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Towards quantum sensing with molecular spins

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ABSTRACT

Molecular spins have shown genuine quantum properties, both as collections of independent units and as individual objects. Their properties and performances can be engineered at molecular level, while advanced technologies to coherently manipulate magnetic objects and to address them with unprecedented spatial and energy resolution have emerged in the last years. Here we address the question on how to exploit quantum features of molecular spins for quantum sensing. To this end, we summarise some basic ideas and discuss some examples where molecular spins can play a role in the field.

1. Introduction

Scientific discoveries and development of novel technologies are often driven by advances in the design of measuring apparata [1] and by the corresponding enhancement of their precision. At the same time, any detector is a physical system itself and, when a new physical effect is discovered, it may be used to improve measuring techniques and their accuracy. A recent and fruitful example of this interplay, causing a major change in the paradigms of metrology, is that of quantum sensing (Q-sensing) [2–5], i.e. the art of exploiting the peculiar features of quantum systems to realise novel enhanced sensors and measuring protocols.

Quantum systems may be prepared in superpositions of states and this peculiarity leads to phenomena known as *quantum coherence* and *entanglement*. Q-sensing exploits both these features in order to get advantages with respect to the performances of classical sensors. Coherence and entanglement may be used to make composite quantum systems sensible to the action of an external agent, even if only a portion of the probe has interacted with the external source of perturbation. On the other hand, the inherent fragility of quantum coherence and entanglement against decoherence may itself be exploited, and suggests the possibility of using quantum systems as probes of the surrounding environment.

1.1. Quantum sensing in a nutshell

As for quantum computation, basic requirements for a system to work as quantum probe can be summarised in few (DiVincenzo) criteria: 1) the quantum sensor has well defined energy-resolved levels; 2) it must be possible to initialise it and read out its final state; 3) it can be coherently manipulated. This latter condition, however, is not strictly required and sensing with continuous or relaxation measurements may well do the job too. An additional and specific request for sensing is the capability of the quantum system to interact with the parameter X to be sensed. This generally implies a shift or a transition between energy levels, or the acquisition of a quantum phase. Alternatively, read out of an observable of choice (Y) can be used in different schemes of measurement. A preliminary issue is actually related to the choice of the observable that optimises the quantum measurement. This is a general problem of quantum information theory that we shall discuss in the next section.

Broadly speaking, the sensing protocol includes three steps: first, one prepares the quantum probe in a state that contains a dependence on the unknown parameter X; in a second step, one performs a measurement of an observable of choice; finally, the value of the parameter is inferred from the outcome of the measurement. The advantages in using genuine quantum features are related to the performances of the quantum sensor, that, ideally, should not be achievable with classical sensors. Thus, for instance, any operation that is not allowed by classical probe certainly brings some *quantum advantage*. Likewise, when nanometer scale resolution is required, single atoms or molecules may perform better than any classical sensor. As far as the preparation step is concerned, it has been shown that a quantum advantage typically results from the use of highly nonclassical states, which exhibit entanglement between subsystems (in the case of a composite quantum probe) or linear superpositions between semiclassical and

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macroscopically distinct states (the so-called *Schrödinger cat*). In particular, the use of such nonclassical states can lead to a faster scaling of the precision with the size of the system with respect to states that don't exhibit genuine quantum features. A key role is thus played by the phase coherence and by the possibility of preserving such coherence in the presence of noise. Thus, in all those cases in which it is requested to perform the entire sensing protocol with nonclassical states, long coherence time T^* is an essential characteristic for the quantum sensor.

Different figures of merit can be used to evaluate the efficiency of sensing, depending on the performances to be optimized. For instance, the sensitivity, i.e. the minimum detectable signal per unit time, is a parameter commonly used to evaluate the efficiency of an experimental protocol. We refer the interested reader to review articles on quantum sensing [2] for rigorous treatment of the problem, while in the next paragraphs we shall focus only on quantities relevant for specific experiments discussed. Here we just point out that there are several factors that may limit the accuracy of the measurement. Among these, any experimental apparatus presents technical limitations that result in a background noise. Thus, the signal-to-noise ratio is another key indicator in quantum sensing. The process of extracting information on the unknown parameter by performing measurements on the quantum probe is also subject to fundamental limitations resulting from the measurement back action. Moreover, since quantum properties need often to be detected at single-unit level, fundamental limits, such as those imposed by Heisenberg indetermination principle, may also arise in quantum sensing. For instance, energy resolution requires sufficiently long acquisition time or, moreover, different components of the magnetic moment cannot be determined with the arbitrary precision at the same time.

