Computational Design of Magnetic Molecules and their Environment: From Quantum Chemistry to Machine Learning and Multi-Scale Simulations.

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Having served as playground for fundamental studies on the physics of d and f electrons for almost a century, magnetic molecules are today becoming increasingly important for technological applications, such as magnetic resonance, data storage, spintronics and quantum information. In all these, one requires the preservation and control of spins in time, an ability hampered by the interaction with the environment, namely with other spins, conduction electrons, molecular vibrations and electromagnetic fields. Thus, the design of a novel magnetic molecule with tailored properties is a formidable task, which does not only concern its electronic structures but also calls for a deep understanding of the interaction among all the degrees of freedom at play. This review describes how state-of-the-art *ab initio* computational methods, combined with data-driven approaches to materials modelling, can be integrated into a fully multi-scale strategy capable of defining design rules for molecular magnets.

The ability to understand and rationalise magnetism represents one of the earliest successes of quantum mechanics.[1,2] The initial interest was driven by the need to explain the magnetic order in inorganic solids, but the early '30s also witnessed the first evidence of magnetic phenomena in molecules.[3–5] Since then, molecular magnetism, namely the study of the magnetic interaction in molecules, either in solution, molecular-crystal or single-molecule form, has been continuously growing in popularity and now it encompasses a vast community of researchers across multiple disciplines. In general, a magnetic molecule is a metal-organic complex bearing a stable net spin moment, which originates either from a single magnetic ion, a transition metal or a rare earth, or from a collection of exchange-coupled ones (see Figure 1).[6,7] The many magnetic ions available, combined with the extreme flexibility of coordination chemistry, offer the possibility to synthesise molecules with an enormous range of geometries. X-ray diffraction and nuclear magnetic resonance provide extremely precise information about a molecule's structure, while electron paramagnetic resonance (EPR) accurately characterises its spin properties[8]. Thus, these experimental tools have allowed us to establish extremely detailed structure-to-property relations, in particular thanks to the fact that molecules are often mono-dispersed. As such, molecular magnetism represents one of the most rich and versatile playground where to study magnetism at its foundation and in its finest details.

Theory and modelling have played an important role in understanding molecular magnetism since the early days, and have constantly evolved as the field was moving forward. Initially, spin algebra and crystal-field-based computational methods were used to interpret EPR measurements, providing a direct link between the measured spin

response and microscopic spin models.[8] Subsequently, a significantly wider and diverse body of computational studies started to appear in the '90s, signaling a much tighter interplay between theory and experiments. This was in response to a major experimental breakthrough, namely the detection of low-temperature magnetic hysteresis in a single molecule, Mn_{12}.[9] Hysteresis is the hallmark of macroscopic magnetism, establishing the ability of a magnet to retain the magnetization direction for long times. This discovery suggested the possibility to use molecules for high-density magnetic recording and entered molecular magnetism in a new *design* phase, where the goalpost shifted from understanding the phenomena to engineering molecules with desired properties. The study of the blocking temperature, T_B, namely the temperature at which the magnetization have a relaxation time long enough to enable a desired application[10,11], revealed that the design criterion for magnetic recording with transition metal complexes is the coexistence of large crystal uni-axial magnetic anisotropy, namely a large zero-field splitting parameter D, and a large spin moment, S. This is because the total magnetic anisotropy energy is proportional to the product DS^2 (see Box 1). Theory was then needed to drive the synthetic effort and fully parameter-free *ab initio* methods became the essential tool. These, in particular, include density functional theory (DFT),[12,13] correlated wave-function (cWFN) methods[14] and various computational schemes for computing the magnetic anisotropy (see Box 2).

A key result from this phase of investigation is the discovery that the magnetic anisotropy, DS^2, of poly-nuclear molecules is almost independent of the ground state's value S, as D scales as $(1/S^2)$[16]. This pointed towards increasing the total number of metal ions in the cluster and their single-ion anisotropy instead of promoting ferromagnetic coupling over ferri-magnetic among them. However, the strategy of high nuclearity clusters also comes with its own severe challenges, such as the con-
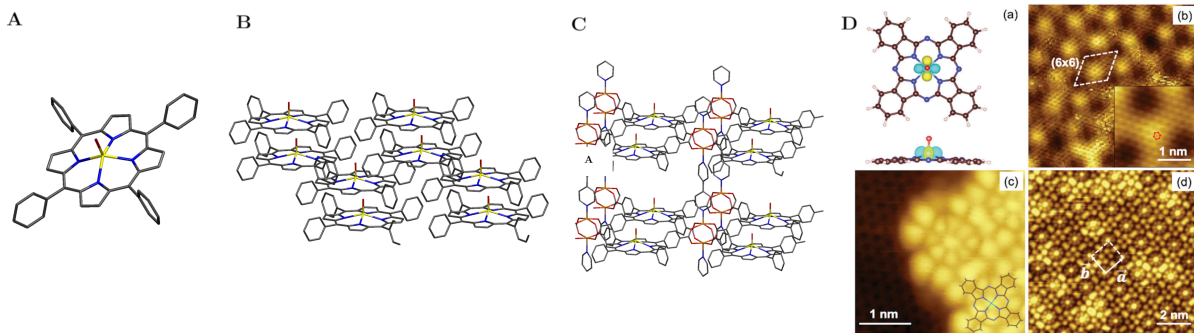
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FIG. 1. **Example of magnetic molecules and their solid-state environments.** The Vanadyl Phtalocyanine (VOPc) or Porphirine (VOP) groups can be found in several crystalline environments. Panel A) displays the molecular structure of Vanadyl tetraphenylporphyrinate (VOTPP), while panel B) reports its bulk crystal structure. Panel C) shows the same molecular core functionalized with Zn_2-4,4′-bipyridyl to give a 3d-metal-organic-framework. Panel D) presents the molecular structure of VOPc with the unpaired electron d orbital [sub-panel D(a)], and the STM imaging of an ordered monolayer of VOPc on Graphene/SiC(0001) at different zooms [sub-panels D(b)-D(d)]. Reproduced from Ref.[15] with permission from the Royal Society of Chemistry.

trol of the cluster symmetry to prevent cancellation effects coming from non-collinear arrangement of the ion's easy axis.[17] As a result, molecules comprising a single magnetic ion, but extremely large anisotropy, seems to offer the best starting point towards room-temperature single-molecule magnets, instigating research on single-ion rare-earth-based compounds. Such change in design rules did not require a change in the theoretical approach, which remained grounded in electronic structure theory.

More recently, however, strong experimental evidence has emerged suggesting that the static electronic structure alone cannot account for the spin relaxation in single-molecule magnets. Such evidence calls for a new update of the designing rules. In particular, it was shown that in many instances the spin-lattice relaxation times (see Box 3) are much shorter than what expected from the magnetic anisotropy.[18–21] This means that some energy scale, other than the one set by the anisotropy, is relevant for the relaxation and that a thorough understanding of the actual spin dynamics is needed. A completely new range of theoretical tools is then required and new theoretical challenges emerge. In particular, one now has to model, at the microscopic level, how spins exchange energy and angular momentum with other elementary degrees of freedom, namely other spins (either electronic or nuclear), phonons, photons and free electrons.

Crucially, the same level of microscopic understanding is also necessary to determine whether magnetic molecules can be employed in quantum technologies, which are rapidly becoming the main application space for molecular magnetism[22–26]. In these, the need for room-temperature macroscopic relaxation times is replaced by that of having long low-temperature coherence ones.[27] However, this is not the only design rule. By adapting DiVincenzo's general criteria for the physical implementation of quantum computation,[28] molecular spins now 1) should have long coherence times, 2)

should be able to interact among each other in a scalable way, 3) should be singularly addressable, and their states 4) should be easy to initialize and 5) to manipulate. It is then clear that the ultimate task for theory is not only to understand how spins interact with their environment, but also how such interaction can be controlled and tuned. This is the realm of electronic structure theory for quantum open systems,[29] which can be formulated rigorously, but for real materials, at present, can be implemented only in the form of multi-scale approaches combining complementary numerical techniques.

The main scope of this review is to demonstrate how modern electronic structure theory can tackle such complex, multiscale problem. This is a formidable theoretical task requiring the microscopic description of all the relevant interactions for a time-dependent problem evolving over relatively long times and involving up to several thousands atoms. Furthermore, the theory should ideally have enough throughput to allow systematic design. With the main concepts in molecular magnetism, electronic structure methods, and spin relaxation time-scales introduced in Box 1-3, we will start this review by introducing the main philosophy behind the multiscale approach. We will highlight the benefits and the limitations of the methods working at different scales and how they interlink among each other. Then, we will pass through the lens the various interactions of the spins with the environment, namely the crystal field, spin-spin, spin-lattice and spin-free-electron. Finally, we will present an outlook on how the advent of machine-learning and artificial-intelligence methods can be used to match any remaining throughput gap and allow one to perform efficient molecular design.
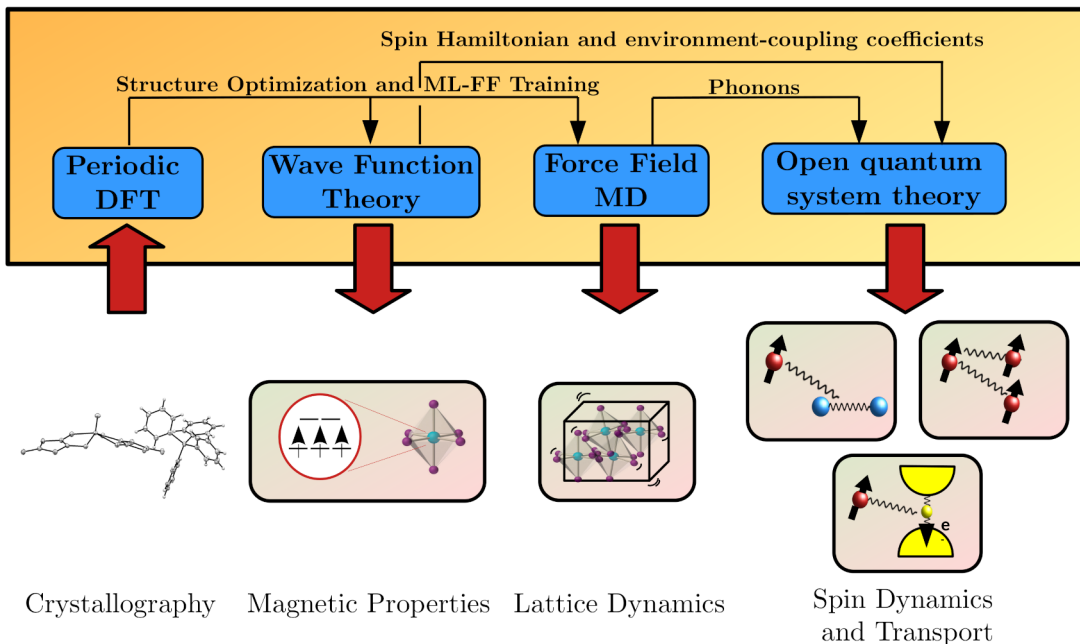
FIG. 2. **Multiscale computational modelling of magnetic molecules.** The crystallographic coordinates are at the start of the computational pipeline. After the atomic positions and the lattice parameters have been optimized with DFT, cWFN theory can be use to predict static magnetic properties and spin-phonon coupling coefficients. At the same time, DFT can be employed to parametrize machine-learning force fields to run molecular dynamics and phonons calculations. Finally, all these ingredients flow into the *ab initio* theory for open quantum system, leading to predictions of time-dependent properties.

