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Abstract. Most muon spin rotation (μSR) experiments are based on the coupling between a muon (a quantum, spin-$\frac{1}{2}$ particle) and a macroscopic magnetic field, either applied externally (as is often the case for experiments on superconductors) or produced internally (due to, for example, the alignment of spins in an ordered magnet). This article will review some experiments which have exploited this, essentially classical, interaction, but then will consider cases in which a more intrinsically quantum mechanical approach is needed. In these cases, one cannot ignore the back reaction of the muon's effect on the system it is probing. It can be profitable to consider the muon as a qubit, evaluating the decoherence of quantum information injected by the muon into the environmental spin system. Experiments focussed on this approach are underpinned by DFT+μ calculations (density functional theory with an included muon) and give rise to an excellent agreement between theory and experiment and open up new ways of using the muon as a probe.

1. Introduction

Muon spin rotation (μSR) relies on the phenomenon of Larmor precession. A magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\boldsymbol{B}$ experiences a torque $\boldsymbol{G} = \boldsymbol{\mu} \times \boldsymbol{B}$ which is equal to the rate of change of angular momentum $\boldsymbol{S}$ where $\boldsymbol{\mu} = \gamma \boldsymbol{S}$ (with γ the gyromagnetic ratio) and hence precession occurs with angular frequency $\omega = \gamma B$. But the phenomenon can also be considered using a quantum-mechanical, rather than a classical, argument: a Hamiltonian $\hat{H} = \hbar\gamma B\hat{\sigma}_z/2$ acting on a state $|\uparrow_x\rangle = \frac{1}{\sqrt{2}}(|\uparrow_z\rangle + |\downarrow_z\rangle)$ results in interference terms in the superposition which lead to the same outcome, precession at $\omega = \gamma B$ (for details, see Chapter 4 of [1]). So is μSR a classical or quantum phenomenon? It would seem from the above discussion that either account will do.

This article will consider this question in detail, but first in Section 2, I will set it in the context of my own work in μSR. Then, in Section 3, I will answer the question by providing an example in which the quantum mechanical nature of the muon spin cannot be ignored. In Section 4, I will provide a further case in which quantum mechanics plays a determinative role in what is observed in a muon experiment and in the final section I will give an outlook for the implications for studies on frustrated magnets with muons.

2. The muon interacting with magnetic fields of macroscopic origin

The application of μSR to studies in magnetism usually proceeds by measuring the temperature dependence of the internal field. A simple example would be the cubic ferromagnet EuO [2], though this was an experiment that proved hard to perform due to the reactivity of EuO with air. Such studies seem straightforward, but there are a number of surprising subtleties which I outline in this section.

2.1. Organic magnets

μSR was initially applied to materials which were chemically rather simple. Nevertheless, a growing field in the last few decades has been that of organic magnetism [3], substantially stimulated by the discovery of a purely organic ferromagnet, *para*-nitrophenyl nitroxide (*p*-NPNN) [4]. The magnetic moment arises from the nitrophenyl nitroxide radical, but the chemical groups to which the radical is joined determine the crystal structure, and this determines the intermolecular overlaps which are only sometimes of the right form to give rise to a ferromagnetic ground state. Despite its chemical complexity, *p*-NPNN exhibited a clear, single frequency μSR signal [5,6], and hence spawned a series of studies in related nitrophenyl nitroxide systems [7–12]. This led to the discovery of some highly idealised one-dimensional ferromagnets [13,14], and also to a study of a chiral nitronyl nitroxide system [1].

The transition temperatures of purely organic systems have remained rather low, and so greater interest has been shown in molecular systems in which the magnetic moment may arise from a transition metal or lanthanide ion, but with the groups linking up the ions being organic [15]. Of particular importance are single molecule magnets, in which a small well-defined cluster of magnetic ions are linked by organic groups to form a molecular unit. These are used to study quantum tunnelling of magnetism [16] and have applications as potential qubits [17]. Comparison of μSR data on single molecule magnets with protonated or deuterated ligands demonstrate that the muon spin polarization is relaxed by electron spin fluctuations which themselves are dephased by the nuclear spin bath [18], and μSR has also been used to probe the low-temperature dipolar ordering in crystals of single molecule magnets [19].

