemSusChem*, 12(15), 3509–3514. <https://doi.org/10.1002/cssc.201901404>
- Montanaro, A. (2016). Quantum algorithms: An overview. *Npj Quantum Information*, 2(1), 15023. <https://doi.org/10.1038/npjqi.2015.23>
- Moreno-Pineda, E., Damjanović, M., Fuhr, O., Wernsdorfer, W., & Ruben, M. (2017). Nuclear Spin Isomers: Engineering a Et<sub>4</sub>N[DyPc<sub>2</sub>] Spin Qudit. *Angewandte Chemie - International Edition*, 56(33), 9915–9919. <https://doi.org/10.1002/anie.201706181>
- Moreno-Pineda, E., Godfrin, C., Balestro, F., Wernsdorfer, W., & Ruben, M. (2018). Molecular spin qudits for quantum algorithms. *Chemical Society Reviews*, 47(2), 501–513. <https://doi.org/10.1039/c5cs00933b>
- Moreno-Pineda, E., Klyatskaya, S., Du, P., Damjanović, M., Taran, G., Wernsdorfer, W., & Ruben, M. (2018). Observation of Cooperative Electronic Quantum Tunneling: Increasing Accessible Nuclear States in a Molecular Qudit. *Inorganic Chemistry*, 57(16), 9873–9879. <https://doi.org/10.1021/acs.inorgchem.8b00823>
- Moreno-Pineda, E., & Wernsdorfer, W. (2021). Measuring molecular magnets for quantum technologies. *Nature Reviews Physics*, 3(9), 645–659. <https://doi.org/10.1038/s42254-021-00340-3>
- Moreno Pineda, E., Komeda, T., Katoh, K., Yamashita, M., & Ruben, M. (2016). Surface confinement of TbPc<sub>2</sub>-SMMs: structural, electronic and magnetic properties. *Dalton Transactions*, 45(46), 18417–18433. <https://doi.org/10.1039/c6dt03298b>

- Morley, G. W. (2014). Chapter 3. Towards spintronic quantum technologies with dopants in silicon (pp. 62–76). <https://doi.org/10.1039/9781782620280-00062>
- Nakazawa, S., Nishida, S., Ise, T., Yoshino, T., Mori, N., Rahimi, R. D., ... Takui, T. (2012). A synthetic two-spin quantum bit: G-engineered exchange-coupled biradical designed for controlled-NOT gate operations. *Angewandte Chemie - International Edition*, 51(39), 9860–9864. <https://doi.org/10.1002/anie.201204489>
- Neeley, M., Ansmann, M., Bialczak, R. C., Hofheinz, M., Lucero, E., O’Connell, A. D., ... Martinis, J. M. (2009). Emulation of a quantum spin with a superconducting phase qudit. *Science*, 325(5941), 722–725. <https://doi.org/10.1126/science.1173440>
- Neves, L., Lima, G., Gómez, J. G. A., Monken, C. H., Saavedra, C., & Pádua, S. (2005). Generation of entangled states of qudits using twin photons. *Physical Review Letters*, 94(10), 100501. <https://doi.org/10.1103/PhysRevLett.94.100501>
- Nielsen, M. A., & Chuang, I. L. (2012). Quantum Computation and Quantum Information. Cambridge University Press, Cambridge Physics, Englad. Cambridge University Press. <https://doi.org/10.1017/CBO9780511976667>
- Nossa, J. F., Islam, M. F., Canali, C. M., & Pederson, M. R. (2013). Electric control of a {Fe<sub>4</sub>} single-molecule magnet in a single-electron transistor. *Physical Review B - Condensed Matter and Materials Physics*, 88(22), 224423. <https://doi.org/10.1103/PhysRevB.88.224423>
- Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., ... Firsov, A. A. (2004). Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306(5696), 666–669. <https://doi.org/10.1126/science.1102896>
- O’Leary, D. P., Brennen, G. K., & Bullock, S. S. (2006). Parallelism for quantum computation with qudits. *Physical Review A - Atomic, Molecular, and Optical Physics*, 74(3), 032334. <https://doi.org/10.1103/PhysRevA.74.032334>
- Ohshima, T., Satoh, T., Kraus, H., Astakhov, G. V., Dyakonov, V., & Baranov, P. G. (2018). Creation of silicon vacancy in silicon carbide by proton beam writing toward quantum sensing applications. *J. Phys. D: Appl. Phys.* 51(33). <https://doi.org/10.1088/1361-6463/aad0ec>
- Otterbach, J. S., Manenti, R., Alidoust, N., Bestwick, A., Block, M., Bloom, B., ... Rigetti, C. (2017). Unsupervised Machine Learning on a Hybrid Quantum Computer. *arXiv:1712.05771*. <https://doi.org/10.48550/arXiv.1712.05771>
- Panajotov, K. P., Arizaleta, M., Gomez, V., Koltys, K., Tabaka, A., Sciamanna, M., ... Thienpont, H. (2004). Semiconductor lasers for quantum sensing. In *Proceedings Quantum Sensing and Nanophotonic Devices*, 5359(360). <https://doi.org/10.1117/12.518317>
- Pedersen, K. S., Ariciu, A. M., McAdams, S., Weihe, H., Bendix, J., Tuna, F., & Piligkos, S. (2016). Toward molecular 4f single-ion magnet qubits. *Journal of the American Chemical Society*, 138(18), 5801–5804. <https://doi.org/10.1021/jacs.6b02702>
- Popov, A., Kiktenko, E., Fedorov, A., & Man’ko, V. I. (2016). Information Processing Using Three-Qubit and Qubit–Qutrit Encodings of Noncomposite Quantum Systems. *Journal of Russian Laser Research*, 37(6), 581–590. <https://doi.org/10.1007/s10946-016-9610-8>
- Radu, V., Price, J. C., Levett, S. J., Narayanasamy, K. K., Bateman- Price, T. D., Wilson, P. B., & Mather, M. L. (2020). Dynamic Quantum Sensing of Paramagnetic Species Using Nitrogen-Vacancy Centers in Diamond. *ACS Sensors*, 5(3), 703–710. <https://doi.org/10.1021/acssensors.9b01903>
- Ralph, T. C., Resch, K. J., & Gilchrist, A. (2007). Efficient Toffoli gates using qudits. *Physical Review A - Atomic, Molecular, and Optical Physics*, 75(2), 022313. <https://doi.org/10.1103/PhysRevA.75.022313>
- Richart, D., Fischer, Y., & Weinfurter, H. (2012). Experimental implementation of higher dimensional time-energy entanglement. *Applied Physics B: Lasers and Optics*, 106(3), 543–550. <https://doi.org/10.1007/s00340-011-4854-z>
- Rungta, P., Munro, W. J., Nemoto, K., Deuar, P., Milburn, G. J., & Caves, C. M. (2007). Qudit Entanglement. *Directions in Quantum Optics*, (1), 149–164. [https://doi.org/10.1007/3-540-40894-0\\_14](https://doi.org/10.1007/3-540-40894-0_14)

- Sangregorio, C., Ohm, T., Paulsen, C., Sessoli, R., & Gatteschi, D. (1997). Quantum Tunneling of the Magnetization in an Iron Cluster Nanomagnet. *Physical Review Letters*, 78(24), 4645–4648. <https://doi.org/10.1103/PhysRevLett.78.4645>