FIRST-PRINCIPLES, MULTI-SCALE MODELLING AND MACHINE LEARNING

The computational design of magnetic molecules with optimal properties for specific applications, either as single-molecule magnets or in quantum technologies, is a multifaceted challenge, spanning across both time and length scales. On the one hand, typical relaxation times for molecules of interest vary from μs to s over a temperature range between a few K and room temperature (see Box 3). On the other hand, single molecules may be as small as a handful of atoms, most typically in the 30-300 range, but usually they pack in crystal structures with unit cells containing multiple molecules. Alternatively, they may be deposited on surfaces in either a single molecule form or in planar regular arrangements so that the typical simulation cells contain a few hundreds atoms. As an example, Fig. 1 illustrates prototypical porphyrin and phtalocyanin metal complexes, which have been studied in many different phases because of their interesting and versatile magnetic and structural properties[30–32]. Given the complexity of the problem, it is clear that a single electronic structure theory method alone cannot predict the electronic and magnetic properties of molecules in realistic thermodynamic conditions, and at the same time accurately model how the magnetic degrees of freedom evolve in time under the effect of the environment and external stimuli.

The only practical computational strategy is then a multi-scale approach, where a hierarchy of methods, specifically tailored to address the different time/length scales of the problem, are combined together.[33]

In general, small length and short time scales are described by accurate, but computational demanding, electronic structure methods. These are used to parametrize the models used for a coarse-grained description at longer and larger scales. Only a limited number of information is transferred from one stage to the next, a task achieved by integrating out those degrees of freedom that do not need to be treated explicitly and for which a statistical description is appropriate. Most importantly, the accuracy of the information transferred should be high enough not to require adjustments from experiments. In practice, the modelling of the entire spin dynamics in magnetic molecules requires a number of steps: 1) the determination of the magnetic properties resulting from the electronic structure, 2) the determination of realistic molecular geometries, 3) the description of thermodynamical effects, such as temperature, pressure, and disorder, 4) the evolution of the spin population and its coherence under *external* dynamical factors, such as external fields, lattice vibrations and electric currents. Figure 2 schematically represents how these steps are interconnected.

Electronic Structure. The natural starting point for the first step is the description of the electronic and magnetic structure of the molecules in their gas-phase. In most situations, the molecule geometry is experimentally known from X-ray diffraction and available either in databases[34] or directly from the relevant literature. As the size of the typical calculation remains limited, very accurate quantum-chemistry methods, based on multi-reference wave-function theory, are feasible. In particular, complete active space self-consistent field (CASSCF)[14] combined with second-order perturbation theory (NEVPT2 or CASPT2)[35] represents the workhorse electronic structure approach for transition-metal and lanthanide single-ion compounds.[36] ORCA[37] and Molcas[38] are the *to-go* codes as they combine flexible cWFN engines and dedicated post-processing tools for the extraction of spin Hamiltonian parameters. Unfortunately, the practical capability range of CASSCF+NEVPT2/CASPT2 is limited to systems with about 100 atoms (depending on computational resources), which usually is not enough for molecular crystals and molecules on surfaces. This, of course, becomes even more problematic if the calculations need to be performed multiple times, for instance in a geometry relaxation. At this length scale, wave-function methods need to be replaced by DFT[12], whose linear-scale numerical implementations are now available[39–45] and routinely used to tackle systems with several thousands atoms.[46]. At this level forces are readily computed, giving access to molecule relaxation and vibrational spectra. In general, there is a multitude of electronic structure codes implementing different methodologies and care is needed to select the optimal one for a specific task[47].

Structural Optimization. DFT, in particular when used with lightweight approximations of the exchange-correlation energy (e.g. local-density or generalised-gradient), can accurately describe molecular geometries, but at the same time it struggles with the electronic structure of the localised d and f electrons. Among other reasons, this is mainly due to the self-interaction error,[48] which can be partially removed by higher-level approximations, such as hybrid functionals.[49–51] However, for magnetic molecules the choice of functional may not be trivial in the absence of experimental information, so that blind predictions become difficult to make.[52,53] One can then take an hybrid approach, where DFT is used to compute the structure and its perturbation due to the environment, and then perform accurate quantum-chemistry calculations for the magnetic properties at the DFT-relaxed geometries. When the electronic structure of the molecule itself is affected by the presence of the environment beyond the indirect effect of steric hindrance, as in the case of charge-transfer, or when the orbitals of the environments are strongly admixed with the molecular ones, quantum-chemistry methods can still be applied within the framework of embedded-cluster approaches.[54,55] In these, the atoms close to the magnetic molecule are treated explicitly with electronic structure methods, whilst distant atoms are modelled as electrostatic charges.

Statistical Sampling. The third step in our modelling pipeline, namely the description of realistic thermodynamical conditions (structural disorder, liquid states, frozen solutions, surface-assembled systems, finite-temperature), requires sampling many conformations of the molecule and its environment. Configurations are generally drawn from a canonical (NVT) or isothermal-isobaric (NPT) distribution by mean of sampling strategies based on molecular dynamics or Monte Carlo schemes. DFT can still be used for these calculations but at a generally large computational cost and only for small system sizes (a few hundred atoms) and short time scales (a few pico-seconds). A better strategy requires a further significant multi-scale step through the introduction of force fields,[56] namely parametric functions designed to reproduce the real *ab initio* potential energy surface needed for molecular-dynamics simulations.

As the electronic degrees of freedom are integrated out and replaced by inter-atomic potentials, the computational efficiency makes a gigantic leap forward. In fact, eliminated the explicit treatment of the electrons, it is possible to compute energy and forces of systems containing from several thousands to millions atoms with relatively little effort[57]. This allows one to exhaustively sample the conformational space at the desired thermodynamic conditions. The challenge of connecting this step with the previous two rests on the generation of accurate force fields for the system of interest. Until recently, the philosophy behind the construction of force fields was to parametrize the different interactions by maintaining a physical meaning of the various contributions to the total energy, e.g. by assuming a harmonic potential for each chemical bond or angle bending. The accuracy of such first-generation force fields remains relatively modest, unless their use is restricted to particular classes of chemical bonds as, for instance, to organic molecules.[58,59]

The application of machine-learning schemes to this problem has completely revolutionized the field and paved the way to the quantum-accurate and efficient description of coordination compounds and their molecular dynamics (see Box 4).[60] In these, the atomic structure of a compound is expanded over a set of translational and rotational invariant descriptors,[61,62] and energy models are constructed through various machine-learning schemes, including linear regression,[63] kernel methods[64] and neural networks.[61,65] Machine-learning force fields have the perfect attributes to be included into a multi-scale pipeline, since they can be automatically generated starting from a number of sample DFT calculations and their accuracy can be arbitrarily converged by increasing the size of the training data. Most importantly, machine-learning force fields are agnostic to the specific chemical nature of the system[66,67] and are flexible enough to adapt to the potential energy sur-

face of transition metals, including spin-crossover compounds, reactive species, and systems presenting Jahn-Teller distortion[67]. This level of accuracy is unprecedented in the force-field description of coordination and magnetic compounds. Furthermore, the same approach can be extended to quantities different from the energy, such as molecular anisotropy.[68]

Spin Dynamics. The theoretical tools outlined so far cover the first three steps of a magnetic-molecule design strategy, as they establish how the structure and the external conditions affect the ground state. This machinery allows one to engineer compounds with specific equilibrium properties. However, a complete design strategy also requires the determination of those magnetic transient properties of central importance to technological applications, namely spin-spin and spin-lattice relaxation times, and spin currents. These all require the study of the evolution of the electronic structure of a molecule in time. Real-time *ab initio* methods, rooted in either multi-configurational wave-function theory or DFT, are in principles available[69] and some of these methods have been used to understand the ultra-fast demagnetization of clusters[70–72] and solids.[73,74] However, time-dependent electronic structure approaches remain limited by the small size of the system that can be realistically investigated, a few atoms, and by the duration of the real-time simulations. The latter rarely exceed hundred femtoseconds, and remains far away from the timescales relevant for molecular magnetism (see Box 3).

Hence, in order to capture the non-equilibrium spin physics taking place in such open systems, the theory requires a higher level of coarse-grained description. This is obtained through effective Hamiltonian operators (see Box 1).[7] Somehow similarly to force field representing a potential energy surface, an effective Hamiltonian is a parametric operator based on a restricted number of quantum variables associated to the total electronic and nuclear Hamiltonian. The spin Hamiltonian, $\hat{H}(\vec{\mathbf{S}})$, is part of this class of operators, as it describes a low-energy manifold of electronic states and it is only a function of the ground-state effective spin operator, $\vec{\mathbf{S}}$. The spin Hamiltonian, in fact, represents the basis for the treatment of non-equilibrium spin properties. The theory is then constructed by introducing Hamiltonian terms, $\hat{H}(\boldsymbol{\sigma}_\alpha)$, describing other relevant degrees of freedom, $\boldsymbol{\sigma}_\alpha$ (phonons, nuclear spins, free electrons, etc.), and their interaction with the spin, $\hat{H}_{\text{int}}(\vec{\mathbf{S}}, \boldsymbol{\sigma}_\alpha)$. Thus, the entire system (spin+environment) is described by a complete Hamiltonian of a generic form,

$$\hat{H} = \hat{H}(\vec{\mathbf{S}}) + \sum_\alpha \hat{H}(\boldsymbol{\sigma}_\alpha) + \sum_\alpha \hat{H}_{\text{int}}(\vec{\mathbf{S}}, \boldsymbol{\sigma}_\alpha). \quad (1)$$

As it stands, Eq. (1) cannot be solved, since it represents a many-body problem comprising infinite degrees of freedom. However, since the typical spin-environment interactions are weak, different flavour of perturbation theory can often be applied, resulting in a spin dynamics dictated by the Redfield equation[75] or their possible

extensions.[29] Furthermore, the spin dynamics in magnetic molecules usually takes place at a timescale significantly longer than those needed to thermalize the other degrees of freedom, which then can be treated as an equilibrium thermal bath. Exceptions include the phonon-bottleneck effects,[76] namely situations in which the phonon-lifetime of some modes is comparable with the spin-dynamics time scale.