2.2. Correlated oxides

μSR data on various oxide systems, such as nickelates [20, 21] and manganites [22, 23] have been used to demonstrate the effect of doping on the magnetic structure across a family of materials. Sometimes the muon signal can be remarkably complex, such as found in the charge-ordered triangular antiferromagnet $AgNiO_2$ which exhibits six distinct muon precession signals [24]. Muon data have also been pivotal in identifying spin Jahn-Teller antiferromagnetism in compounds where a magnetically-driven lattice distortion is necessary for establishing magnetic order [25, 26]. Although neutron diffraction remains the technique of choice for identifying magnetic ground states [27], μSR is particularly effective when the ordered moment is weak and arises from an element that hinders neutron measurements, such as osmium [28, 29] or iridium [30, 31].

2.3. Low-dimensional molecular magnets

Quasi-one-dimensional magnets exhibit a large anisotropy in their magnetic exchange constants. A prototypical example is Sr_2CuO_3 in which copper-oxygen chains show a strong intrachain exchange of around 1300 K, but the weak interchain interactions result in a magnetic ordering temperature of only 5 K, as determined by μSR [32]. In an attempt to find an isostructural material based on cobalt, $LaSrCoO_3$ was synthesized by a novel topotactic method that would have left the cobalt in an unusual Co^{I} oxidation state. This compound was difficult to characterise with laboratory susceptibility methods since the novel synthesis route resulted in nanoscopic elemental cobalt impurities which dominated the response in a SQUID. μSR is ideal in this application since it responds to the majority phase, and the experiment exhibited a precession signal that persisted to well above room temperature [33] [Fig. 1(a)]. This pointed to extremely strong interchain interactions, and these were found to be due to the presence of hydride (H^-) ions that had become incorporated into the structure; the compound was actually $LaSrCoO_3H_{0.7}$, although the presence of hydrogen was not apparent from laboratory x-ray diffraction. This experiment demonstrated the effectiveness of the filled $1s^2$ orbital in the hydride ion as a mediator of superexchange interactions [33].