1.2. Spins as quantum probes

Here, we are interested on the use of spin systems as quantum probes. Recently, the use of spin systems for quantum sensing has been actively pursued [2]. A spin can be used as a probe for estimating external physical parameters, such as temperature, electrical or magnetic field but they are also ideal probes for detecting related quantities like, for instance, faint currents or exotic topological states such as vortices in superconductors. In the last years, a burst of interest in the field has been given by Nitrogen Vacancy (NV) centers in diamond [6]. NV centers have long coherence time even at room temperature, they can be addressed individually and quickly respond to several external stimuli, being protected by hard diamond shell at the same time. While NV's performances seem optimal for quantum sensing and they provide a playground to test novel schemes, other spin impurities in solids and magnetic systems, including molecular spins, may offer complementary features and have potentialities as quantum probes. Since the discovery of quantum effects in molecular nanomagnets, the possibility to exploit genuine quantum properties of these systems to perform unconventional operations has been considered. In the last decade understanding the decoherence mechanisms in molecules have made huge progresses, and Rabi oscillations have been reported in several molecular spin systems, even at room temperature. Proposals for using molecular as building blocks (qubits) for performing quantum computation or simulation are today attracting the interest of physicists and chemists [7]. In this perspective, controlling the decoherence mechanisms represents a fundamental prerequisite [8–12].

As an important point, the use of molecules with large number of paramagnetic metal ions embedded in a ligand shell can lead to high values of the total spin S (up to several tens of $\hbar$), well beyond the ones that can be achieved by single ions or by a single defect in solid-state systems. Larger values of S in principle result with higher precisions in a transduction of a spin state or in the possibility of generating Schrödinger cat states, which are known to represent a resource in the estimation of homogeneous or staggered magnetic fields [13,14]. While the use of single high spin molecules might combine a precise measurement with a high spatial resolution, it turns out that some of the estimation protocols can also be implemented with spin ensembles [2]. We shall explicitly address this issue by discussing cases of quantum sensing with spin ensembles (Section 3.3).

Mononuclear paramagnetic centres can be simple-almost isotropic-spin 1/2. Yet, a peculiarity of molecular spins is the possibility to engineer the magnetic characteristics (the Lande' g-factor and its anisotropy, the zero field splitting etc.) of the spin probe by tailoring the molecular features at synthetic level. These can be relevant in different schemes for Q-sensing as we shall discuss in the following paragraph.

2. Theoretical background and examples

Q-sensing offers the possibility of developing a radically new approach to probe complex systems, based on the quantification and optimisation of the information that can be obtained by an interacting quantum probe, as opposed to a classical one. In this framework, the basic techniques to optimize the extraction of information are provided by *(local) quantum estimation theory*, which allows one to account for the effect of quantum fluctuations in any measurement and which provides a tool for the characterization of signals and devices. The precision eventually achieved in the estimation protocol thus depends quite critically on the choice of the observable, and also on the kind of measurement that is performed. Within the framework of quantum estimation theory, one can establish which observable is in principle optimal and derive a theoretical maximum, which can be used as a benchmark for the performance of a given observable. The precision that can be achieved in the parameter estimation depends not only on the chosen observable, but also on the kind (for example, ensemble or projective) of measurement that is performed.

The mathematical concepts involved in this optimisation are the so-called *symmetric logarithmic derivative*, which helps in identifying and assessing optimal measuring techniques, and the *quantum Fisher information*, which quantifies the ultimate bounds to precision [15,16].

There are two main paradigmatic configurations for quantum sensing, which are schematically illustrated in the two panels of Fig. 1. In the first one (upper panel), a well known quantum system is prepared in a given initial state and then interacts with the system under investigation (red area). This may be a region of space where an external field is acting, or a generic sample characterized by an unknown parameter of interest (e.g., temperature, chemical potential, or some spectral parameter). After the interaction, which imprints in the system state an information on the parameter of interest, the system is subject to a measurement, in order to extract such information [17–24]. The second scheme consists of a quantum system embedded in a larger structure, thus the quantum probe represents a subsystem of the system under investigation, such as an individual spin within a spin cluster.

In any case, the estimation problem may be formulated as follows: a quantum system (the probe) is prepared in a state that belongs to the parametric family of density matrices $\hat{\varrho}_\gamma$, and an optimal detection scheme is devised in order to effectively estimate the actual value of γ. We consider a generic measurement performed on the quantum system, and denote by Y the measured observable; $p(y|\gamma) = \langle y|\hat{\varrho}_\gamma|y\rangle$ is the probability of the measurement outcome y, for a given value of γ. After repeating the measurement N times, the collected data can be represented by the vector $\mathbf{y} = \{y_1, ...,y_N\}$. This vector is then processed using an *estimator*$\hat{\gamma} \equiv \hat{\gamma}(\mathbf{y})$, i.e. a function of the data that provides a likely value of the unknown parameter. The estimator has an expectation value, which is obtained by the sum over all the possible measurement outcomes, weighted by the corresponding probabilities:

$$\overline{\gamma} = \int d\mathbf{y}\, p\left(\mathbf{y}\middle|\gamma\right)\hat{\gamma}(\mathbf{y}), \tag{1}$$

where $p(\mathbf{y}|\gamma) = \Pi_{k=1}^{N} p(y_k|\gamma)$, since the repeated measurements are independent on each other. The *precision* of this estimation is quantified