In any case, the parameters of the effective spin Hamiltonian can be determined by requiring that its eigenvalues and eigenvectors match the relevant subset of eigenstates obtained from *ab initio* calculations, and so is the case for the others degrees of freedom.[77] As a consequence, one can derive a fully *ab initio* description of the dynamical problem, where no experimental data are needed, except for a general knowledge of the chemical composition and structure of the compound of interest. This means that the theoretical study of magnetic molecules is effectively a multi-scale *ab inito* approach, able to tackle every aspect, going from the details of electronic correlation to the quantum evolution of a spin entangled with its environment. In the next sections we will detail the success and the challenges of such approach, proceeding by singling out the various interactions of the spins with the other degrees of freedom.

SPIN-ENVIRONMENT INTERACTIONS UNDER THE LENS OF COMPUTER SIMULATIONS

Single-ion magnetic properties

The interplay between spin-orbit coupling, electron-electron interactions and the crystal field experienced by the d/f electrons, is at the origin of molecular magnetic properties. The design of a compound thus requires the careful choice of the ions, their oxidation state and, most importantly, their chemical coordination. The possibility to predict magnetic properties from the knowledge of the molecular structure plays a central role in molecular magnetism as it allows one to rationalize and interpret experimental observations. In the first part of this section we will review the most important *ab initio* methods for this task with an outlook to future directions. However, there is more to the prediction of accurate molecular magnetic properties than supporting experimental investigations. Indeed, a reliable electronic structure method also enables the exploration of new molecular prototypes without the need to synthesize them in advance and to systematically investigate new chemical scenarios. In the second part of this section we will review some of the successes of this strategy and show how electronic structure methods have already suggested new synthetic routes towards slow relaxing magnetic molecules.

Early attempts at computing the single-ion anisotropy tensor of transition metals, **D**, saw at the center stage DFT and cWFN-based perturbative treatments of the

spin-orbit coupling.[78–82] Important lessons on the role of the coordination environment and the symmetry were learnt, revealing the difficulty of aligning different single-ion tensors into a unique effective giant spin with large anisotropy (the $D \propto 1/S^2$ problem mentioned before).[17,83] Such result focused the field on the design of single-ion anisotropy rather than on increasing the clusters nuclearity. These early approaches proved to be quite accurate, but only as long as the underlying perturbative regime holds its validity. The condition is fulfilled by coordination compounds with an orbitally non-degenerate ground state, such as Fe^{3+} or Mn^{4+} in an octahedral crystal field[84,85]. This limit was soon reached in the context of single-molecule magnets, where ions with a strong spin-orbit coupling interaction were been deliberately synthesized in order to slow down spin relaxation[86–88].

cWNF methods usually outperform DFT[89–92], and in the quest for large single-ion anisotropy, DFT eventually gave in to multi-reference methods. In the realm of cWFN, perturbative approaches could be successfully substituted by a more general scheme based on a direct mapping between the low-lying electronic states describing the magnetic manifold and the spin Hamiltonian itself.[93] In a nutshell, one chooses a spin Hamiltonian, whose terms are selected based on physical intuition, and then tries to fit the model parameters to match the eigenstates and eigenvalues of the electronic Hamiltonian. The accuracy of cWFN methods stems from including all the relevant electron excitations into a variational wave function with the correct spin symmetry. Although this offers a systematic approach to converge results to an arbitrary level of accuracy, it rapidly leads to numerically intractable problems. Several computational schemes have then been devised to make the problem solvable. They all represent a different rule of thumb to guess *a priori* what subspace of orbitals and electrons is going to contribute to the multi-determinant wave-function of the ground and low-lying electronic states. CASSCF is among the most used method to describe the electronic structure of magnetic molecules thanks to the localized nature of d and f electrons and their little mixing with ligands' orbitals. In its simpler implementation only electronic excitations involving d/f electrons in d/f-like orbitals are included. Already at this level of approximation, single-ion magnetic properties are semi-quantitatively reproduced, especially for those ions with a low level of covalency.[36,94]

For most cases, the inclusion of multi-reference perturbation theory corrections, such as NEVPT2[35] or CASPT2[95], over a CASSCF simulation, is enough to quantitatively predict single-ion magnetic properties. Additionally, one can include in the CASSCF simulations some orbitals belonging to the ligands or a second shell of d/f orbitals to provide more flexibility to the wave-function[96]. This method proved to be extremely efficient and very versatile, and it now represents the workhorse for the prediction of single-ion spin Hamil-

tonian terms for any strength of spin-orbit interaction. This includes the case of magnetic molecules containing lanthanide ions, where un-quenched angular momentum and strong spin-orbit coupling lead to zero-field-splitting of the M_J levels of thousands of cm^{-1}. In comparison, the size of the zero-field splitting in coordination compounds, where the perturbative approaches are still valid, is of the order of one cm^{-1} or fractions. In contrast, the simulation of lanthanides (Ln), or in general systems with large spin-orbit coupling, with DFT is still a challenge. Although it is possible to include spin-orbit coupling beyond perturbation theory, DFT seems to fail in capturing the full effect of this interaction on the magnetic anisotropy.[97–99] This issue can be traced back to the single-determinant nature of DFT. Indeed, a large zero-field-splitting due to spin-orbit coupling is invariably associated to an orbitally degenerate, or quasi-degenerate, electronic ground state. The electronic structure of such states is multi-determinant in nature and available exchange-correlation functionals are not able to capture the electronic-correlation effects.

CASSCF-based methods have been widely used to both interpret experimental observations as well as to suggest new synthetic strategies. Following seminal synthetic breakthroughs[87,88], early applications of these methods to transition metal coordination compounds made it possible to individuate quasi-degeneracy electronic ground states as key to realize ions with large single-ion magnetic anisotropy[83,100]. For instance, these insights contributed to the design of coordination compounds of Fe^{2+}[19,101], Fe^{1+}[102] and Co^{2+}[103] elements with bulky or rigid ligands, where Jahn-Teller distortions are largely suppressed and a degenerate ground state was achieved. These compounds holds the record magnetic anisotropy barrier for single-ion transition metal complexes and their design was strongly supported by electronic structure simulations.

The design of lanthanides-based magnetic molecules has followed a similar trajectory. The realization that single-ion Ln coordination complexes could support extraordinarily large magnetic anisotropy[86] spurred a large body of theoretical studies. The work based on electrostatic models from Rinehart et al. provided the first conceptual framework for understanding how ligand-field symmetry affects the magnetic anisotropy of Ln ions.[104] In a nutshell, the states with maximum and minimum magnetic moment z-component, M_j, in Ln ions are often associated to an electronic density of ellipsoid shape with opposite aspect-ratio, namely prolate against oblate. Ligand field symmetry can then be exploited to split the energy with different M_j value. For instance, the $M_j = 15/2$ state of Dy^{3+} ions possesses an oblate electron distribution, while the state with $M_j = 1/2$ have a prolate symmetry. Therefore, an axial ligand field will strongly stabilize the energy of the former with respect to the latter, leading to a large magnetic anisotropy. *Ab initio* studies quickly followed, providing a more robust estimation of anisotropy barriers and helping in identify-

ing key relations between structural symmetries and slow magnetic relaxation.[105–109]. A strong interplay between electronic structure methods and synthesis continue to this day, with many successful stories that includes the design of new coordination geometries[110–112] and the elucidation of electrostatic and covalent contributions to the crystal field[113–115], just to name a few examples.

Although modifying the first coordination shell of an ion is the most effective strategy to the modulation of its magnetic properties, other strategies can be exploited. For instance, it is also possible to act on the molecular structure by modifying its chemical environment, such as depositing the molecule on a substrate, or by applying external pressure[116,117]. *Ab initio* molecular dynamics simulations have been used to tackle the challenge of understanding molecule-surface interactions and their role on the magnetism.[118–122]. For instance, *ab initio* molecular dynamics was used to unravel the presence of structural disorder due to multiple absorption minima,[120] an effect verified experimentally only years later thanks to technical advances in surface characterization.[123]

As mentioned before when discussing the multi-scale strategy, once an accurate parameterization of the system's potential energy surface is available, a significant boost in computational throughput makes it possible to sample extended time- and length-scales. Early attempts to generating a force field for single-molecule magnets was carried out to simulate the dynamics of the prototypical a tetra-nuclear Iron cluster on Au(111) and Terbium double-decker on Graphite.[118,124] Such studies paved the way to understanding the complexity of self-assembled monolayers and the impact of 2D molecular packing on the molecular anisotropy.[125] With the advent of quantum-accurate machine-learning force fields, it is natural to expect that the range of applicability of molecular dynamics will be significantly extended, opening up the possibility of routinely simulate adsorbed molecules, glasses and liquid solutions.

Spin-Spin Interactions

Spin-spin interactions play different roles in molecular magnetism. On the one hand, they can be used to strongly couple different magnetic units, thus creating ground states with large spin values. This has the aim to increase the robustness of spin relaxation time and coherence with respect to temperature, fields fluctuations and quantum tunneling of the magnetization (QTM). On the other hand, uncontrolled spin-spin interactions, as those mediated by long-range dipole fields between the molecular spins, or between the molecular and the various nuclear spins, can lead to fast spin diffusion and decoherence. In both cases, computational methods can play a decisive role in the optimization of these interactions, by shedding light on their origin, so that new synthetic solutions can be designed.

The prediction of the scalar exchange coupling con-

stants, J, of the Heisenberg Hamiltonian for multi-ion clusters of transition metals has been among the first attempts at quantifying spin-spin interactions. Both strategies based on molecular orbitals (Hartree-Fock and DFT) and cWFN have been largely explored. Once the the solutions of a single-determinant method, such as DFT or Hartree-Fock, are correctly interpreted as the eigenstates of the single-ion $\hat{S}_z$ operators,[126,127] namely broken-symmetry solutions, it is possible to perform a direct mapping between the Heisenberg Hamiltonian and the energy difference of states with local spins aligned in different directions.[128] Interestingly, the same approach can be used together with coupled-cluster solutions.[129] As often the case with DFT, the choice of the functional is key to achieve results in good agreement with experiments, with hybrid functionals usually representing the safest choice. Hence, the non-demanding nature of these calculations and the relative-good accuracy of standard hybrid functionals,[85,130] makes the DFT approach among the most popular for the calculation of the exchange coupling parameters.