- Santanni, F., Albino, A., Atzori, M., Ranieri, D., Salvadori, E., Chiesa, M., ... Sessoli, R. (2021). Probing Vibrational Symmetry Effects and Nuclear Spin Economy Principles in Molecular Spin Qubits. *Inorg. Chem.*, 60(1), 140–151. <https://doi.org/10.1021/acs.inorgchem.0c02573>
- Schrödinger, E. (1926). Quantisierung als Eigenwertproblem. *Annalen Der Physik*, 385(13), 437–490. <https://doi.org/10.1002/andp.19263851302>
- Sessoli, R., Gatteschi, D., Caneschi, A., & Novak, M. A. (1993). Magnetic bistability in a metal-ion cluster. *Nature*, 365(6442), 141–143. <https://doi.org/10.1038/365141a0>
- Shi, F., Zhang, Q., Wang, P., Sun, H., Wang, J., Rong, X., ... Du, J. (2015). Single-protein spin resonance spectroscopy under ambient conditions. *Science*, 347(6226), 1135–1138. <https://www.science.org/doi/10.1126/science.aaa2253>
- Shiddiq, M., Komijani, D., Duan, Y., Gaita-Ariño, A., Coronado, E., & Hill, S. (2016). Enhancing coherence in molecular spin qubits via atomic clock transitions. *Nature*, 531(7594), 348–351. <https://doi.org/10.1038/nature16984>
- Shor, P. W. (1997). Polynomial-time algorithms for prime factorization and discrete logarithms on a quantum computer. *SIAM Journal on Computing*, 26(5), 1484–1509. <https://doi.org/10.1137/S0097539795293172>
- Stepanenko, D., Trif, M., & Loss, D. (2008). Quantum computing with molecular magnets. *Inorganica Chimica Acta*, 361(14–15), 3740–3745. <https://doi.org/10.1016/j.ica.2008.02.066>
- Sugisaki, K., Nakazawa, S., Toyota, K., Sato, K., Shiomi, D., & Takui, T. (2019). Quantum chemistry on quantum computers: Quantum simulations of the time evolution of wave functions under the S<sup>2</sup> operator and determination of the spin quantum number: S. *Phys. Chem. Chem. Phys.*, 21(28), 15356–15361. <https://doi.org/10.1039/c9cp02546d>
- Sun, Y., & Rogers, J. A. (2007). Inorganic semiconductors for flexible electronics. *Advanced Materials*, 19(15), 1897–1916. <https://doi.org/10.1002/adma.200602223>
- Tacchino, F., Chiesa, A., Sessoli, R., Tavernelli, I., & Carretta, S. (2021). A proposal for using molecular spin qubits as quantum simulators of light-matter interactions. *Journal of Materials Chemistry C*, 9(32), 10266–10275. <https://doi.org/10.1039/d1tc00851j>
- Taran, G., Bonet, E., & Wernsdorfer, W. (2019). The role of the quadrupolar interaction in the tunneling dynamics of lanthanide molecular magnets. *Journal of Applied Physics*, 125(14), 142903. <https://doi.org/10.1063/1.5079453>
- Tesi, L., Lucaccini, E., Cimatti, I., Perfetti, M., Mannini, M., Atzori, M., ... Sessoli, R. (2016). Quantum coherence in a processable vanadyl complex: New tools for the search of molecular spin qubits. *Chemical Science*, 7(3), 2074–2083. <https://doi.org/10.1039/c5sc04295j>
- Thiele, S., Vincent, R., Holzmann, M., Klyatskaya, S., Ruben, M., Balestro, F., & Wernsdorfer, W. (2013). Electrical readout of individual nuclear spin trajectories in a single-molecule magnet spin transistor. *Physical Review Letters*, 111(3), 037203.