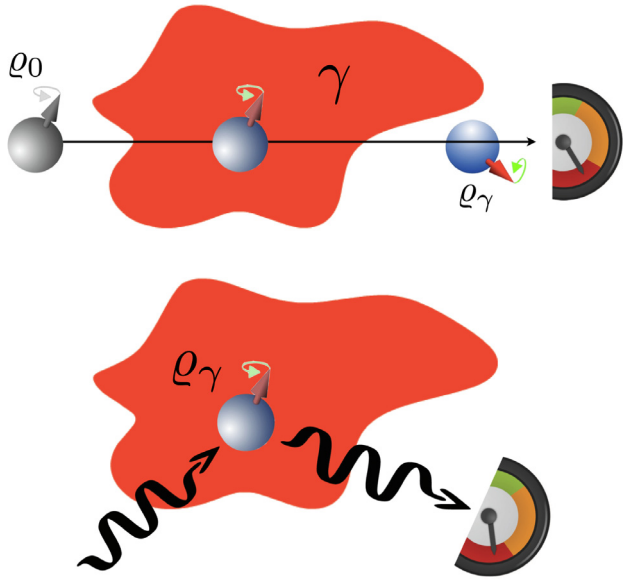

Fig. 1. Paradigmatic configurations for quantum sensing. In the upper panel, we consider a scheme where a quantum system is prepared in a given initial state ϱ_0, and then interacts with an external system or field under investigation (red area), which is characterized by the unknown parameter γ. After the interaction, which imprints information about γ into the state of the quantum probe, this is subject to a measurement, in order to extract such information. The lower panel describes a situation where the quantum probe is embedded in a larger structure, and its state contains information on some internal parameter of interest.

by the variance of the estimator:

$$V_\gamma = \int d\mathbf{y} p\left(\mathbf{y}\middle|\gamma\right)[\hat{\gamma}(\mathbf{y}) - \overline{\gamma}]^2. \tag{2}$$

The smaller is V_γ, the more precise is the estimation strategy. The precision of any unbiased estimator (i.e. an estimator such that $\overline{\gamma} \to \gamma$ for $N \gg 1$), is bounded by the so-called Cramèr-Rao (CR) inequality [25]:

$$V_\gamma \geqslant \frac{1}{NF_\gamma}, \tag{3}$$

where F_γ is the Fisher information (FI) of Y, which is given by

$$F_\gamma = \int dy\, p\left(y\middle|\gamma\right)[\partial_\gamma \log p(y|\gamma)]^2\,. \tag{4}$$

The Fisher information thus quantifies the information on γ that can be extracted by performing measurements of the observable Y on the state ϱ_γ. The best measurement, i.e. the one that allows the most precise estimate of γ, is the measurement that maximizes the FI, where the maximization is performed over all the possible quantum measurements.

The maximum is achieved for any observable having the same spectral measure of the so-called *symmetric logarithmic derivative* L_γ, i.e. the selfadjoint operator satisfying the equation:

$$2\partial_\gamma \varrho_\gamma = L_\gamma \varrho_\gamma + \varrho_\gamma L_\gamma. \tag{5}$$

The corresponding FI is usually referred to as the *quantum Fisher information* (QFI) and may be expressed as $H_\gamma = \mathrm{Tr}[\varrho_\gamma L_\gamma^2]$. Since $F_\gamma \leqslant H_\gamma$, the ultimate bound to precision in estimating γ by performing quantum measurements on ϱ_γ is given by the quantum CR bound:

$$V_\gamma \geqslant \frac{1}{NH_\gamma}. \tag{6}$$

In the following two Subsections, we consider two representative examples of parameter estimation through a generic spin of length S. This can in principle coincide with the spin of a single molecular nanomagnet, or with the collective spin of an ensemble of molecules. We start by considering the case of a spin that is prepared in an eigenstate of the spin projection along a given axis and that is probed in order to estimate the orientation of such axis. We then consider the case of a spin coupled to a magnetic field and in thermal equilibrium with a bath, which is used as a quantum thermometer.

2.1. Orientation of the quantization axis

We consider the case where the spin is initialized in an eigenstate $|M\rangle_\theta$ of the spin projection $S_\theta = \hat{\mathbf{n}}_\theta \cdot \mathbf{S} = \cos\theta S_z + \sin\theta S_x$ corresponding to the eigenvalue M. The goal is to estimate the value of the angle θ, which defines the quantization axis, by probing the state $|M\rangle_\theta$ through the measurement of an observable Y. In order for such estimate to be precise, two conditions need to be met: (*i*) the state $|M\rangle_\theta$ should depend strongly on the parameter θ (i.e. $|M\rangle_{\theta+\delta\theta}$ is supposed to differ as much as possible from $|M\rangle_\theta$); (*ii*) the observable Y should capture such dependence, through the dependence on θ of its statistics or expectation value.