The multi-reference nature of cWFN theory makes it the natural formalism for studying the exchange coupling in magnetic molecules beyond DFT. Obtaining quantitative predictions is, however, a much harder challenge than that encountered when computing single-ion properties, such as the g-tensor and the zero-field splitting. Firstly, having multiple metallic centers corresponds to having a large minimal active space. Furthermore, the participation of the ligands orbitals to the exchange mechanism may require a correct treatment also of their electronic correlation. A possible solution to this problem consists in applying either perturbative methods, such as CASPT2 and NEVPT2, or multi-reference configuration interaction schemes on top of the CASSCF solutions. Examples of this family include multi-reference single and double configuration interaction and difference-dedicated configuration interaction methods.[131] Perturbative strategies are often found to be not accurate enough, while multi-reference configuration-interaction approaches become numerically prohibitive very rapidly with the number of excitations considered.[132] Alternative approaches rely on systematically extending the active space to include ligands contributions. This is made possible by the use of adaptive methods, which iteratively select the relevant excitations among the many spanned by the active space.[133–135] For instance, density-matrix renormalization group (DMRG) shows systematic convergence, although a fully quantitative agreement is often precluded by the computational overheads.[136] The development of methods that combine the strengths of cWFN with DFT are a promising area of recent development. For instance, multi-configurational pair-density functional theory[137] (MCPDFT) augments a DFT description of the dynamical correlations with multi-configurational wave functions and has been shown to predict the scalar exchange coupling of Cr^{+3} dimers at an unprecedented level of accuracy.[138]

More recently, there has been an interest shift from the study of the exchange in pure-$3d$ compounds[139,140] to that among more exotic ions and topologies. These include any combination of organic radicals, and d/f ions[141–143]. In an attempt to combine large single-ion anisotropies proper of $4f$ elements, it has been shown that the creation of low-energy exchange spin states can lead to fast spin-phonon relaxation[144] and that strong exchange coupling and collinearity between single-ion anisotropies is therefore necessary to achieve slow relaxation and zero-field QTM quench. The use of radical bridges among lanthanides has become one of the main synthetic strategies to this goal.[145] Indeed, the very contracted $4f$ shell does not in general allow for efficient super-exchange, thus leading to very small exchange coupling constants. However, when a radical is used to mediate the interaction, large exchange coupling constants and quenching of zero-field QTM have been obtained[146,147]. Similarly, the use of diffuse $3d/4d$ orbitals to mediate strong exchange coupling among Lanthanide ions has been successfully used to mitigate QTM and increase relaxation time at low temperature.[148–153] Another very successful chemical strategy is to create exchange interactions by direct metal-metal orbitals' overlap[154]. This has been first investigated in endohedral fullerene systems[155,156], where multiple ions are caged inside the carbon structure and kept at a close distance, resulting in large exchange coupling constants[157]. The same principle has also been realized in canonical coordination compounds[158,159], where two Ln ions form a metal-metal bond that mediates a very large exchange coupling between the $4f$ electrons. This strategy has been proved particularly successful in the design of the mixed-valence linear Ln dimers [(Cp^{iPr5})$_2$Ln$_2$I$_3$, with Ln=Tb,Dy and Cp^{iPr5}=pentaisopropylcyclopentadienyl], which show record-breaking magnetic anisotropy and coercive field[160]. State-of-the-art *ab initio* methods have been used to understand the electronic structure and magnetism of (Cp^{iPr5})$_2$Ln$_2$I$_3$ dimers. CASSCF and MCPDFT have been used to provide insights into the Ln ions' $4f/5d$ orbital interaction, revealing the formation of a delocalized σ bonding orbital due to the overlap of the $5d_{z^2}$ states from each metal ion. Such a picture is corroborated by comparing experimental and theoretical electronic excitations at the level of CASSCF and TD-DFT. Furthermore, CASSCF, DMRG, MCPDFT and DFT have all been used to rationalise the exchange mechanism, showing that the direct exchange between $4f$ and $5d$ electrons is responsible for the very large ferromagnetic exchange coupling constant ($J \sim 390$) between the ions and the unpaired delocalized electron in the σ orbital.[160] This study summarises common theoretical approaches to deal with the increasing complexity of polynuclear systems, where CASSCF-based methods are used for the determination of single ion states, while exchange parameters can be computed in different ways, including the use of CASSCF-based techniques[160–162],

DFT[149,154,163], and hybrid schemes involving fitting to experimental data[164].

In conclusion, despite the tremendous advancements of both cWFN and DFT, a universally robust and efficient approach to the prediction of the exchange coupling in polynuclear coordination compounds is still missing, and further methodological development and benchmarking are needed. Until then, both cWFN and DFT methods can be used, although with some care, to unveil how the exchange coupling arises from the electronic structure, including effects such as anisotropic exchange[165] and Dzyaloshinskii-Moriya interactions[166].

So far, we have discussed spin-spin interactions as a mean to rationally link different magnetic units in creating large nuclearity clusters or even extended systems. Namely, we have discussed exchange interaction mediated by the chemical bond. However, through-space dipolar spin-spin interactions also play a role in molecular magnetism, being at the origin of spin relaxation and decoherence. The relevant mechanism is known as spin diffusion and involves the exchange of energy and angular momentum among different spins without any intermediate quasi-particle, such as lattice vibrations. This is a T-independent mechanism that, away from severe magnetic dilutions, always limits spin coherence. Predicting coherent spin dynamics is an enormous computational challenge that partially mirrors the problem of electronic correlation in quantum chemistry: the entire Hilbert space required to describe exactly the system is virtually infinite and space-reduction techniques are needed to make the simulations feasible. Fortunately, spin systems often only explore a very small portion of the entire Hilbert space (they access only low-lying excitations or maintain a low degree of entanglement). This allows us, at least in principle, to reduce the complexity of the problem, and several schemes have been designed to achieve this purpose.

In general, when the problem consists of a central spin surrounded by a spin bath, the effect of small groups of spins can be considered separately, thus avoiding an exponential growth of the Hilbert-space dimension. These approaches are collectively called cluster methods.[167,168] Adopting a similar philosophy, Liouville[169] or Hilbert[170] space truncation techniques are often used, if the relevant set of states is known *a priori*. This condition is often fulfilled for low-T dynamics, where Lanczos[171] and Krylov schemes[172,173] can also be employed. Some of these strategies have been used to provide detailed information about the role of nuclear spin flip-flop transitions driving electronic spin relaxation,[174] the role of magnetic dilution over spin coherence[170,175] and diffusion-barrier effects.[176] DMRG-based methods are largely employed for similar purposes by the community working on quantum thermodynamics and many-body physics, with a good success for low-dimensional systems.[177] Little work, however, exists for magnetic molecules. The limitation of all these methods is set by the ability to identify the relevant part of the Hilbert space and to represent

it in a compact mathematical form. Noteworthy, machine learning has been shown to provide an excellent way around this problem and, when combined with quantum Monte Carlo, it can provide virtually exact simulations of many-body systems.[178] Unfortunately, to date the interplay between the many-body physics and the molecular magnetism communities remains limited, but we expect that strong synergy may develop in a near future.

Spin-Lattice Interactions

The electronic structure of magnetic molecules is extremely sensitive to the atomic position of their coordination shell. Therefore, it is not surprising that the atomic motion due to thermal fluctuations has a major impact on the spin properties. In general, the oscillatory motion of atoms, as described by a phonon $\hat{q}_\alpha$ with angular frequency ω_α, elicits a time-dependent perturbation on the crystal field of the magnetic ion. In turns, the modulation of the crystal field induces a perturbation on the spin degrees of freedom thanks to the presence of spin-spin interactions or spin-orbit coupling. These time-dependent electronic interactions are the main driver for molecular spin relaxation and they are generally grouped together under the name of spin-phonon coupling and described in terms of the derivatives of the spin Hamiltonian coefficients.

The theory of spin-phonon relaxation based on perturbation theory and model Hamiltonian operators has been developed decades ago by Orbach.[179] The details of spin-phonon processes have been debated for a long time, but the complexity of the theory and the drastic approximations taken[180] obstructed the emergence of a clear microscopic picture of spin-phonon relaxation in molecular materials. The complexity of the phenomenon thus makes it a fertile ground for the development of *ab initio* strategies, where microscopic insights at the molecular level, hard to obtain from experiments, can serve to design new compounds[181].

Different *ab initio* approaches have been recently applied to the spin-phonon relaxation problem and, despite variations in methodology, all the contributions to date share the same underlying philosophy: vibrational properties are computed by finite-difference methods with DFT, while the spin-phonon coupling coefficients are computed as numeral derivatives of the spin Hamiltonian, obtained with CASSCF or similar methods.[77,111,182–184] In what follows we summarize the main achievements in identifying the dominant relaxation pathways (see Box 3).

The simplest form of spin-phonon relaxation in molecular magnetism is represented by the *direct* relaxation mechanism, where one phonon is exchanged with the lattice and, at the same time, the spin orientation is reversed (see Fig. 6A,B). This process can be simulated by considering a linear spin-phonon coupling and second-order time-depended perturbation theory. At this level the for-

malism leads to a phonon-induced transition rate among spin states i and j, W_{ij}, that is reminiscent of the Fermi's golden rule in optics[181]. For one-phonon absorption it reads

$$W_{ij} \sim \sum_\alpha \left| \langle i | \hat{V}^\alpha_{sph} | j \rangle \right|^2 \bar{n}_\alpha \delta(\omega_{ij} - \omega_\alpha), \qquad (2)$$

where $|i\rangle$ and $\hbar\omega_{ij}$ represent spin wavefunctions and spin excitation energies, respectively, and $\bar{n}_\alpha$ is the Bose-Einstein population of the α-mode. The latter is the sole term of Eq. 3 to depend on temperature. Here $\hat{V}^\alpha_{sph}$ is the linear derivative of the relevant spin Hamiltonian with respect to the phonon displacement vector; for instance, for the Zeeman interaction we have

$$\hat{V}^\alpha_{sph} = \mu_B \, \vec{S} \cdot \left(\frac{\partial \mathbf{g}}{\partial q_\alpha} \right) \cdot \vec{B}, \qquad (3)$$

where μ_B is the electron's Bohr magneton, $\mathbf{g}$ is the Landè tensor and $\vec{B}$ is the external magnetic field.

The direct process is mostly relevant for $S = 1/2$ (and pseudo-1/2 spin systems), where the energy splitting is in the $0.01 - 10.0$ cm^{-1} range, namely at a scale canonically associated to acoustic phonons. In order to include acoustic phonons in the spin-relaxation calculation one has to consider the full phonons' dispersion, as demonstrated for molecular qubits based on the Vanadyl group.[187] In this particular case, a super-cell approach to lattice vibrations was employed, revealing a picture of direct relaxation based on the modulation of the hyperfine coupling and the g-tensor by the intra-molecular component of the acoustic phonons[187]. The DFT accuracy in evaluating the phonons' dispersions was also tested against 4D inelastic neutron scattering measurements, with an excellent qualitative agreement, rest apart a rigid shift of the low-energy frequencies.[46] This is not an uncommon situation with DFT, and similar effects have been observed for both vibrational and cohesive properties of molecular crystals.[188–191] *Ab initio* simulations of direct relaxation in $S = 1/2$ molecules confirm the relation of $\tau \sim T^{-1}$ in the high-T regime, as depicted in the left panel of Fig. 3. A combined ligand-field-theory and *ab initio* analysis of spin-phonon coupling coefficients due to the modulation of the g-tensor showed that the presence of low-lying electronic excited states contributing to the g-shift also increases the spin-phonon coupling[192–195]. Moreover, the study of spin-phonon coupling in model systems allowed to extrapolate simple rules to predict the spin-phonon coupling strength of specific modes based on their symmetry[196,197]. Such studies thus provide an effective way to studying the effect of different coordination environments on spin relaxation time of molecular qubits.