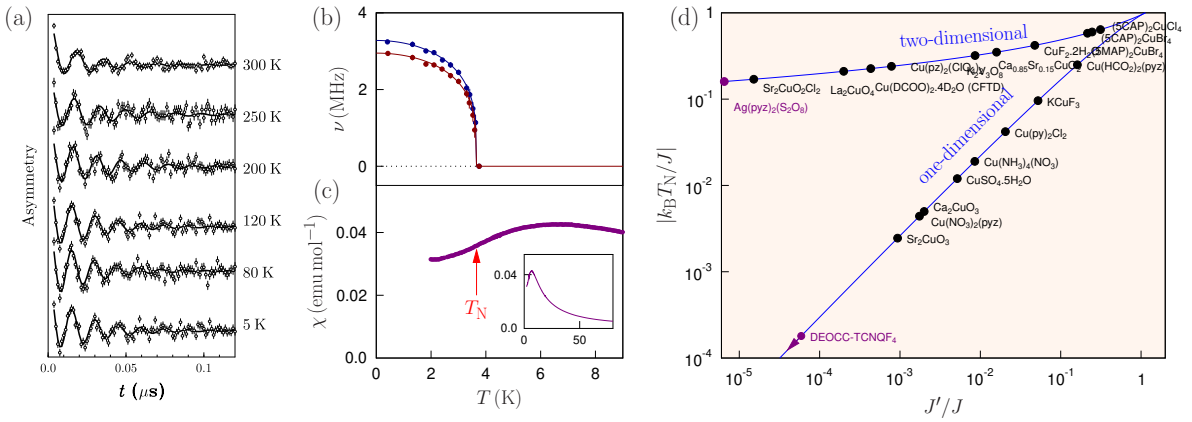

Figure 1. (a) The precession signals measured in $LaSrCoO_3H_{0.7}$ [33]. The measured (b) μSR precession signal and (c) magnetic susceptibility χ (measured by Jamie L. Manson) in the mixed-anion coordination polymer $Cu(HCO_2)(NO_3)(pyz)$ [34]. The inset in (c) shows a wider temperature dependence and illustrates the large hump which is associated with the correlations developing along the chains. The transition to three-dimensional ordering is invisible in χ, but glaringly obvious from the μSR measurement. (d) The Néel temperature T_N scaled by J as a function of the anisotropy of quasi-one-dimensional and quasi-two-dimensional antiferromagnetic spin-half chains with T_N determined from μSR. The anisotropy $|J'/J|$ is evaluated from $|J'/J| = \exp(b - 4\pi\rho_s/(k_B T_N))$ (one-dimensional) and $|J'/J| = (4cx)^{-1}[\ln(\lambda x) + \frac{1}{2}\ln\ln(\lambda x)]^{-1/2}$ where $x = J/(k_B T_N)$, $\rho_s = 0.183J$, $b = 2.43$, $c = 0.233$ and $\lambda = 2.6$ [35]. For $DEOCC\text{-}TCNQF_4$, T_N has not been determined, but it is known that $T_N < 0.02K$ and $|J'/J| < 10^{-4}$ [36, 37].

It is not just the insensitivity to impurity phases that gives μSR an advantage; three-dimensional order in intrinsically low-dimensional systems can be challenging to identify by other methods, but is straightforward for μSR. For example, copper pyrazine dinitrate $[Cu(C_4H_4N_2)(NO_3)]$ contains $S = \frac{1}{2}$ Cu^{2+} ions are linked via pyrazine molecules to form chains. The intrachain exchange $J/k_B \approx 10.3$ K) [38], but no 3D long–range order was found by heat capacity measurements performed down to 70 mK [39]. However, μSR experiments have shown that magnetic order sets in below $T_N = 107(1)$ mK, leading to a value of the ratio $|k_B T_N/J| = 0.0103(1)$ [40]. Bulk thermodynamic measurements are rather ineffective at determining the onset of three-dimensional order in highly anisotropic systems, principally because the entropy associated with such transitions can be very small so that the onset of magnetic order makes a negligible contribution to the measured heat capacity or susceptibility [see, for example, Fig. 1(c)]. As the correlation length ξ in an antiferromagnetically-coupled spin chain increases on cooling, the heat capacity exhibits a rather broad maximum centred around $T \sim J$ as the spin entropy falls as the spins begin to correlate. When three-dimensional ordering finally becomes established (driven by the weaker interchain exchange J' which allows the system at low temperature $T \ll J/k_B$ to respond to the fact that it is, in fact, three-dimensional), there is little entropy left to expel and the peak in the heat capacity (or feature in the susceptibility) will be tiny, its size decreasing with the anisotropy $|J'/J|$, as has been demonstrated in simulations [41]. In contrast, μSR identifies such transitions extremely easily, as once three-dimensional order is established, a beautiful spin precession signal suddenly appears [see, for example, Fig. 1(b)], as has been shown in numerous studies on low-dimensional molecular magnetic systems [34, 42–49]. μSR measurements determine T_N and hence allow an estimate of the anisotropy [37] [some collected results are given in Fig. 1(d)]. This approach has led to the discovery of the most idealised spin-$\frac{1}{2}$ Heisenberg antiferromagnetic quasi-one-dimensional [36]

and quasi-two-dimensional systems [46]. Moreover, low-dimensional magnets can also exhibit interesting chiral behaviour [50] and potentially realise Kitaev interactions, a field to which μSR has contributed by studying the low-temperature ground states [31, 51].