We start by considering the case of an ensemble measurement, where the measurement outcome is deterministic and coincides with the expectation value of the observable Y. In particular, if Y corresponds to the spin projection S_z, the precision in the parameter estimation can be identified with

$$P\left(\left|M\right\rangle_\theta, S_z\right) = \frac{|\partial_\theta \langle S_z\rangle_\theta|^2}{\mathrm{Var}_\theta(S_z)} = \frac{2M^2}{S(S+1) - M^2}, \tag{7}$$

being $\langle S_z\rangle_\theta = M\cos\theta$ and $\mathrm{Var}_\theta(S_z) = \frac{1}{2}[S(S+1) - M^2]\sin^2\theta$. We note that P is independent on θ, and thus on the particular spin projection (in the xz plane) that is chosen as an observable. This results from the fact that the angular dependence of the numerator coincides with that of the denominator. For example, for small values of θ, the expectation value $\langle S_z\rangle_\theta$ depends weakly on θ, but also the fluctuations in the value of S_z are small; for $\theta \simeq \pi/2$, instead, both terms are large. From the above equation it also follows that the highest precision is achieved with the states that display the largest spin projection ($|\langle \mathbf{S}\rangle| = |M| = S$), whereas the state $M = |\langle \mathbf{S}\rangle| = 0$ is of no use for the parameter estimation (being $P = 0$). This result is in agreement with intuition: the longer the vector $\langle \mathbf{S}\rangle$, the better one can detect small variations in its orientation.

If one considers projective measurements, the relevant figures of merit are represented by the quantum and the classical Fisher information. The quantum Fisher information $H_\theta = H(|M\rangle_\theta)$ allows one to establish to which extent the above condition (*i*) is met for a given parameter-dependent state. In fact, according to the quantum Cramer-Rao inequality, H_θ gives the highest precision that can be achieved in the estimate of θ by performing a single measurement on the spin. In the present case, one can show that

$$H(|M\rangle_\theta) = 4[\langle K_\theta|K_\theta\rangle - |\langle K_\theta|M\rangle_\theta|^2] = 2[S(S+1) - M^2], \tag{8}$$

where $|K_\theta\rangle \equiv \partial_\theta|M\rangle_\theta$. Therefore, rather counterintuitively and unlike what is found for the case of ensemble measurements, the dependence of the state $|M\rangle_\theta$ on the angle is minimal ($H_\theta = 2S$) for $|M| = S$, and maximal ($H_\theta = 2S(S+1)$, assuming an integer S) for $M = 0$, which corresponds to a vanishing expectation value of all components of the spin operator ($\langle \mathbf{S}\rangle = 0$). It's also worth stressing that the scaling of the precision with the spin length is linear in the former case and quadratic in the latter one. This suggests that the projective measurement allows one to exploit the quantum features of the spin states in order to outperform the precision that can be achieved with the semiclassical (spin coherent) states $M = \pm S$. It's also worth noting that, if one has N copies of the spin state $|M\rangle_\theta$ and can thus repeat the measurement N times, both the classical and the quantum Fisher information (and thus the

precision that can be achieved in the estimate of θ) are enhanced by a factor N. This is not the case with an ensemble measurement, where the measurement outcome always corresponds to the expectation value of the observable, and thus the repetition doesn't provide any additional information on the system state.

The classical Fisher information $F_\theta = F(|M\rangle_\theta, Y)$ allows one to establish to which extent the above condition (*ii*) is met. In fact, through the classical Cramer-Rao bound, it gives the highest precision that is achievable in the estimate of the parameter θ by using a given observable Y. For the case $Y = S_z$, one can show that [26]

$$F(|M\rangle_\theta, S_z) = 2[S(S+1) - M^2] = H(|M\rangle_\theta), \tag{9}$$

independently on the angle θ. This means that any spin projection along the xz plane (where $\hat{\mathbf{n}}_\theta$varies locally) has a statistics that is maximally dependent on θ, and thus represents an optimal observable.

To summarize, the results of the present Subsection show that the parameter θ, which defines the quantization axis, can be estimated with the highest possible precision by measuring any spin projection in the xz plane, irrespective of the kind of measurement. The semiclassical states represent the best or the worst choice, depending on whether one performs ensemble or projective measurements, and they give rise to the same values of the precision in the two cases. In the case of projective measurements, the precision is maximized by the nonclassical states $M = 0$, for which it increases as a quadratic function of the spin length.

In molecular magnetism, the directions in the spin space are typically inequivalent, due to the crystal field interactions, reflected by the presence of anisotropic terms in the spin Hamiltonian. The anisotropic terms can play an important role in the estimation schemes discussed above. For example, if the field is oriented along the hard axis of a molecule, one can have a ground state that coincides with any of the above mentioned $|M\rangle_\theta$ states by properly tuning the intensity of the field. More generally, the anisotropies and their interplay with the magnetic field can be used to define different parametric families of (ground) states $|\psi\rangle_\lambda$ in which the system can be initialized and that can represent a resource for quantum sensing. (In particular, one should look for those anisotropies that enhance the dependence of the system state on e.g. the direction of the applied field, and thus increase the quantum Fisher information with respect to case of an isotropic system.) As far as the observables are concerned, there are experimental techniques that give access to the expectation value of a spin projection. These include the magnetization and torque measurements. In the former case one typically performs an ensemble measurement of the spin projection along the direction of the applied magnetic field, while in the latter one the relevant spin projection is perprendicular to the applied field and its expectation value can be nonzero only in the presence of magnetic anisotropy [27,28]. Projective measurements of single molecular spin states, which would allow to fully exploit the quantum features of the molecule states, have been realized in spin transistor geometries.