In case a direct transition among the $M_S = \pm S$ states is not possible, like in the case of Kramers systems with large effective spin and axial crystal field, intermediate spin states can still mediate the relaxation. Eq. 2 can be used to describe this process, provided that the Zero-field
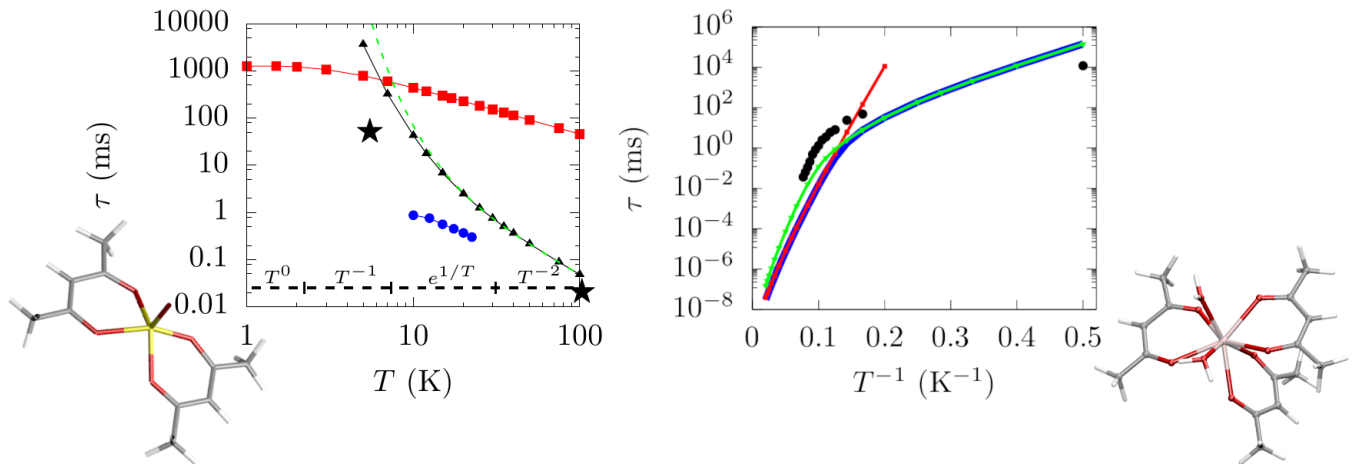
FIG. 3. **Ab initio spin-dynamics results.** Left Panel: The spin-phonon relaxation time of $VO(acac)_2$ computed with *ab initio* spin dynamics at 5 Tesla and including the effect of the direct (red squares and line) and Raman mechanism (black triangles and line). Experimental results coming from magnetometry (blue dots) and X-Band EPR inversion recovery (black stars) are also included.[185] Right panel: computed spin-phonon relaxation time for $Dy(acac)_3H_2O)_3$. Simulations of the Orbach mechanism are reported in red, Raman relaxation in green, and their sum in blue. The black dots mark the experimental results. Reproduced from Refs.[185] and[186] with permission from the American Chemical Society.

splitting terms of the spin Hamiltonian are accounted for in Eq. 3. The Orbach mechanism then involves a series of one-phonon processes that progressively populate intermediate spin states until the reversal is complete (see Fig. 6A,C). Initial *ab initio* studies include the calculation of the spin-phonon relaxation, based on Redfield equations, for a Fe^{2+} single-ion magnet[77,182]. These studies suggested that low-energy optical phonons out of resonance with spin transitions may play a crucial role for under-barrier relaxation and provided a first proof that intra-molecular distortions are the main drive for spin-phonon coupling, thus pointing to increase molecular rigidity and shifting up low-energy vibrations as possible strategies to mitigate the effect of phonons on spin lifetime. *Ab initio* spin relaxation studies on lanthanide-based single-ion magnets also provided important insights on the role of optical phonons in Orbach relaxation[111], pointing to increasing the rigidity of certain modes in resonance with spin levels. These first attempts, although not quantitatively accurate across the entire temperature range, provided a wealth of new information regarding the spin-phonon interaction. Furthermore, they established that the design of long-living single-ion magnets cannot take into account only the static crystal field, but an estimate of the Orbach relaxation rates is also crucial.[186,198–204] In fact, there is now a general consensus that spin-phonon relaxation in magnetic molecules with large effective spins $(S > 1/2)$ is driven by the fluctuations of the single-ion anisotropy due to optical phonons, at least once the dipolar and hyperfine fields are removed by magnetic dilution and isotopic substitution[205]. Combined experimental and *ab initio* simulations of magnetic field-dependent far-infrared and Raman spectroscopies

can play an important role in this area by determining the nature of optical phonons in resonance with excited spin states mediating Orbach relaxation[184,204,206–208]. The inclusion of hyperfine fields in *ab initio* spin-phonon relaxation simulation of $S > 1/2$ systems has not been attempted yet, but represents an interesting new aspect needed to complete the picture[209–211].

One-phonon transitions, accounting for the direct and Orbach mechanisms, do not explain spin relaxation over all the temperature and magnetic-field range. In order to achieve a complete level of description it is necessary to account also for two-phonon processes. In these, a pair of phonons simultaneously exchange energy with the spin, leading to what is generally called Raman relaxation (see Fig. 6A,D). Somehow creating confusion in literature, there are two different mechanisms that fall under the name of Raman relaxation. In one case, the two-phonon nature is brought by the quadratic dependence of the spin Hamiltonian on the atomic displacements,

$$\hat{V}_{sph}^{\alpha\beta} = \mu_B \, \vec{S} \cdot \left(\frac{\partial^2 \mathbf{g}}{\partial q_\alpha \partial q_\beta} \right) \cdot \vec{B} \,, \qquad (4)$$

and equivalently for the modulation of the hyperfine tensor or other spin-Hamiltonian terms. This mechanism appears to be relevant in explaining the high-T profile of the spin-lattice relaxation time of $S = 1/2$ systems, correctly recovering the T^{-2} limit often observed in experiments.[185] The left panel of Fig. 3 reports a comparison between the computed direct and Raman relaxation time for the $S=1/2$ molecule $VO(acac)_2$ (acac=acetylacetonate) due to the modulation of the hyperfine coupling between Vanadium electronic and nuclear spins. At variance with the direct relaxation, THz

intra-molecular phonons were found to dominate the Raman channel. This suggests that possible modifications of the metal's ligands may contribute in suppressing Raman relaxation.

The second type of Raman process instead originates from the linear coupling, $\hat{V}_{sph}^{\alpha}$, between the spin and the lattice degrees of freedom, but a fourth-order time-dependent perturbation theory. In this circumstance, Eq. 2 must be substituted with terms of the form

$$W_{ij} \sim \sum_{\alpha,\beta} \left| \sum_k \frac{\langle i|\hat{V}_{sph}^{\alpha}|k\rangle \langle k|\hat{V}_{sph}^{\beta}|j\rangle}{E_k - E_j - \hbar\omega_\beta} + ... \right|^2 \quad (5)$$

$$\bar{n}_\beta(\bar{n}_\alpha + 1)\delta(\omega_{ij} + \omega_\alpha - \omega_\beta) , \quad (6)$$

where for this specific example a phonon α is emitted and a phonon β is absorbed thanks to the presence of spin excited states with energy E_k. A fully *ab initio* approach involving the use of both Eqs. 2 and 6 has been applied to both lanthanide- and transition-metal-based magnetic molecules with $S > 1/2$ and large zero-field splitting, demonstrating that the formalism is able to explain the dependence of relaxation time at all temperatures[186,199]. As depicted in the right panel of Fig. 3, simulations predict that spin-phonon relaxation follows a relation

$$\tau^{-1} = \tau_0^{-1} e^{U_{\text{eff}}/k_B T} + \tilde{V} \frac{e^{\hbar\tilde{\omega}/k_B T}}{(e^{\hbar\tilde{\omega}/k_B T} - 1)^2} , \quad (7)$$

where U_{eff} and τ_0^{-1} are the effective anisotropy barrier and pre-exponential coefficient driving the Orbach relaxation rate, while $\hbar\tilde{\omega}$ is a value of energy consistent with the energy of the first available optical modes, generally starting at ~ 10 cm^{-1}. A similar picture has also been obtained by Chiesa *et al.*[212] and Gu *et al.*[213], who employed a semi-*ab-initio* strategy to analyze Kramers and non-Kramers single-ion magnets, respectively. All these studies point to the low-energy optical phonons of magnetic molecules as the primary responsible for Raman relaxation.

The development of an efficient and accurate computational strategy is among the most significant challenges in the simulation of spin-phonon relaxation. Also on this count, machine learning offers a new prospect towards the reduction of the computational overheads. It was shown, for a Co-based single-ion magnet, that it is possible to develop *ab initio*-accurate machine learning force fields able to reproduce the phonons of a super-cell at a training cost lower than that needed for a unit-cell DFT calculation.[199] Similarly, the simulation of the quadratic terms of the spin-phonon coupling Hamiltonian requires a colossal number of *ab initio* simulations. This challenge was also solved by developing a machine-learning method able to predict the values of the spin Hamiltonian parameters as a function of the molecular structure at almost *ab inito* accuracy[185,214]. A possible alternative to machine-learning to reducing the overhead of calculating spin-phonon coupling coefficients involves the use of crystal field theory instead of *ab initio* methods[200].

When an accurate and reliable parametrization of the crystal field operators is available, these methods may become incredibility efficient. Another possible strategy is to develop hybrid approaches, where relaxation models are partly computed with electronic structure methods and other are parametrized to match experimental results[194,196,212,213,215–218]. Although lacking predictive power, these approaches can shed light on important features of spin relaxation without the burden of running expensive electronic structure simulations.

The *ab initio* determination of the spin-phonon relaxation represents a new cornerstone in the modelling and design of magnetic molecules. However, before this can be deployed as a truly predictive tool, several challenges must be overcome. Most importantly, quantitative predictions so far have remained elusive, with the typical deviation between theory and experiments remaining as large as one or two orders of magnitude.[185,186,199,202] It has recently been shown that once the dynamics of the full density matrix is considered, as opposite to that of the sole diagonal elements, a close and systematic agreement with experiments carried out on magnetically diluted molecular crystals can be achieved[219]. However, at the same time, an exhaustive benchmark of the predictive power of these methods is still missing and only a handful of systems have been investigated. The improvement of the method accuracy is also related to the necessity to closely review and verify the appropriateness of the approximations underpinning Redfield's relaxation theory and the accuracy of the underlying electronic-structure methods.

Spin-Electron Interactions

At the fundamental level, the spin of an atom or a molecule itself is the result of the interaction among electrons, so that an adiabatic separation of the spin and the electronic degrees of freedom, as in the case of phonons, is conceptually much more difficult to justify and construct. Moreover, at a practical level, the spin-electron interaction strength may vary significantly depending on the system and the environmental conditions, so that a perturbative approach may not apply in all situations. The most direct way to tackle the problem would be that of solving a purely electronic one, either in the time domain of through electronic structure theory in the grand canonical ensemble. We have already discussed the complexity of the first approach in the case of molecular magnetism. Concerning the second one, a formulation of DFT in the grand canonical ensemble has been proposed a long time ago,[220] but no real practical implementation has emerged so far. As such, even in this case one has to rely on a multi-scale approach of some kind.