2.4. Frustrated magnets

Ordered ground states are easily studied by μSR, but the technique is arguably even more useful when order is avoided by frustration and μSR reveals a slowly fluctuating ground state that is realised in a variety of disparate systems [18, 52–54]. A particularly interesting case is that of spin ice, in which μSR established a very large internal field due to the frozen spin ice state [55]. Magnetic monopoles emerge as the natural excitations in this system [56], but in this emergent picture the "vacuum" that has been substracted is a strongly magnetic background [57]. The role of muons in spin ice became controversial following a report of a determination of the magnetic monopole charge from low transverse-field μSR data [58], but this was refuted by a subsequent experiment [59] and the earlier data were shown to be consistent with demagnetization fields in the sample holder [60]. Demagnetization fields are of course important for the correct interpretation of μSR data on ferromagnets or on other systems which are magnetized by the application of a magnetic field during the experiment [61].

In fact, it is possible to gain information from studying the effect of demagnetizing fields outside a frustrated sample [62]. If low-energy muons can be made to operate at very low-temperatures, this proximal magnetometry method could be an attractive method of studying spin fluctuations due to monopole excitations in spin ice [63], although similar effects can be obtained using SQUID magnetometry of the spin noise [64].

2.5. Superconductors

μSR has been extensively used to study superconductors [65], extracting the penetration depth and hence the superfluid stiffness [66–68], examining vortex lattice melting [69] and determining the nature of the pairing. Wherever the muon sits inside the crystallographic unit cell, it will uniformly sample the magnetic field distribution produced by the vortex lattice produced by the applied magnetic field. The technique was well placed to make a major contribution in studying the iron-based superconductors discovered towards the end of the first decade of this century (see e.g. [70–75]). A particular highlight was the effect of molecular intercalation on FeSe which had the potential to induce a fivefold increase in the superconducting transition temperature [76], an effect which in some systems could be chemically controllable [77, 78].

2.6. Muon sites

Though μSR provides a direct measurement of the magnetic field at the muon site, the precise location of that muon site inside the unit cell has been hard to tie down. Moreover, the unknown effect of the positively-charged muon on its local environment raises the important question of how much of the probed behaviour is intrinsic to the material or an effect of the presence of the implanted muon itself. If the final muon stopping state involves relatively little contact hyperfine coupling, then the stopped muon can be treated as a bare particle, albeit 'dressed' by interactions with the electronic system, perhaps by acquiring a screening cloud of electronic charge in a conducting system, or perhaps by acquiring a strain field in an insulator. If instead the muon forms a bound paramagnetic state such as muonium, or induces a large spin density at its position, the muon's effect on its environment can be significant. This effect is not necessarily a drawback, but can be exploited as studied extensively in semiconductors [79, 80]. Moreover, in conducting polymers the reaction of muonium and the conjugated chain produces a highly mobile unpaired electronic spin which is injected into the polymer chain. Every time this electronic excitation briefly revisits the muon, the muon–electron hyperfine coupling is turned on and then off, so that successive visits progressively relax the muon polarization. Measurement of

the magnetic field dependence of this relaxation yields the spectral density function associated with the excitation random walk (because the muon spin relaxation rate is connected with the noise power (or spectral density), in the fluctuating magnetic field at the muon Larmor frequency [81–83]. Even without an injected electronic excitation, a muoniated radical state can be used to infer molecular dynamics in many organic systems, for example liquid crystals [84].

An avoidance strategy that has been deployed in the quest for muon-site determination is to deny that knowledge of the muon site is even necessary. If the goal is to measure a magnetic moment of a particular magnetic ion in a structure, perhaps the muon site is not really needed and one could include our quantified ignorance of it in the calculation? This approach leads to a Bayesian method [85] that is based on the fact that evaluating the dipolar field, given the muon site and the magnetic moment, is an easy problem [86], but the reverse problem (inferring the magnetic moment given the experimentally measured dipolar field) is hard. The inversion between the two calculations is accomplished using Bayes' theorem and is surprisingly effective.

Nevertheless, a more direct attack on the muon-site problem is clearly needed and therefore a density functional theory (DFT) ab-initio approach [87] has been developed to determine the muon site [88, 89]. This method can be termed DFT+μ, since it is an electronic structure calculation with an included muon. The total energy of a supercell of the structure to be modelled is evaluated but with a muon located at a trial site. The positions of the atoms in the super- cell are then relaxed so that the muon can move and nearby ions distort. If this is carried out with a large number of initial trial sites then the lowest-energy site can be identified, as well as any associated muon-induced distortions predicted and characterised [90–92]. In most cases, it seems that the effect of the muon is relatively benign (e.g. in superconductors that exhibit time-reversal symmetry breaking [49]) but there are cases where the muon can play an important role, such as Pr-based pyrochlores [93], an important case I will return to.