2.2. Spin as a quantum thermometer

Here we consider the case of a spin that is coupled to a magnetic field and in thermal equilibrium with a bath [29]. The spin can be used as a quantum probe in order to estimate the temperature T of the bath. As a starting point, we write the equilibrium state of the spin, which is given by:

$$\rho_T = \sum_{M=-S}^{S} p_M \Big|M\rangle\langle M\Big| = \frac{1}{Z}\sum_{M=-S}^{S} e^{-M\Delta/k_BT}\Big|M\rangle\langle M\Big|, \tag{10}$$

where Δ is the Zeeman splitting induced by the field and $Z = \sum_{M=-S}^{S} e^{-M\Delta/k_BT}$ is the partition function. The equilibrium state depends on the temperature through the occupation probabilities p_M of the states $|M\rangle$. The observable S_z is be the best suited to capture such dependence (see below). This is generally true since one can show that, if the system is prepared in the equilibrium state and it is probed in order to estimate the temperature, the Hamiltonian always represents an optimal observable.

As discussed in the previous Subsection, the precision allowed by an ensemble measurement can be identified with the ratio

$$P\left(\rho_T, S_z\right) = \frac{|\partial_T\langle S_z\rangle_T|^2}{\mathrm{Var}_T(S_z)}. \tag{11}$$

The derivative with respect to T of the expectation value of S_z is given by

$$\partial_T\left\langle S_z\right\rangle_T = \sum_{M=-S}^{S}\left(\partial_T p_M\right)M = \frac{\Delta}{k_BT^2}\mathrm{Var}_T(S_z), \tag{12}$$

being $\partial_T p_M = p_M(\langle S_z\rangle_T - M)$. The expectation value of S_z and its variance can be expressed as analytical functions of the temperature through the expressions:

$$\langle S_z\rangle_T = (1/2)f_{1/2} - (S+1/2)f_{S+1/2} \tag{13}$$

$$\mathrm{Var}_T(S_z) = S(S+1) + \langle S_z\rangle_T(f_{1/2} - \langle S_z\rangle_T), \tag{14}$$

where $f_\alpha \equiv \coth(\alpha\Delta/k_BT)$.

In the case of a projective measurement, the highest precision achievable in the estimation of the temperature is given by the quantum Fisher information of ρ_T, which can be shown to coincide with the classical Fisher information of the observable S_z. In fact, both the classical and the quantum Fisher information are given by:

$$H(\rho_T) = F\left(\rho_T, S_z\right) = \frac{\Delta^2}{k_B^2T^4}\mathrm{Var}_T(S_z). \tag{15}$$

From the above equations it follows that the values of $P(\rho_T, S_z)$ and $F(\rho_T, S_z)$ coincide for all values of the temperature and of the spin length S. Temperature estimation obtained through ensemble and projective measurements are thus equally precise. This results from the peculiarity of the Zeeman Hamiltonian, where the energy levels are all equally spaced. In the case of projective measurements, however, one can always increase the precision by repeating the measurement.

3. Some experimental cases

In the following, a special case of relaxation measurements in a molecular spin transistor is first discussed as an experimental realisation of local temperature sensor (Section 3.1). Few further cases in which spins can be used as local probes are also mentioned (Section 3.2). An intriguing case in which microwave photons are used for detection spin excitation in ensemble is then presented (Section 3.3).

3.1. Molecular spin transistor as local temperature sensor

The case of a single spin continuously measured by an auxiliary system can be considered as a further scheme for temperature sensing. Experiments on molecular spin transistor under microwave pulses have been recently reported in [30] and represent an example of local temperature sensor that merits further analysis. The molecular spin transistor consists of a single $TbPc_2$ molecule embedded in gold electrodes used in several spectacular experiments reported by the group of Prof. Wernsdorfer in Grenoble. In previous experiments, it has been clarified that the charge current passes through the organic radical in the phthalocyanine, which acts as quantum dot for electrical read out [31]. Due to the uniaxial anisotropy of the ligand field, the electronic magnetic moment of Tb lays in the ground $\pm$ 6 doublet. This is exchange coupled to the radical in the phthalocyanine and it is continuously measured by the charge current passing in the quantum dot: each flip generates a well defined jump in the conductance of this molecular transistor.