The nature and type of phenomena related to spin-electron interaction are determined by the relative strength of the electron correlation within the molecule and by the coupling between the molecule and an elec-
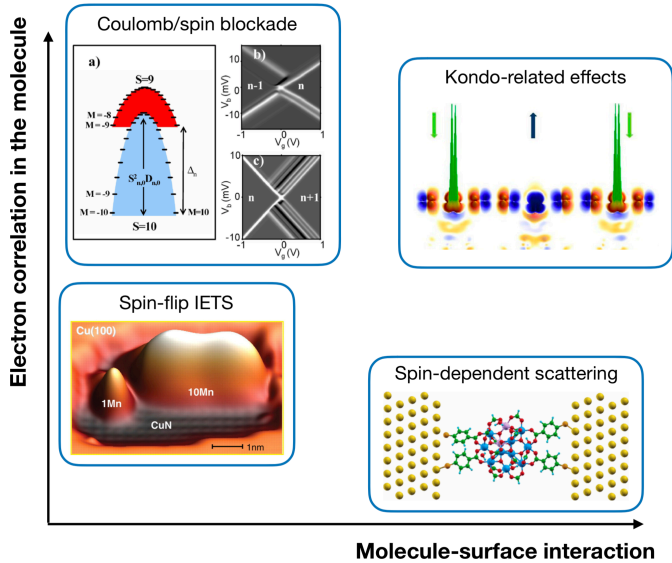
FIG. 4. **Different phenomena driven by spin-electron interaction in molecules.** In general the type and nature of spin-electron phenomena depend on the electron correlation of the molecule and the coupling between the molecule and the electronic bath (e.g. the surface). This latter determines the characteristic time an electron can reside on the molecule. Reproduced from Refs.[221–224] with permission from the American Physical Society, the American Association for the Advancement of Science, and the American Chemical Society.

tronic bath (see Figure 4). This is associated to the surface where the molecule is deposited on, and by the possible presence of an external driving voltage. The same physical characteristics also define the best method to theoretically tackle the problem.

Perhaps the simplest situation is when the coupling between the surface and the molecule is strong but correlation can be neglected. In this case the molecular orbitals are strongly hybridized with the electronic continuum and their lifetime is extremely short. An electronic current, in general, will not affect the internal degrees of freedom of the molecule. One can then study how the scattering potential generated by the molecule affects the current flow, namely the molecule electrical resistance. The most common way to approach the problem is offered by the non-equilibrium Green's functions (NEGF) method[225] combined with DFT.[226–228] In this case one uses the Kohn-Sham system as an effective mean-field single-particle theory in a fully *ab initio* self-consistent scheme. In practice, the electronic structure is computed in the presence of appropriate boundary conditions describing the coupling of a scattering region (the molecule) with one or multiple electronic reservoirs (the circuit's leads), possibly including the action of an external bias voltage (either driving or gating). Then, the conductance, and hence the current, is obtained via

Landauer's theory.[229,230] The method is not free from fundamental ambiguities, mostly related to interpreting the Kohn-Sham spectra as actual removal energies, and practical issues connected to the actual position of the Kohn-Sham states and their shift upon charging.[231–234] Nevertheless, NEGF+DFT has been used many times to understand how the magnetic properties of single-molecule magnets[221,235–241] and spin qubits[242] determine the tunneling current of two-probe junctions (in some cases DFT is replaced by a tight-binding electronic structure). In general, one finds that the presence of the spin-split $3d$ manifold near the junction Fermi level results in a spin-polarised transmission coefficient, similarly to what happens in standard spin-polarised scanning tunnel microscopy.[243] Whether or not a spin-polarised current can be sustained, however, depends on the spin-relaxation time of the molecule, which should be longer than the time needed to detect such spin polarization (in a magnetic tunnel junction experiment, T_1 must be longer than the typical tunneling time). Several of these calculations also observe a negative differential resistance in the current-voltage curve, usually attributed to the unavoidable asymmetric electronic coupling of the molecule to the electrodes[244] and to complex orbitals rehybridization under bias.[221] An intriguing idea emerging by these electron scattering studies is that the current can be used to read the magnetic state of bi-stable molecules, such as spin-crossover[245,246] and valence-tautomeric[247] compounds, and that the bias voltage can be used to induce the switching.[248–250] Notably, some of these switching effects have been observed in experiments.[251]

The theoretical description becomes sensibly more complex when the coupling between the molecule and the electron bath reduces, so that a transport electron has enough time to excite the molecule. If the interaction between the electron and the molecule is weak, it can be treated at the level of perturbation theory. This is, for instance, the case of spin-flip inelastic electron tunnel spectroscopy (SF-IETS),[222,252] in which the tunnelling electrons induces a spin transition opening an inelastic transport channel. As a result, one typically observes a step in the differential conductance spectrum, corresponding to the excitation energy. In this situation a model spin Hamiltonian can be used together with the NEGF method for transport. Typically the electron-spin coupling is simulated by an appropriate self-energy, obtained from perturbation theory.[253–255] Alternative single-particle approaches consider tunnel Hamiltonian or the standard Tersoff-Hamann description of the current.[256–259] Additional details can be included in the model by taking into account the effects related to current-generated non-equilibrium spin populations.[260,261] All these single-particle perturbative methods are amenable to be treated at the *ab initio* level. For example, DFT combined with many-body perturbation theory, a general framework to evaluate the different contributions to the spin susceptibility,[262] has been used to compute the inelastic tunneling spectra of various

magnetic adatoms on surfaces.[263] In this case the system remains in equilibrium, and any transport-related non-equilibrium effects are not taken into account.

Still in the weak molecule-surface coupling limit, the final level of complexity is found in situations where the electron transport is strongly correlated. This, for instance, is the case of the Coulomb blockade regime,[264] where the electron flow is determined by the charging state of the molecule. Now one can treat the coupling between the molecule and the electron bath as perturbation and solve some correlated equations of motion for the molecule in different charging and spin states. The most common theoretical approach is that of using some type of master equation.[265] This is then combined with various effective spin Hamiltonian, describing the particular molecule at hand. In addition to charge blockade, the method is capable of explaining spin blockade and the associated negative differential resistance, arising from selection-rule forbidden transitions across the molecule excitation spectrum.[224,266] Similar approaches have been also used to investigate the interplay between spin dynamics and electron transport in lanthanide-based single-molecule magnets,[267,268] in which a spin-valve behaviour has been observed experimentally.[269]

The final and most complex situation is encountered in the strong coupling limit where the molecule is correlated. In this scenario perturbation theory is now no longer applicable and the physics is dominated by the Kondo effect,[270] namely the dynamical screening of the atom's spin by the free electrons in the metal. The literature on the Kondo effect is vast, in particular at the level of model Hamiltonian for which a broad variety of models and numerical techniques have been developed over the years. These have helped enormously in understanding experiments and in identifying their fundamental features. Not pretending to be exhaustive, here we will only offer a brief overview on the most recent development among the *ab initio* approaches. In general, the theory passes through a multi-scale approach, where the electronic structure is mapped onto an effective electronic Hamiltonian.

The first step always consists in performing electronic structure calculations (mostly DFT) in order to extract the parameters needed by an Anderson-type impurity model.[271] This consists in a strongly correlated electronic electron manifold (the atomic/molecular shell hosting the spin) interacting with a non-correlated electron bath. Once the relevant manifold is identified, one has to calculate its Coulomb repulsion energy (more generally a Coulomb matrix), similarly to a DFT+U approach, and the hybridization function of such manifold with the electron continuum. Some of the choices concerning the correlated electron manifold are not different from those one has to make when using cWFN schemes for the electronic structure. This can be done by using supercell calculations, which are possible with essentially any standard DFT package,[272,273] and with some orbital-projection scheme such as that provided by the maxi-

mally localised Wannier functions.[274] Alternatively, the hybridization function can be extracted from the self-energies of the electrodes in a NEGF transport calculation setup.[275,276] As with many other multi-scale approaches based on projecting a complex electronic structure onto a model Hamiltonian, the scheme is not free of ambiguity. In fact, the choice of the correlated manifold may be non trivial. In particular, it is legitimate to ask whether the orbitals associated to the ligands must be included, or alternatively for molecules, whether molecular orbitals should be used instead of the atomic ones.

Once the Anderson impurity model is constructed the remaining step consists in computing the spectral function (density of state) and from this the conductance. The simplest way is that of using known results when available, although these are usually limited to very specific situations (e.g. $S = 1/2$, particle-hole symmetry, etc.). At a more general level, there are several computational strategies differing for their range of applicability and computational costs. These are all grouped under a class of algorithms named impurity solvers. Numerical renormalization group[277] is in principle exact and can be used with smooth hybridization functions and by availing of symmetries.[278] A powerful alternative is offered by the continuous-time quantum Monte Carlo scheme,[279] which can deal with arbitrary hybridization functions and general Coulomb matrices (non-diagonal in the orbital subspace). Despite its general numerical complexity, the method has been already used many times to describe the Kondo physics of atoms on a broad variety of surfaces.[273,280,281]

Finally, let us conclude this section by briefly discussing a few of the outstanding problems when dealing with spin-electron interaction in a completely non-perturbative way. Firstly, it is important to point out that the electron transmission spectrum, when computed, is essentially obtained from elastic scattering to the correlated spectral function.[282] As such the theory does not describe, on the same footing, the Kondo physics and inelastic spin flip. Likewise, all the current implementations of many-body spin scattering are not self-consistent, namely the hybridization function and Coulomb matrix are computed only once from a converged DFT calculation. Achieving self-consistency, at present, remains extremely challenging. Another difficulty is that of including finite-bias effects. The issue is not related to the impurity solvers, which have been extended to non-equilibrium situations,[283] but to their interface with *ab initio* electronic structure codes, which at present is not available. Finally, the vast majority of the studies to date deal with single impurity problems, while several experimental investigations look at more complex spin structures comprising exchanged-coupled spins either through bonds[223] or mediated by the electrons in the substrate.[284,285] In principle, multi-spin-center calculations are possible, but these require the definition of large correlated-orbital manifolds so that the solution of the impurity problem may be practically impossible with

the current algorithms.