- Thiele, Stefan, Balestro, F., Ballou, R., Klyatskaya, S., Ruben, M., & Wernsdorfer, W. (2014). Electrically driven nuclear spin resonance in single-molecule magnets. *Science*, 344(6188), 1135–1138. <https://doi.org/10.1126/science.1249802>
- Thomas, L., Lioni, F., Ballou, R., Gatteschi, D., Sessoli, R., & Barbara, B. (1996). Macroscopic quantum tunnelling of magnetization in a single crystal of nanomagnets. *Nature*, 383(6596), 145–147. <https://doi.org/10.1038/383145a0>
- Timco, G. A., Carretta, S., Troiani, F., Tuna, F., Pritchard, R. J., Muryn, C. A., ... Winpenny, R. E. P. (2009). Engineering the coupling between molecular spin qubits by coordination chemistry. *Nature Nanotechnology*, 4(3), 173–178. <https://doi.org/10.1038/nnano.2008.404>



- Troiani, F., Carretta, S., & Santini, P. (2013). Detection of entanglement between collective spins. *Physical Review B - Condensed Matter and Materials Physics*, 88(19), 195421. <https://doi.org/10.1103/PhysRevB.88.195421>
- Troiani, F., Ghirri, A., Affronte, M., Carretta, S., Santini, P., Amoretti, G., ... Winpenny, R. E. P. (2005). Molecular engineering of antiferromagnetic rings for quantum computation. *Physical Review Letters*, 94(20), 207208. <https://doi.org/10.1103/PhysRevLett.94.207208>
- Troiani, F., Ghirri, A., Paris, M. G. A., Bonizzoni, C., & Affronte, M. (2019). Towards quantum sensing with molecular spins. *Journal of Magnetism and Magnetic Materials*, 491, 165534. <https://doi.org/10.1016/j.jmmm.2019.165534>
- Urdampilleta, M., Klyatskaya, S., Cleuziou, J. P., Ruben, M., & Wernsdorfer, W. (2011). Supramolecular spin valves. *Nature Materials*, 10(7), 502–506. <https://doi.org/10.1038/nmat3050>
- Urdampilleta, M., Klyatskaya, S., Ruben, M., & Wernsdorfer, W. (2013). Landau-Zener tunneling of a single Tb<sup>3+</sup> magnetic moment allowing the electronic read-out of a nuclear spin. *Physical Review B*, 87(19), 195412. <https://doi.org/10.1103/PhysRevB.87.195412>
- Urdampilleta, M., Klyatskaya, S., Ruben, M., & Wernsdorfer, W. (2015). Magnetic interaction between a radical spin and a single- molecule magnet in a molecular spin-valve. *ACS Nano*, 9(4), 4458– 4464. <https://doi.org/10.1021/acs.nano.5b01056>
- Vincent, R., Klyatskaya, S., Ruben, M., Wernsdorfer, W., & Balestro, F. (2012). Electronic read-out of a single nuclear spin using a molecular spin transistor. *Nature*, 488(7411), 357–360. <https://doi.org/10.1038/nature11341>
- Wasielewski, M. R., Forbes, M. D. E., Frank, N. L., Kowalski, K., Scholes, G. D., Yuen-Zhou, J., ... Whaley, K. B. (2020). Exploiting chemistry and molecular systems for quantum information science. *Nature Reviews Chemistry*, 4(9), 490–504. <https://doi.org/10.1038/s41570-020-0200-5>
- Watson, T. F., Philips, S. G. J., Kawakami, E., Ward, D. R., Scarlino, P., Veldhorst, M., ... Vandersypen, L. M. K. (2018). A programmable two-qubit quantum processor in silicon. *Nature*, 555(7698), 633–637. <https://doi.org/10.1038/nature25766>
- Wedge, C. J., Timco, G. A., Spielberg, E. T., George, R. E., Tuna, F., Rigby, S., ... Ardavan, A. (2012). Chemical Engineering of Molecular Qubits. *Physical Review Letters*, 108(10), 107204. <https://doi.org/10.1103/PhysRevLett.108.107204>
- Wernsdorfer, W., Soler, M., Christou, G., & Hendrickson, D. N. (2002). Quantum phase interference (Berry phase) in single-molecule magnets of [Mn<sub>12</sub>]<sup>2-</sup>. *Journal of Applied Physics*, 91(10 I), 7164–7166. <https://doi.org/10.1063/1.1450788>
