# Muon relaxation functions

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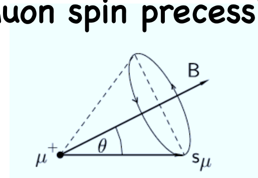
*Muon training course - 2010*


## Lecture plan

- Static distributions - what is a Kubo-Toyabe?
- Gaussian or Lorentzian?
- Dynamic relaxation functions - what happens when the muons get a bit jumpy?
- Stretched exponentials - dangerous evil or answer to all problems?
- When quantum mechanics shines on the experiment!

## Muon spin precession

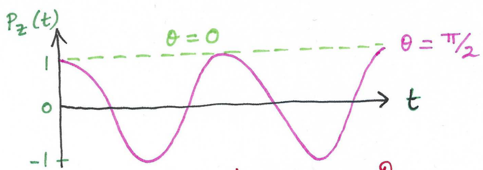



$$P_z(t) = \cos^2\theta + \sin^2\theta\cos(\gamma_\mu |B| t)$$

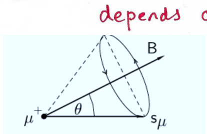
$|B|$ is the *modulus* of the local dipolar field

## Spin precession

$$P_z(t) = \cos^2\theta + \sin^2\theta \cos[\gamma_\mu B t]$$




depends on $\theta$.



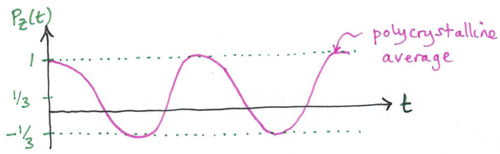

$$P_z(t) = \cos^2\theta + \sin^2\theta\cos(\gamma_\mu |B| t)$$

Angular averages: $\langle \cos^2\theta \rangle = \frac{1}{3}$

$\langle \sin^2\theta \rangle = \frac{2}{3}$

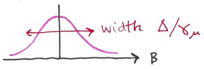
average taken over a sphere

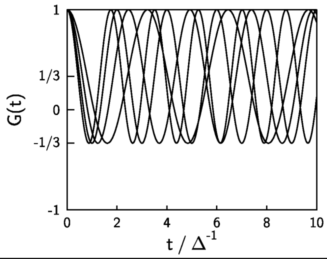
$\therefore \quad P_z(t) = \frac{1}{3} + \frac{2}{3}\cos[\gamma_\mu B t]$



Now, assume B is distributed according to a Gaussian distribution:

$$\text{prob}(B) \propto B^2\, e^{-\gamma_\mu^2 B^2/2\Delta^2}$$

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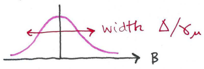


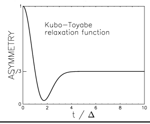

Standard integrals: $\int_0^\infty x^2 e^{-a^2x^2}\,dx = \frac{\sqrt{\pi}}{4a^3}$ and

$$\int_0^\infty x^2 e^{-a^2x^2}\cos bx\,dx = \frac{\sqrt{\pi}}{4a^3}\, e^{-b^2/4a^2}\left(1-\frac{b^2}{2a^2}\right)$$

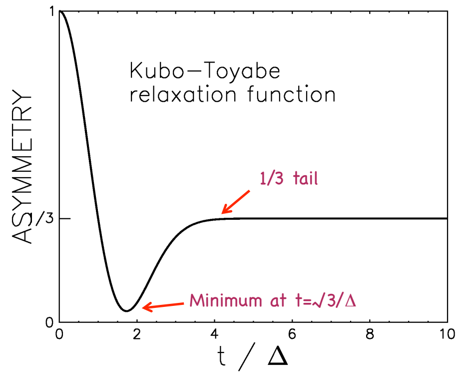
$$\Rightarrow \quad P_z(t) = \frac{1}{3} + \frac{2}{3}\, e^{-\frac{1}{2}\Delta^2 t^2}\left(1-\Delta^2t^2\right)$$

ZERO-FIELD KUBO-TOYABE FUNCTION.