In the latest experiments reported in [30], the Tb magnetic moment ("spin" hereafter for simplicity) is polarised along one direction of the easy axis by an external magnetic field (60 mT). At the lowest temperature (40 mK), very few spin flip events can be observed during a long laps of time (seconds), due to the exceptional stability of the system. The experiments reported in [30] consist in monitoring the rate of spin flip after the application of heat (electromagnetic) pulses of different duration and intensity. The microwave frequency was not resonant with the possible electron or nuclear transitions, thus we can reasonably assume that this radiation was absorbed by the local environment rather than the molecular spin itself [32]. The protocol of pump (microwave pulse) and probe (electrical read out) can be repeated many times, and the probability of spin flip estimated by statistical analysis starting from the number of jumps in the conductance observed under different conditions (duration and intensity of microwave irradiation). It turns out that probability of spin flip follows an exponential relaxation whose characteristic time shortens as the power of microwave increases, as reasonably expected for a local temperature increase. If we assume that the local environment relaxes in a time scale longer than what we observe, we can infer the local temperature from the relaxation time of our Tb spin probe. Due to the difficulties in performing an independent set of measurements for calibration, we indirectly inferred the temperature from similar experiments performed on $TbPc_2$ molecule detected by a carbon nanotube [33]. From this experiment we learn that the main advantage in using this single molecule probe is the possibility to exploit the small size of this sensor (few nm), combined with the low energy ($< 10\,\mu$eV for one spin flip) of the molecular quantum dot. This allows one to detect small temperature variations with little perturbations of the local thermal bath. It is true that the actual experiments on molecular spin transistor are at present very challenging. Yet the scheme described here contains several features that can be exported in other contexts such as, for instance, spin impurities in solid state (P,Bi) coupled to (semiconducting) quantum dots for the electrical read out. Even more interesting can be spin sensors coupled to light emitters for the read out. Examples of optically detected EPR transitions in NV centers used as local temperature sensors have been reported in the literature [34–36].

3.2. Single spins as local probes

It turns out from previous discussion that the use of single spin as local probe represents a technological challenge but also a giant step ahead with respect to any classical sensor. Recently the possibility to use scanning microscope to detect single spin has been demonstrated in different geometries and this opens new perspectives for detection of local quantities. For instance, as concerns thermal properties, imaging thermal conductivity has been recently demonstrated by using scanning probe microscope with NV centres [37]. Thanks to their robustness at finite (>1 K) temperature, NV centres have been successfully used also for imaging the stray magnetic field in proximity of vortices in a high T_c superconductors [38]. In both the previous cases, optically detected ESR technique was employed to probe NV centre. It is interesting to note that the sensitivity achieved by this technique when used in continuos wave mode typically achieves $\mu T\,Hz^{-1}$ while sensitivities as high as $nT\,Hz^{-1}$ can be obtained in the pulsed wave regime (i.e. fully exploiting the long coherence times and the coherent manipulation of the NV centers).

A further remarkable experimental set-up makes use of Scanning Tunnelling Microscope (STM) combined with electromagnetic radiation: the application of microwave may induce electron transitions between the lowest spin levels of single spin centre and change the population of its levels that, in turns, is detected by the spin polarised STM tip. This technique has been recently applied to study the coherence life time of isolated Fe atom on MgO [39] as well as the r^{-3} power law scaling of the dipolar interaction between Fe spin centers on MgO with nanometric resolution [40]. A similar STM set up with radio frequency has been recently applied to detect resonant transitions within the electron and nuclear manifold of $TbPc_2$ molecules [41]. These scanning techniques with enhanced energy and spatial resolution for the study of molecular nanomagnets are very promising and can be used in different ways. For instance, we just mention here that the theoretical and experimental tools developed for estimating external physical parameters (such as temperature or magnetic field) can also be used for optimizing the estimate of the parameters entering the spin Hamiltonian. In fact, although the magnetic properties of nanomagnets and the parameters entering in their spin Hamiltonian can in principle derived through ab initio approaches, the most practical and widely applicable approach remains that of inferring their value from the experimental results.

To conclude this section we finally mention that further peculiarities of molecular spins can be exploited for quantum sensing at nanometer scale. Proposal to use the high spin of some molecules as an "amplifier" for local magnetic field sensors was discussed in [42]. Mononuclear molecules already offer a wide palette of interesting cases for which the zero field splitting of the ground multiplet can be tailored by a rational choice of the ligands thus providing the possibility to tune the ESR resonant frequency. On the other hand, the link to external world by organic ligands may offer the possibility to establish a direct (superexchange) coupling with the environment, thus providing alternative paths to probe electrical and magnetic features at distances below 10 nm. In particular, the possibility to place molecular centers directly on a functionalized surface or hybrid nano-architecture is very appealing for sensing applications.

Optical read out schemes, such as Optically detected ESR implemented with nitrogen-vacancy defects and extensively applied also for pentacene [43], can be envisioned in suitably functionalized molecular magnets [44] and open the way for the use of single molecule as local probe.