CONCLUSION AND OUTLOOK

The close interplay between computer simulations and experiments has allowed the field of molecular magnetism to thrive for many years, witnessing examples of both experiments driving theory and vice-versa. As discussed in this review, until recently the design of magnetic molecules has mainly required accurate electronic structure theory together with the rationale provided by crystal-field engineering. This is no longer enough and it is now necessary to go beyond the static picture of molecular magnetism and also look at the design of dynamical properties. A multi-scale approach, as reviewed here, is the only practical way to build such strategy and has the potential to act as a blue-print for a complete *ab initio* approach to the design of novel magnetic molecules. Importantly, many of the concepts discussed here are not unique to single-molecule magnets or molecular qubits and can also be applied to other important spin systems, such as spin-crossover systems[286], colored defects in semiconductors[287], organic radicals[288], nuclear spins[289], and delocalised spins in graphitic fragments.[290,291] Moreover, the same theoretical toolbox can also be exported to other application areas of computational materials science, for instance in the design of solid catalysts[292] or metal-organic frameworks.[293]

A final question, however, remains: *is the ability to accurately predict molecular properties a sufficient requirement to the computational design of new compounds with specific properties without any input from experiments and minimal human intervention?* This is a question that goes well beyond the field of molecular magnetism and that has recently become a central topic of computational materials science at large. We believe that the actual design of a new magnetic molecule requires two additional steps beyond the comprehensive computational strategy highlighted in this review. In facts, one requires the ability i) to predict all the relevant properties with a minimal computational cost but sufficient accuracy, so ii) to be able to screen different chemical compositions and structures in an automated and systematic fashion.

High-throughput[294] and machine-learning-guided materials screening[295,296] have recently emerged as very promising pathways for materials design, which satisfy the two principles stated above. High-throughput strategies involve the selection of a large part of the chemical space for the target materials and the systematic computation of all the relevant structures, compositions and properties, usually by DFT methods. Besides providing an estimate of the materials characteristics, high-throughput approaches also allow for empirical laws to emerge. In turn, these can be used to further guide the selection of new candidates and they provide qualitative structure-to-property relations. Machine learning is emerging as a new paradigm for scientific investigation, going well beyond computational materials science.[297] In materials design, machine learning holds the promise to substitute not only human intuition, but also the human ability to translate ideas into algorithms. By learning from examples as the human mind does, machine learning can go beyond the set of rules provided by the scientists and adapt itself to new circumstances as they present themselves through new data.

As illustrated in this review, seminal steps in the field of coordination compounds and magnetic molecules have only recently been taken. These include the use of data mining for database creation[298], high-throughput screening of transition metal complexes[299], and the machine-learning prediction of i) structural parameters[300], ii) potential energy surfaces[67], iii) spin splittings[301], and iv) spin Hamiltonian parameters as function of atomic coordinates[68,214,302–304]. Although much more work will be needed before machine learning can become a black-box approach to chemical design, other areas of chemistry, without the complications brought by the magnetic degrees of freedom and the coordination bond, are showing promising results. For instance, highly accurate and exportable machine-learning force field for organic compounds and small molecules are now routinely produced[305,306], proof-of-concept generation of new materials based on statistical inference has been shown[307,308], and examples of self-driving AI controlled laboratories are already available.[309,310]

Finally, it is important to remark that in a near future machine-learning and high-throughput methods are expected to become tightly integrated at the methodological level. This means that machine-learning accelerators will be part of electronic structure algorithms, which in turn will provide either a higher throughput or a higher accuracy than conventional schemes. Much work, for instance, has been dedicated to the design of machine-learning-based kinetic density functionals for orbital-free DFT.[311] If delivered, these will allow one to perform linear-scaling DFT calculations by avoiding the Kohn-Sham construct, with the potential access to large-scale simulations. Such strategy is still affected by issues connected to the representation of the charge density, the differentiability of the functional and by the generally limited transferability, but notable progress has been made.[312–314] Using the same philosophy one can also engineer new energy functionals either translating a Kohn-Sham approach into an orbital-free one[315] or by training on a high-level quantum chemistry theory.[316–318] This approach has the potential to both increase throughput and accuracy.

An interesting result arising from the development of orbital-free kinetic density functionals is the observation that often even an approximated charge density can serve as good descriptor for a more accurate calculation. This has inspired a range of methods, collectively called Δ-DFT, where approximated charge densities are used to predict either accurate total energies obtained from wave-function quantum chemistry methods[319–322], or directly

physical observables.[323] All in all, Δ-DFT schemes, if demonstrated universal, will hold the potential to bring electronic structure calculations at a quantum-chemistry accuracy with the computational overheads of a local DFT approach. Intriguingly, machine-learning accelerators can also help in improving the efficiency of pure wave-function methods, for instance by optimising the sampling in configuration interaction and complete active space methods[324–328], or by providing a more compact way to write the wave function ansatz in quantum Monte Carlo calculations[329]. In general, we expect that such hybrid electronic-structure/machine-learning schemes will speed up significantly the computation of materials properties and thus will improve our ability to perform accurate predictions ahead of experiments.

Although the focus of this review article is on theory and algorithms, it is worth mentioning that quantum computers will also play an important role in the design of accurate and efficient computational solutions to the problems of molecular magnetism[330]. Seminal works have shown that near-term noisy quantum computers are already able to tackle electronic structure problems for simple molecules[331] as well as computing many-body dynamics of spin systems[332]. The advent of new hardware with a large number of physical qubits and the development of quantum-error correction strategies[333] hold the promise of unlocking the virtually exact simulation of today's intractable quantum problems[334–338]. Another recent and interesting solution to the hardware bottleneck instead comes comes from the classical world. Tensor processing units, originally designed for running large-scale deep learning architectures, they have recently used to speed up both electronic structure and many-body simulations[339,340].

As presented in this review, molecular magnetism is well on its way to complete a multi-scale pipeline of first-principles methods able to predict all the relevant figures of merit for key technological applications, such as quantum technology and spintronics. Although this is a remarkable achievement in itself, it is only the tip of iceberg. In the future we envisage a full integration of multi-scale approaches with high-throughput and machine-learning strategies. This will lead to a complete paradigm shift with the possibility to perform unbiased real molecules design.

ACKNOWLEDGMENT

Box 1: Spin Hamiltonian and magnetic molecules. Slow relaxation of the magnetization at the molecular level can be obtained either by applying an external field or in the presence of magnetic anisotropy (also known as zero-field splitting)[6,7]. The first case is relevant for $S = 1/2$ systems, often employed as quantum bits for quantum applications, and the relevant energy scales are due to the Zeeman interaction, gauged by the Lande' tensor $\mathbf{g}^{22}$. In the second case, we can instead talk about single-molecule magnets, which maintain their magnetization even in absence of external fields. In the early days, research studies focused on transition-metal complexes and their spin properties can be modelled with the spin Hamiltonian $\hat{H}_s(\vec{\mathbf{S}}) = D\hat{S}_z^2 + E(\hat{S}_x^2 + \hat{S}_y^2)$, where D is the axiality of the magnetic anisotropy, and E its rhombicity[341]. For $D < 0$ the states with maximum spin momentum projection along z, namely $\langle \hat{S}_z \rangle$, are the ground state, as depicted in Fig. 5A. Larger the value of DS^2, the slower the inter-conversion between $\pm S_z$ is expected, giving rise to the single molecule magnet behaviour. Magnetic bistability can be improved by coupling multiple ions through exchange interactions. Spin-spin interactions of this kind can be described by Heisenberg exchange Hamiltonian $\hat{H}_s = \sum_{ij} J_{ij} \vec{\mathbf{S}}_i \cdot \vec{\mathbf{S}}_j$, where the sum runs over the different metallic centre and $J_{ij} < 0$ (> 0) accounts for a ferromagnetic (anti-ferromagnetic) interactions[8]. Fig. 5B reports a classical example of SMMs based on four exchange-coupled Fe^{3+} ions with a total ground state $S = 5^{341}$. Single-ion coordination complexes can also support high values of magnetic anisotropy, as in the case of lanthanide compounds, which are able to reach spin splittings up to 2000 K, as depicted in Fig. 5C,D for a Dysprosium metallocene compound[111]. Ln complexes often possess a non-vanishing orbital angular momentum and their states need to be described in terms of total angular momentum J and a generalization of the simple zero-field splitting Hamiltonian: $\hat{H}_{CF}(\vec{\mathbf{J}}) = \sum_{l=2}^{l_{max}} \sum_{m=-l}^{l} B_m^l \hat{O}_m^l(\vec{\mathbf{J}})$, where l and m are the order and component of a tesseral operator $\hat{O}_m^l$ and l takes even values with an upper limit $l_{max} = 2J^{342}$.
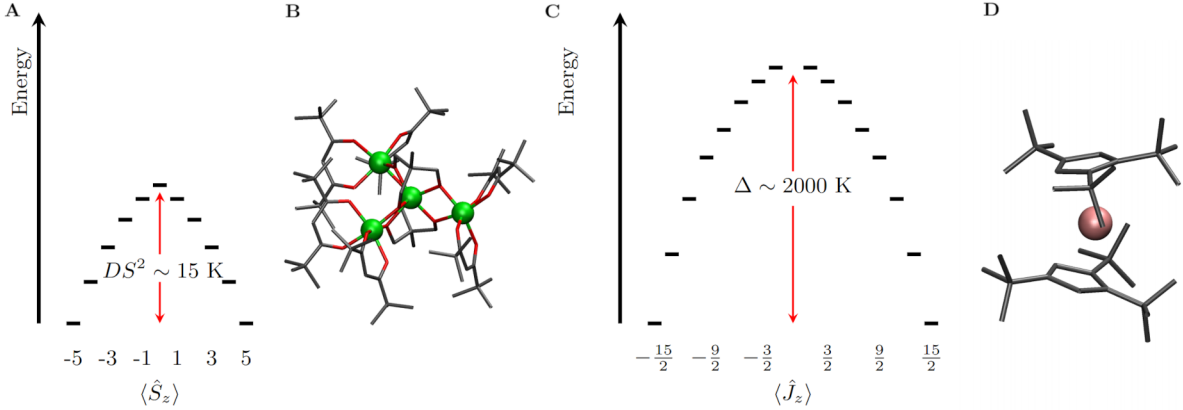

FIG. 5. **Prototypical single-molecule magnets.** Panel A and B show the spin energy levels and the molecular structure of a tetra-nuclear Iron cluster, whose maximum magnetic anisotropy is in the range of 15 K[341]. Panels C and D show spin energy levels and the molecular structure of a Dy-based single-ion magnet with a record magnetic anisotropy of ~ 2000 K[111].