Ryogo Kubo (1920-1995)

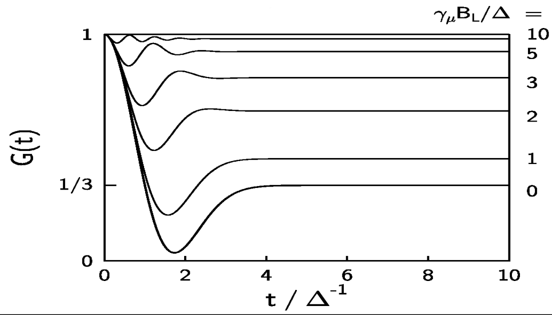



$G(t)=1/3 + 2/3\,(1-\Delta^2t^2)\, e^{-\Delta^2t^2/2}$




## Apply a longitudinal field:

see a recovery of the K-T function!

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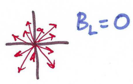
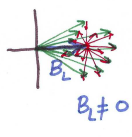



- random fields in all directions
  - $\sim 1/3$ parallel or antiparallel to the muon-spin
  - $\sim 2/3$ perpendicular $\Rightarrow$ depolarize on a time $\sim 1/\Delta$




- now add a longitudinal component boosts the $\frac{1}{3}$ fraction along z

$$P_z(t) = \langle \cos^2\theta \rangle + \langle \sin^2\theta \cdot \cos\gamma_\mu B t \rangle$$

BOOSTED "RINGS" at $\sim\gamma_\mu B_L$.

Analytical calculation:

$$P(B_x) = \frac{\gamma_\mu}{(2\pi)^{1/2}\Delta}\, e^{-\gamma_\mu^2 B_x^2/2\Delta^2}$$

$$P(B_y) = \frac{\gamma_\mu}{(2\pi)^{1/2}\Delta}\, e^{-\gamma_\mu^2 B_y^2/2\Delta^2}$$

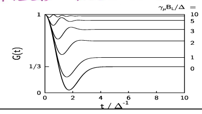
$$P(B_z) = \frac{\gamma_\mu}{(2\pi)^{1/2}\Delta}\, e^{-\gamma_\mu^2 (B_z - B_L)^2/2\Delta^2}$$

Gaussian distribution with offset

$$P_z(t) = \int d^3B \left[\cos^2\theta + \sin^2\theta\,\cos(\gamma_\mu B t)\right] P(B_x)P(B_y)P(B_z)$$

$$\Rightarrow \boxed{P_z(t) = 1 - \frac{2\Delta^2}{(\gamma_\mu B_L)^2}\left(1 - e^{-\frac{1}{2}\Delta^2t^2}\cos\gamma_\mu B_L t\right) + \frac{2\Delta^4}{(\gamma_\mu B_L)^3}\int_0^t e^{-\frac{1}{2}\Delta^2\tau^2}\sin\gamma_\mu B_L\tau\, d\tau}$$

LONGITUDINAL-FIELD KUBO TOYABE FUNCTION



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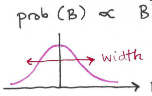
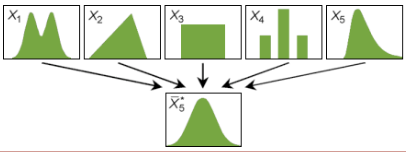
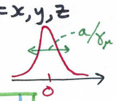



The Gaussian distribution is justified by the CENTRAL-LIMIT THEOREM; other distributions are possible.