3.3. Use of spin ensembles

Spins are ideal sensors of the magnetic field. While nm-scale spatial resolution can be achieved with the detection of single spins, one may wonder whether the use of spin *ensembles* can still bring some quantum advantage. Actually, nuclear spin ensembles and NMR protocols are intensively explored for quantum sensing [2,45]. Electron spins have larger magnetic moments and their Larmor frequency in a static magnetic field of 0.1 to few Tesla falls in the microwave (MW) range. Under particular conditions (spin systems in cavity), efficient transfer of magnetic excitations to MW photons occurs. Single MW photon detection is nowadays feasible thanks to the most advanced techniques [46]. The detection of few magnetic excitations in a spin ensemble is achievable by efficient conversion to MW photons [47], as depicted in Fig. 2. Briefly, the magnetic system is inserted in a microwave cavity and it achieves the so-called strong coupling regime, for which the spin-photon coupling Ω is larger than both the cavity decay rate κ and the line width Γ of the spin system [48]. The use of an ensemble allows one to enhance the naturally small coupling of single magnetic dipole to photons by a factor $\sqrt{N}$, being N the number of the coupled spins [49]. At the same time, it allows one to achieve an efficient transfer of information from the spin system to photons and to enhance the probability of radiative emission in the cavity, thanks to the Purcell effect [50]. On the other hand, the use of large number of spins has the drawback of introducing inhomogeneous broadening and, therefore, an enhancement of the line width Γ. The detrimental effect of such line broadening can be reduced in the strong coupling regime by means of the cavity protection effect [51,52].

3.3.1. Application to dark matter particles detection

An intriguing application of the use of spin ensembles has been recently proposed for the detection of "cold" dark matter particles, namely the *axions*[53]. The detection relies on the fact that the axions

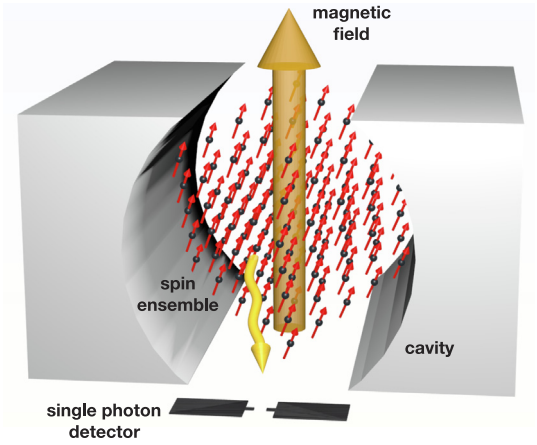

Fig. 2. Spin ensemble in a microwave cavity. At low temperature the system is driven in strong coupling regime for which an efficient transfer of magnetic excitation to microwave photon occur. The detection of single microwave photon may allow sensing few/one of the collective magnetic excitation in spin ensemble [47].

generate an effective oscillating magnetic field (B_a) that may interact with spins [54]. The expected mass of the axions typically spans from the 0.1 to 1 meV, corresponding to B_a values 10^{-22} T< B_a < 10^{-21} T and to equivalent frequencies in the 10 to 200 GHz range. A spin ensemble in its ground state, at vanishing temperature and in a static magnetic field B_0, oscillates at a Larmor frequency that can be tuned at resonance with the effective axions's field B_a (*i.e.* with the desired target mass). When the resonance condition is met, a spin excitation is generated by the interaction with dark matter particles. Since these events are very rare, their detection requires the spin state lifetime to be sufficiently long and the implementation of an efficient read out of the spin excitation (see above). The experiment proposed for the axion detection [53,55] thus requires that the power of the microwave photon emitted after axion-spin event should be larger than the noise of the whole apparatus, including the magnetic system, the microwave cavity and the (single) photon detector. As discussed in Ref. [53], the power generated by the axion-spin interaction is estimated to be proportional to the number N of the spins and to the lifetime of the magnetic excitations. Thus, also taking into account the long de Broglie wavelength of axions, large spin ensembles are required. Suitable spin systems should be characterized by high spin-photon coupling ($\Omega \gtrsim 10$ MHz) and sharp line widths (Γ smaller than a few MHz). At present these requirements are fulfilled by the best specimens of Yttrium Iron Garnet ($Y_2Fe_5O_{12}$) [56], which are typically available in spheres of ≈ 1 mm diameter [55]).

3.3.2. Coherent coupling molecular spin ensembles to microwave

In this context the relevant figures of merit for the magnetic detectors are the lifetime of the spin ensemble (or equivalently the line width Γ) and the spin photon coupling. It is interesting to see how the characteristic Ω and Γ values of molecular spins compare with those of inorganic systems. In principle, one can start to enhance the coupling of each single magnetic moment in the ensemble with the effective field B_a by using high spin centers and large g-factors, as provided by rare earths diluted in a non-magnetic (molecular) matrix [57]. Yet, high spins also enhance the dipole-dipole inter-molecular interaction with the result that large dilutions are required to have narrow line widths. This also has the drawback of reducing the number of spins per unit of volume available for the coupling to the resonator mode. Single ion molecules based on low spin metal centers, such as copper or oxo-vanadium (vanadyl), may exhibit sharper line widths, with concentrations of few per cents in non magnetic matrix, as reported for $Cu(mnt)_2$ and VOPc derivatives [48]. For the latter molecule, the high cooperativity regime ($\Omega^2/\Gamma\kappa > 1$) has been experimentally demonstrated [58]. Although still far from values achieved for YIG [59,56], these systems also exhibit hyperfine splitting of the resonant line that may possibly be exploited for multi-tone detection. An alternative way to reduce inhomogeneous broadening is to exploit the exchange narrowing effect, which is typically exhibited by concentrated samples of organic radicals. This is similar to the narrowing effect observed in atomic vapor cell sensors, where high densities are used to average out the decoherence caused by atomic collisions [60]. For instance, ensembles of DPPH or PyBTM cooperativity values exceeding 10^3 and a strong coupling regime persisting above 30 K can be achieved [61]. Whether these features improve or vanish in the mK range is still matter of research, and has been so far tested only in few experiments [62]. Conversely, the high performances of YIG are related to spin excitations (magnons) in the long range ordered ferrimagnetic state. This suggests to look at spin excitations in insulating molecular systems with long-range magnetic order. For this purpose, cubic systems with low magnetic anisotropy, such as Prussian blue analogues, could be good candidates, and we have actually observed strong coupling values for CsNiCr systems [63]. Unfortunately, these materials tend to form granular samples or, even in the form of (quasi) mono-dispese nanoparticles, to produce line widths much larger than 10 MHz [63]. This problem could be solved by using alternative growth methods. Remarkably, line width as narrow as that in YIG (< 1 MHz) have been recently reported for organic-based ferrimagnetic vanadium tetracyanoethylene thin films [64,65], demonstrating that molecular systems can actually be a valid alternative to inorganic magnets.