Box 2: Quantum chemistry for magnetic molecules. An accurate description of the electronic structure is the starting point for any computational investigation of magnetic molecules. According to the variational theorem it is possible to determine the electronic ground state of a molecular system by minimizing the energy expectation value of the many-body N-electron Hamiltonian, $\hat{H}$, with respect to adjustable parameters (α_i) contained on a trial wave function $|\Psi(\alpha_i)\rangle$[14]. In order to converge to the exact solution, $|\Psi(\alpha_i)\rangle$ must be expressed as linear combination of an infinite number of Slater determinants $(|\phi^{SD}\rangle)$: $|\Psi(\alpha_i)\rangle = \sum_i \alpha_i|\phi_i^{SD}\rangle$. The latter represent a complete basis set of the anti-symmetric portion of the N-electron Hilbert space. In turn, each Slater determinant, must be constructed from a complete mono-electronic basis set, namely the molecular orbitals $|\chi\rangle$, also containing variational parameters that needs optimization. In practice, a variational function $|\Psi\rangle$ containing infinite degrees of freedom cannot be use and neither is required. The Hartree-Fock method is the most drastic *ab initio* approximation and involves approximating the total wave-function to a single determinant $(|\Psi\rangle \sim |\phi^{SD}\rangle)$[14]. Hartree-Fock also represents the starting point for more involved *ab initio* schemes, where the contribution of additional Slater determinants is reintroduced. In the case of magnetic molecules, Complete Active Space (CAS) methods are particularly popular as they are able to selectively correct Hartree-Fock solutions for the magnetic degrees of freedom[14]. For instance generating an expansion of Slater determinants that only involve the d- or f-like molecular orbitals, which are known to be responsible for the magnetic response of a coordination compound[36,96].

Density Functional Theory (DFT) represents an alternative to wave-function-based methods. According to the Hohenberg-Kohn's theorems[13], it is possible to rewrite the electronic variational problem as a functional of only the electron density of the system, instead of the entire wave-function. However, due to the unknown nature of the exact functional, in practice DFT is implemented following the Kohn-Sham scheme, where the many-body N-electron problem is replaced by a non-interacting N-electron problem, sharing the same ground-state energy and density. An addition potential term, the exchange-correlation potential, includes the effect of electronic correlation in the the Kohn-Sham scheme. Several families of exchange-correlation potentials have been derived at different levels of approximation for different properties and chemical systems. In the case of magnetic systems, functional that includes a portion of exact Hartree-Fock exchange[50] (called hybrid functionals) are often found to give the best results, but no universal and accurate DFT recipe exists yet for magnetic molecules[343].

Box 3: Spin Relaxation and Decoherence. Spin lifetime, T_1, (also called longitudinal or spin-lattice/phonon relaxation), namely the time a spin requires to thermalize to equilibrium, is a characterizing feature of magnetic molecules. Indeed, any application that involves controlling the state of the molecule's spin state must drive it on a time scale significantly shorter than T_1. Under normal conditions, the interaction of spin with molecular vibrations is the main driving force for spin relaxation and it is responsible for the temperature behaviour of T_1. There are several possible spin-phonon relaxation mechanisms and the nature of the dominant one depends on both the magnetic properties of the molecule, the nature of molecular vibrations and the thermodynamic conditions. A first classification of relaxation mechanisms distinguishes between one- and two-phonon processes. One-phonon transitions can lead to two types of relaxation: direct and Orbach mechanisms. In the first case the absorption/emission of a single phonon is enough for inverting the spin moment direction. In the case of Orbach relaxation instead it is necessary to sequentially absorb/emit a multitude of phonons as the symmetry of the crystal field prohibits a direct transition. These two mechanisms are depicted in Fig. 6A-C. Direct relaxation is often observed in $S = 1/2$ or non-Kramer systems at very low-temperature, while Orbach relaxation necessary require systems with $S > 1/2$ and high-temperature. Finally, two-phonon processes arise from the simultaneous interaction of spin with two phonons and are responsible for Raman relaxation mechanisms. The latter are generally triggered by the simultaneous absorption and emission of two quasi-degenerate phonons, which induce a spin flip of the total spin moment. Crucially, these phonons do not need to be resonant with any spin level, as depicted in Fig. 6A,D. Raman relaxation dominates at intermediate temperature ranges with respect Direct and Orbach relaxation and is active for any type of spin system. At very low temperature, where the role of phonons is hindered by the lack of populated states, other relaxation mechanisms become relevant. Spin-spin interactions in particular drives spin diffusion, which is particularly important for quantum applications as it limits the coherence of spin states to a timescale denoted as T_2 (also known as spin-spin or transverse relaxation time). The table below reports representative values of T_1 and T_2 for a range of single-ion molecular magnets (upper part) and spin qubit (middle part). Other spin qubits, such as solid-state paramagnetic defects, are also shown for comparison (lower part). For a more detailed and extended analysis we refer the reader to the numerous reviews appeared recently.[25,287,344,345]

Molecule	Spin	T_1	T_2	Ref.
$[Dy(O^tBu)_2(py)_5]^+$	$J = 15/2$	1 s (38) $-$ 0.1 ms (100)		[110]
$[Dy(O^tBu)_2(4\text{-Pdpy})_4]^+$	$J = 15/2$	0.2 s (10) $-$ 25 μs (118)		[346]
$[Co^{II}(L^{2-})_2]^{2-}$	$S = 3/2$	18 ms (5) $-$ 35 μs (25)		[21]
$Fe[N(SiMe_3)(Dipp)]_2$	$S = 2$	1 s (2) $-$ 45 μs (20)		[19]
$[Fe(C(SiMe_3)_3)_2]^-$	$S = 3/2$	1 s (10) $-$ 75 μs (30)		[102]
CuPc	$S = 1/2$	59 ms (5) $-$ 10 μs (80)	2.6 μs (5) $-$ 1 μs (80)	[347]
$(Ph_4P)_2[V(C_8S_8)_3]$	$S = 1/2$	20 ms (10) $-$ 4.9 μs (120)	0.7 ms (10) $-$ 1.2 μs (120)	[27]
$[(Ph)_4P]_2[VO(dmit)_2]$	$S = 1/2$	2.3 ms (2) $-$ 5 μs (300)	3 μs (4) $-$ 1 μs (300)	[348]
CpTi(cot)	$S = 1/2$	20 ms (4.5) $-$ 3 μs (120)	34 μs (4.5) $-$ 1 μs (120)	[349]
$[Cr([D_9]\text{-ddpd})_2](BF_4)_3$	$S = 3/2$	0.3 ms (7) $-$ 8 μs (70)	8.4 μs (7) $-$ 0.6 μs (80)	[350]
Yb(trensal)	$S = 1/2$	6 ms (3.3) $-$ 0.9 μs (15)	0.5 μs (2.7) $-$ 0.2 μs (15)	[351]
$[Gd(phendo)_4](NO_3)_3$		0.2 ms (5) $-$ 4.7 μs (30)	2.7 μs (5) $-$ 0.3 μs (30)	[352]
$[Ho(W_5O_{18})_2]^{9-}$	$J = 8$		8 μs (5)	[353]
NV$^-$ in diamond	$S = 1$	$\sim$6 ms (300)	$\sim$3 ms (300)	[354]
NV$^-$ in nano-diamonds	$S = 1$	$\sim$ 30 μs (300)		[355]

TABLE I. Summary table of spin-lattice and spin-spin relaxation times, respectively T_1 and T_2, for a number of representative molecules. Data are presented over the available temperature range (temperature in K in brackets). The upper part of the table concerns single-molecule magnets, for which T_2 usually is not measured, while the middle part is for spin qubits. The bottom part of the table presents some data for N-V centers in diamond as comparison. The second column displays the value of the angular momentum (either spin or total) relevant for the spin relaxation.
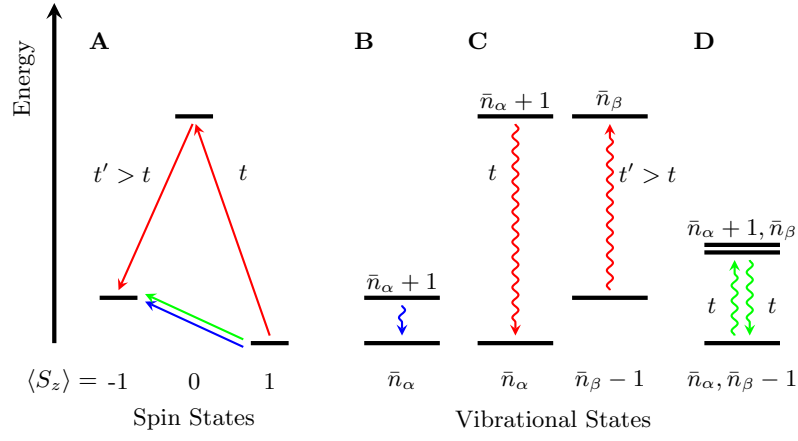
FIG. 6. **Schematic representation of spin relaxation mechanisms.** Panel A represents the energy levels of a S=1 with uni-axial anisotropy in the presence of an external field that removes the $M_S = \pm 1$ states degeneracy. Panel B represents the Direct relaxation mechanism, where the absorption of a phonon resonant with the states $M_S = \pm 1$ diminishes the number of available phonons, $\bar{n}_\alpha$, by one. Panel C represents an Orbach relaxation mechanism due to the time-sequential absorption and emission of a phonon in resonance with the $M_S = \pm 1 - M_S = 0$ transitions. Panel D represents the Raman relaxation mechanism, where two phonons are simultaneously absorbed/emitted to induce a transition among the states $M_S = \pm 1$.

Box 4: Machine learning and chemical science. The last few decades have witnessed an exponentially growing volume of scientific data and their optimal exploitation is an essential ingredient of modern science[297]. Machine learning (ML) provides a set of procedures to numerically learn from data in an automatic and consistent way[356]. One of the most celebrated ML methods is supervised deep learning. In a nutshell, supervised ML is a generalized way to run a regression, where a trial function containing adjustable coefficients is optimized to fit a set of data. One of the big advantages of deep learning is the use of neural networks as scalable trial functions. Indeed, it is possible to demonstrate that any function can be approximated by a neural network with enough neurons and enough data samples to learn from (neural networks with many neurons have a high degree of flexibility to learn from data)[356]. In addition to its flexibility, performing ML also involves the use of numerical strategies to avoid over/under data fitting as well as to monitor the ability of the model to extrapolate to new scenarios as they present themselves[357]. The use of test sets and regularization methods, and active learning are just two examples of how to deal with these problems[356]. A very successful application of ML in molecular science is the learning of potential energy surfaces, namely machine-learning force fields[60,358]. Here a ML model is trained to reproduce several *ab initio* results of energy and/or forces for many different molecular conformations by taking as input a feature vector that represent the chemical structure[62]. If the training is performed correctly, the model will then be able to interpolate the potential energy surface and it can be used to make accurate predictions for new geometries. Different flavours of machine-learning force fields have been successfully applied to condensed-phase systems. The list includes liquids solutions[359], solid-state materials[295], reactivity[360] and catalysis[361] as well as to coordination and magnetic compounds[67,299].

It is worth pointing out that the use of machine learning in materials science is relatively young and that the community has not yet implemented rigorous procedures of quality control and both model transferability and reproducibility. The goodness of a model is usually determined by the value of the loss function and the error over the quantity to predict. However, comparisons between different models are difficult to make and, at variance with conventional electronic structure theory[362], ever rigorous criteria to make such comparison are not well established. Finally, models and data are often shared through dedicated repositories, such as GitHub, pointed by publications. This practice, in principle, enables full reproducibility. Unfortunately, such procedure is not enforced by publishers and so it remains at the good will of the authors.

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