3. The muon as a qubit

3.1. Classical broadening

The preceding section has detailed various cases (mainly focussing on examples from my own work) in which the muon is coupled to a magnetic field, either produced internally to the sample or applied externally. The magnetic field can be static or dynamic, but in either case the key interaction is between the muon and a macroscopic field. Thus Larmor precession (or a dynamic analogue in the case of a fluctuating field) arises because although the muon is influenced by the macroscopic field, the macroscopic field is not influenced by the muon. This rather straightforward observation runs deep in the history of solid state physics and one can see its effect in the phenomenon of the broadening of lines in nuclear magnetic resonance (NMR) [94,95]. Nuclear spins in a solid subjected to a magnetic field gives rise to a resonance line which is broadened due to the effect of coupling to nearby nuclei. Since these nearby nuclei are weakly coupled to each other and to the magnetic field, their orientations are essentially random and the line broadening is close to Gaussian [94]. Similar assumptions underpin the prediction of a zero-field effect due to Gaussian random distributions, the so-called Kubo-Toyabe relaxation function [96], that was so spectacularly confirmed by μSR experiments [97]. The muon passively responds to its statistical environment.

3.2. Quantum systems and their environment

One might have therefore expected to observe a Kubo-Toyabe relaxation function in an inorganic fluoride, such as NaF, which shows no electronic magnetism but has numerous nuclear spins whose orientation is expected to be random. Instead, it is found that the muon couples strongly to two fluorine nuclei, giving rise to coherent oscillations observed in muon spectra [98], an effect that is observed in numerous inorganic fluorides [99, 100], fluoropolymers [101–103] and

fluorine-containing molecular magnets [104]. The effect is distinct from the van Vleck/Kubo-Toyabe scenario because in this environment the muon is no longer passive, but actively engaged in coupling with nearby spins, influencing them as well as being influenced by them. In fact, the effect is a direct result of the entanglement between the fluorine and muon spins in the F–μ–F unit [104]. Fluorine nuclei are the best choice for demonstrating this effect: they have spin $I = \frac{1}{2}$ with 100% abundance, and fluoride ions are very electronegative, making their surroundings particularly attractive sites for positive muons. The fluorine ionic radius is small and a muon can get very close, so that together with the large fluorine nuclear moment the coupling is strong, enhancing the effects of entanglement against environmental decoherence. Although fluorine is special, it is not unique and it is possible to observe somewhat similar effects in systems containing hydride ions [105–107] [coupling to the proton ($I = \frac{1}{2}$)] and even in certain A15 compounds [coupling to ^{51}V ($I = \frac{7}{2}$) or ^{93}Nb ($I = \frac{9}{2}$) nuclei] [108].

The F–μ–F state forms a well-defined quantum system $\mathcal{S}$ which evolves due to the action of the Hamiltonian. The action of interactions with the environment $\mathcal{E}$ cannot however be completely ignored, and these result in decoherence [109], a process whereby quantum information leaks out from $\mathcal{S}$ into $\mathcal{E}$ where it can no longer be discovered. Of course $\mathcal{S} \otimes \mathcal{E}$ undergoes purely unitary evolution and its von Neumann entropy, $S = -\mathrm{Tr}\rho \log_2 \rho$, where ρ is the density matrix of the $\mathcal{S} \otimes \mathcal{E}$ composite object, is constant. However, we are restricted to monitoring the reduced density matrix of the system, $\rho_{\mathcal{S}} = \mathrm{Tr}_{\mathcal{E}}\rho$, obtained by tracing out the degrees of freedom of the environment, and the entropy of $\mathcal{S}$ will tend to increase with time [110]. For example, including the smaller effect of the weaker coupling to the eight next-nearest-neighbour fluorine nuclei in CaF_2 (which adopts a simple fluorite structure in which only the nuclear moments on fluorine need to be included) results in a broadening of the four doublet energy levels in isolated F–μ–F into four bands of energy levels [Fig. 2(a)]. The coherences between these energy levels are shown in the two-dimensional plots, where the size of the point indicates the amplitude of the interference term between energy levels $\hbar\omega_1$ to $\hbar\omega_2$ [Fig. 2(b)]. The overall structure for isolated F–μ–F is retained when including the more distant couplings, but a richer frequency spectrum results and this mixture of frequencies is responsible for the dephasing of the precession signal observed in experiments [111] [see Fig. 2(c)].