Fig. 3 summarises some recent results and gives us the opportunity to compare coupling strength and line width of some representative molecular systems with values reported in the literature. The diagonal line $\Omega = \Gamma$ indicates the threshold above which strong coupling is achieved. Note that, due to dependence of the spin polarization on the temperature, the coupling strength increases as the temperature is

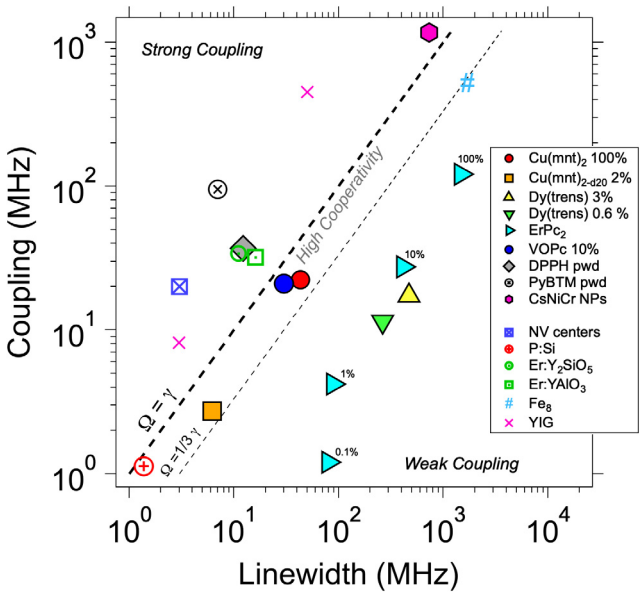

Fig. 3. Collective coupling strength Ω as a function of the ensemble line width Γ measured for different molecular spin systems (see legend) at 2 K (only the point for VOPc is at 0.5 K). The full temperature dependence of the results is given in [48]. Values from literature concerning spin ensembles at low temperatures are added for comparison: NV centers ([66]), Er^{3+} dopant in inorganic crystals (from [67,68]), P impurities in Si (from [69]), Fe_8 (from [70]). Dashed rectangles show the typical working ranges for NV centers (blue) and Er^{3+} ions in inorganic crystals (green) at temperatures between 10 and 50 mK. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

decreased. It's also worth noting that molecular spin systems compare well with other spin impurities in inorganic matrix, like for instance nitrogen vacancy (NV) centers in diamonds or Er^{3+} ions diluted in inorganic crystals.

Finally, it's worth noting that the spin-photon coupling and the coherence time of spin systems are also relevant figures of merit for magnonics and spintronics [59]. Therefore, the optimization of these parameters may allow the use of molecular spin ensembles for further experiments and applications in quantum technologies [64,71].

4. Final remarks

By the time writing, individual spins, especially NV centers in diamond, are becoming reliable quantum probes for estimating values of external electric and magnetic fields, or as thermometers. Molecular spins represent a possible alternative for these applications, with potentialities that are still largely unexplored. These molecular systems are indeed widely engineerable at the synthetic level in terms ground spin state, magnetic anisotropy, energy level pattern, as well as for possibility to choose external ligand to interface the central spin with external world. In this respect, the possibility to use linkers that may selectively bound spin markers to biological systems is particularly appealing for applications. Nuclear and electron spin resonance techniques are widely used in this field and an extensive catalog of organic radicals and spin markers is already available in literature. Here we may wonder whether the long coherence time of some molecular spins, e.g.. radicals, and the use of protocols developed for quantum sensing may enhance conventional magnetic resonance technics or if single molecular spins can be used as local probes. For instance, in order to fully exploit quantum mechanics for sensing, pulse sequences such as Ramsey or Rabi measurements as well as dynamical decoupling protocols have been developed. These can be used for instance to extract the quantum phase of the spin sensor interacting with the signal under investigation [2]. Molecular spins can be potentially employed in this way, as the efficiency of these sequences has been demonstrated for spin ensembles [72], and this aspect may deserve further attention in future.

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