- Wiesendanger, R., G# ntherodt, H. J., G# ntherodt, G., Gambino, R. J., & Ruf, R. (1990). Observation of vacuum tunneling of spin-polarized electrons with the scanning tunneling microscope. *Physical Review Letters*, 65(2), 247–250. <https://doi.org/10.1103/PhysRevLett.65.247>
- Wiesendanger, Roland. (2009). Spin mapping at the nanoscale and atomic scale. *Reviews of Modern Physics*, 81(4), 1495–1550. <https://doi.org/10.1103/RevModPhys.81.1495>
- Willke, P., Bae, Y., Yang, K., Lado, J. L., Ferrón, A., Choi, T., ... Lutz, C. P. (2018). Hyperfine interaction of individual atoms on a surface. *Science*, 362(6412), 336–339. <https://doi.org/10.1126/science.aat7047>
- Willke, P., Paul, W., Natterer, F. D., Yang, K., Bae, Y., Choi, T., ... Lutz, C. P. (2018). Probing quantum coherence in single-atom electron spin resonance. *Science Advances*, 4(2), eaq1543. <https://doi.org/10.1126/sciadv.aaq1543>
- Willke, P., Singha, A., Zhang, X., Esat, T., Lutz, C. P., Heinrich, A. J., & Choi, T. (2019a). Tuning Single-Atom Electron Spin Resonance in a Vector Magnetic Field. *Nano Letters*, 19(11), 8201–8206. <https://doi.org/10.1021/acs.nanolett.9b03559>
- Willke, P., Yang, K., Bae, Y., Heinrich, A. J., & Lutz, C. P. (2019b). Magnetic resonance imaging of single atoms on a surface. *Nature Physics*, 15(10), 1005–1010. <https://doi.org/10.1038/s41567-019-0573-x>
- Xiang, Q., Cheng, B., & Yu, J. (2015). Graphene-Based Photocatalysts for Solar-Fuel Generation. *Angewandte Chemie - International Edition*, 54(39), 11350–11366. <https://doi.org/10.1002/anie.201411096>



- Yang, J., Wang, Y., Wang, Z., Rong, X., Duan, C. K., Su, J. H., & Du, J. (2012). Observing quantum oscillation of ground states in single molecular magnet. *Physical Review Letters*, 108(23), 230501. <https://doi.org/10.1103/PhysRevLett.108.230501>
- Yang, K., Bae, Y., Paul, W., Natterer, F. D., Willke, P., Lado, J. L., ... Lutz, C. P. (2017). Engineering the Eigenstates of Coupled Spin- 1/2 Atoms on a Surface. *Physical Review Letters*, 119(22), 227206. <https://doi.org/10.1103/PhysRevLett.119.227206>
- Yang, K., Paul, W., Phark, S. H., Willke, P., Bae, Y., Choi, T., ... Lutz, C. P. (2019). Coherent spin manipulation of individual atoms on a surface. *Science*, 366(6464), 509–512. <https://doi.org/10.1126/science.aay6779>
- Yu, C. J., Graham, M. J., Zadrozny, J. M., Niklas, J., Krzyaniak, M. D., Wasielewski, M. R., ... Freedman, D. E. (2016). Long Coherence Times in Nuclear Spin-Free Vanadyl Qubits. *Journal of the American Chemical Society*, 138(44), 14678–14685. <https://doi.org/10.1021/jacs.6b08467>
- Yu, C. J., Von Kugelgen, S., Laorenza, D. W., & Freedman, D. E. (2021). A Molecular Approach to Quantum Sensing. *ACS Central Science*, 7(5), 712–723. <https://doi.org/10.1021/acscentsci.0c00737>
- Zadrozny, J. M., Niklas, J., Poluektov, O. G., & Freedman, D. E. (2014). Multiple quantum coherences from hyperfine transitions in a vanadium(IV) complex. *Journal of the American Chemical Society*, 136(45), 15841–15844. <https://doi.org/10.1021/ja507846k>
- Zadrozny, J. M., Niklas, J., Poluektov, O. G., & Freedman, D. E. (2015). Millisecond coherence time in a tunable molecular electronic spin qubit. *ACS Central Science*, 1(9), 488–492. <https://doi.org/10.1021/acscentsci.5b00338>
- Zhang, Y., Zhang, L., & Zhou, C. (2013). Review of chemical vapor deposition of graphene and related applications. *Accounts of Chemical Research*, 46(10), 2329–2339. <https://doi.org/10.1021/ar300203n>