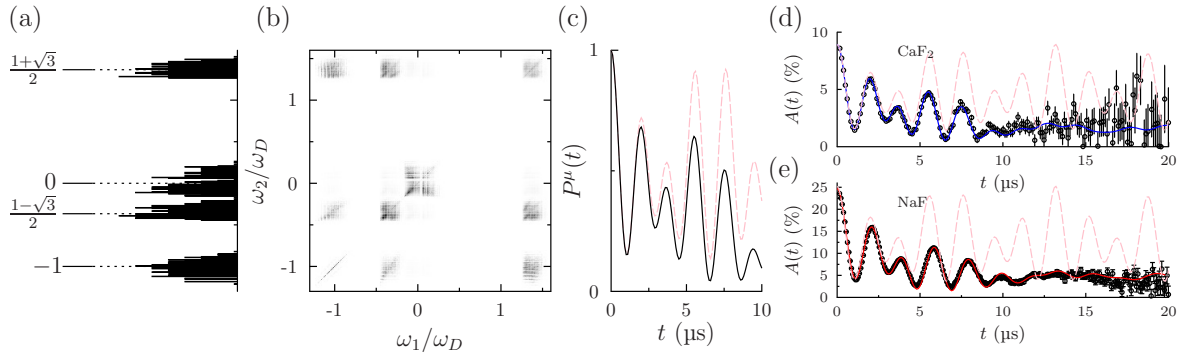

Figure 2. (a) The energy levels of the isolated F–μ–F state (four doublets) broaden into four bands. (b) The amplitude of the quantum interference between energy levels $\hbar\omega_1$ and $\hbar\omega_2$ is represented by a grey scale. (c) This results in the oscillating signal relaxing (solid line) compared to the isolated case (pink dashed line). Data and fit for (d) CaF_2 and (e) NaF. Figure adapted from [111].

One can consider this effect from the point of view of von Neumann entropy. For an isolated F–μ–F state, the spin-polarized muon begins in a pure state with zero entropy (it acts as a

qubit), but this entropy oscillates with time as the quantum information rattles around the F–μ–F unit. The muon does however periodically return to a pure state. Switching on the additional interactions results in the information 'leaking out' of the F–μ–F unit into the wider network of fluorine nuclei and the muon entropy rises to close to unity. The information transferred from the muon remains in the environment and never completely returns to the muon [111]. The muon polarization $P^\mu(t)$, can be calculated as $P^\mu(t) = \frac{1}{2}\left\langle \mathrm{Tr}\left[\sigma^\mu_{\hat{n}} \exp\left(\frac{-\mathrm{i}\hat{\mathcal{H}}t}{\hbar}\right)\sigma^\mu_{\hat{n}} \exp\left(\frac{\mathrm{i}\hat{\mathcal{H}}t}{\hbar}\right)\right]\right\rangle_{\hat{n}}$, where $\langle\ldots\rangle_{\hat{n}}$ represents the angular average over $\hat{n}$ (appropriate for an experiment on a polycrystalline sample), and $\sigma^\mu_{\hat{n}}$ is the Pauli spin operator for the muon in the direction of $\hat{n}$. The problem is that the dimension of the Hilbert space is $2\prod_{i=1}^{M}(2I_i+1)$, where the product is over the M nuclei included in the calculation (and the initial factor of two is due to the muon spin), and this dimension grows exponentially with M, making this method prohibitively computationally expensive when too many nuclei are included. The trick [111] is to evaluate a restricted set of the closest few shells of neighbouring nuclei, but then to slightly enhance the coupling to these shells by an amount given by the contribution to the van Vleck second moment of the nuclear spins we have ignored (a small correction since contributions to the second moment scale as $1/r^6$ where r is the distance to the spins, and the infinite sum is easy to evaluate). In this way, our finite set of neighbours act as a proxy for the entire reservoir of environmental spins. Data can then be fitted using essentially two parameters, one representing this correction (that can be compared with theory) and the other representing the distortion of lattice due to the muon (which pulls in the two fluorine nuclei towards the muon, an effect that can be compared with DFT+μ calculations). The fits and agreement with theory are impressive and have been carried out for CaF_2 [Fig. 2(d)] and NaF [Fig. 2(e)] [111] (the latter case requiring quadrupolar effects to be included), other inorganic fluorides [112], and A15 compounds [108].

4. The muon interacting with a singlet state

Quantum-mechanical effects also become of central interest when the muon interacts with a singlet state. Usually, one would think that the interaction between a muon and a singlet state is non-existent. For example, below the spin-Peierls transition the muon can only respond to defect spins [113] since the non-magnetic spin singlet is invisible. In many solid-state systems, a singlet ground state $|\mathrm{G}\rangle$ is produced by the effect of the crystal field and can take a typical form $|\mathrm{G}\rangle = \frac{1}{\sqrt{2}}(|J\rangle + |-J\rangle)$ with $J > \frac{1}{2}$. This state has zero magnetic moment since $\langle \mathrm{G}|\,\hat{\boldsymbol{J}}\,|\mathrm{G}\rangle = 0$. A muon cannot couple to this state, particularly because there would be no matrix element of the dipolar coupling (the electron and muon cannot flip-flop since $|J\rangle$ and $|-J\rangle$ are separated by more than one unit of angular momentum). There may also be an excited state $|\mathrm{E}\rangle$, orthogonal to $|\mathrm{G}\rangle$, which is separated from the ground state by a crystal field gap Δ and which could take the form $|\mathrm{E}\rangle = \frac{1}{\sqrt{2}}(|J\rangle - |-J\rangle)$. A muon cannot couple to this either, but the presence of a hyperfine coupling $A\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{J}}$ can mix $|\mathrm{G}\rangle$ and $|\mathrm{E}\rangle$, so that they contain small admixtures of each other. The ground state now splits into several levels depending on the nuclear quantum number I_z and these take the form

$$|\mathrm{G}(I_z)\rangle = \frac{1}{\sqrt{2}}(|J\rangle + |-J\rangle) + \frac{AJI_z}{\Delta}\frac{1}{\sqrt{2}}(|J\rangle - |-J\rangle), \tag{1}$$

and now $\langle \mathrm{G}(I_z)|\,\hat{J}_z\,|\mathrm{G}(I_z)\rangle = 2AJ^2I_z/\Delta$, so these states are magnetic [see Fig. 3(a)]. If they are all occupied, there is no average moment (I_z takes both positive and negative values) but the muon can couple to these levels via dipolar coupling to the nuclear degrees of freedom. We then expect the muon to detect a moment intermediate in size between nuclear and electron moments at temperatures $T \ll \Delta/k_\mathrm{B}$ where only the ground state multiplets are occupied. When

$T \gg \Delta/k_B$, the effect should disappear as the multiplets in the excited state produce an opposite effect. The temperature dependence should follow a $\tanh[\Delta/(2k_BT)]$ form. My description above is essentially the zero-field version of an effect predicted by Bleaney for hyperfine enhancement of nuclear moments in singlet state systems in NMR [114].

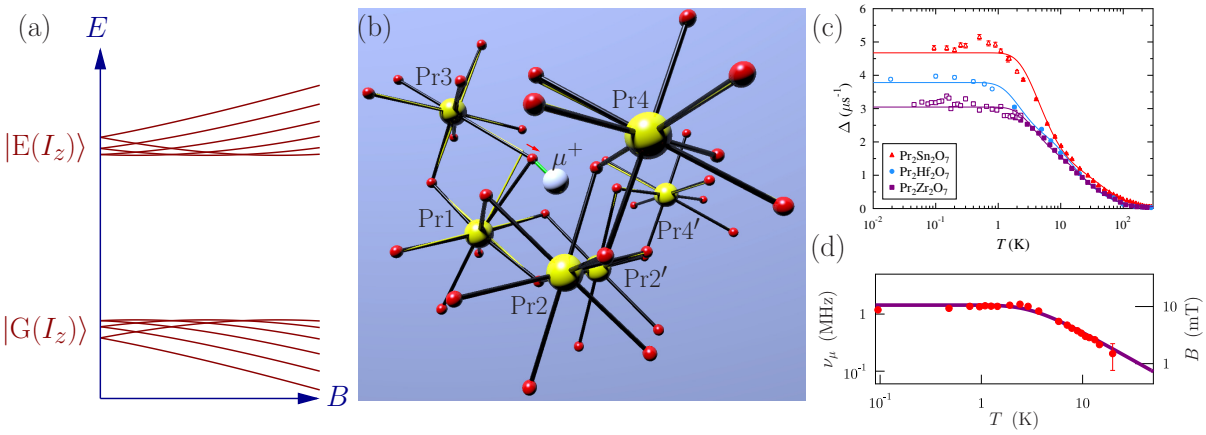

Figure 3. (a) The energy levels of two electronic singlets with the addition of hyperfine coupling (greatly exaggerated). (b) The muon-induced distortion in $Pr_2Sn_2O_7$ and (c) fits of the width of the field distribution in other Pr-based pyrochlores [93]. (d) The precession frequency in $TmNi_2B_2C$ [115], fitted to the model of hyperfine enhanced singlet states.

The effect has been observed in μSR measurements on quantum spin ice materials $Pr_2X_2O_7$ (X=Sn, Zr, Hf) which revealed a static distribution of magnetic moments that appears to grow in strength on cooling [93]. In this material, and without the muon, there is a doublet ground state in the crystal field, resulting in an effective spin-$\frac{1}{2}$ moment leadsing to quantum spin ice behaviour. However, the presence of the muon distorts the local symmetry around the Pr ions, with one Pr–O bond strongly rotated (bent) and another significantly extended [see Fig. 3(b)]. The net result is that the doublet ground state is split on each of the neighbouring Pr cations has a singlet ground state. Then, via the hyperfine enhancement mechanism described above, a distribution of static magnetic moments is produced in which the average moment size grows on cooling [see Fig. 3(c)]. The model (involving DFT+μ calculations of the distortion and crystal field calculations of the resulting Pr environments) produced quantitative agreement with the temperature dependence of the observed muon response, demonstrating the validity of this approach [93].

It is possible that this effect has been observed before, albeit unwittingly in the previous century. The magnetic superconductor $TmNi_2B_2C$ (superconducting below 9.5 K, antiferromagnetic below 1.5 K) exhibits a precession signal which is visible up to nearly 20 K and follows an unusual $\sim 1/T$ form above about 3 K [115]. This seemingly mystifying behaviour could, I now think, in fact be due to a singlet ground state in the Tm^{3+} ion (nuclear moment $-0.232\mu_N$ and $A = -394$ MHz) produced by a muon-induced distortion, with the data consistent with a 1 meV gap between ground state and excited state [see Fig. 3(d)].

5. Conclusion

The intuitions accumulated from these experiments point to an exciting future for μSR where we learn to move beyond treating the muon as a passive responder to macroscopic fields and start to learn how to think of it as an active participant in a quantum-mechanical system, one that can be modelled quantitatively. The results on fluorides have demonstrated that one can abandon

the stretched-exponential background (commonly deployed in previous treatments) if one can model all interactions carefully [111]. The challenge is to apply this approach in a variety of frustrated systems where the details of the persistent spin dynamics frequently observed might be possible to model describe in a quantitative fashion if we can understand all the microscopic quantum-mechanical interactions.

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