Dilute spins $\Rightarrow$ Lorentzian distribution

$$\text{Prob}(B_i) = \frac{\gamma_\mu}{\pi} \frac{a}{a^2 + \gamma_\mu^2 B_i^2} \qquad i = x, y, z$$




and you get a similar result

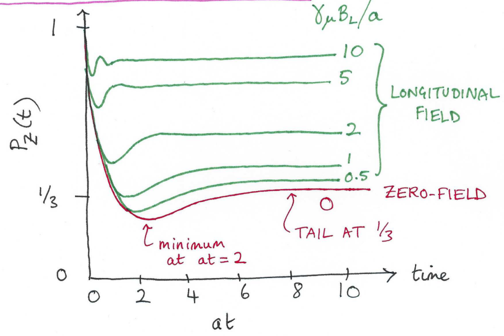
Zero field: $\boxed{P_z(t) = \frac{1}{3} + \frac{2}{3}(1 - at)e^{-at}}$

Longitudinal field:

$$\boxed{\begin{aligned} P_z(t) &= 1 - \frac{a}{\omega_L} j_1(\omega_L t) e^{-at} - \left(\frac{a}{\omega_L}\right)^2 \left[ j_0(\omega_L t) e^{-at} - 1 \right] \\ &\quad - \left[ 1 + \left(\frac{a}{\omega_L}\right)^2 \right] a \int_0^t j_0(\omega_L t) e^{-a\tau} d\tau \end{aligned}}$$

$\omega_L = \gamma_\mu B_L$ ; $j_0$ and $j_1$ are spherical Bessel functions

LORENTZIAN KUBO-TOYABE

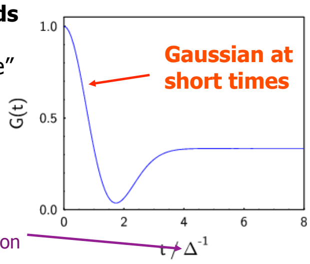



See Larkin et al. Physica B 289, 153 (2000).

## Relaxation functions

**Static distribution of local fields**

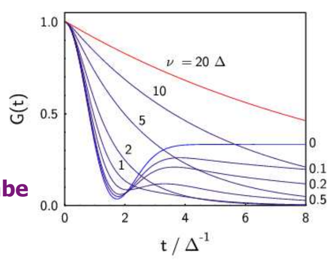
"Kubo-Toyabe" relaxation function




$\Delta$ is the width of the static distribution

## Relaxation functions

One can interpolate between statics and dynamics using a **dynamical Kubo-Toyabe function**




Introduce *dynamics*!

"Strong collision" approximation

(How to get a dynamic relaxation function from a static one)

Assume

1. local field on $\mu^+$ is suddenly changed by a "collision", after which it is randomly distributed with no correlation with field before collision.
2. Collision takes place at rate $\nu$

A Markov process:

$$\frac{\langle B(t) B(0) \rangle}{\langle [B(0)]^2 \rangle} = e^{-\nu t}$$

## Dynamic relaxation function

$G_z(t,\nu) =$ muons that don't collide up to time $t$

$+$ muons that do one collision

$+$ muons that do two collisions

$+ \ldots$

$$= \sum_{n=0}^{\infty} g_z^{(n)}(t)$$

**no jumps**

$$g_z^{(0)}(t) = e^{-\nu t} \; g_z(t)$$

fraction of muons not hopped up to time $t$

the static relaxation function

## one jump at $t_1$

$$g_z^{(1)}(t) = \int_0^t \underbrace{(\nu\, dt_1)}_{\text{jumping probability between } t_1 \text{ and } t_1+dt_1} \underbrace{e^{-\nu(t-t_1)} g_z(t-t_1)}_{\text{after jump}} \underbrace{e^{-\nu t_1} g_z(t_1)}_{\text{before jump}}$$

Sum up all single jumps between 0 and $t$

**two jumps**

$$g_z^{(2)}(t) = \int_{t_2}^{t}\int_0^{t_2} \nu^2\, dt_2\, dt_1\, e^{-\nu(t-t_2)} g_z(t-t_2)\, e^{-\nu(t_2-t_1)} \cdot$$
$$\times\; g_z(t_2-t_1)\, e^{-\nu t_1} g_z(t_1)$$

## SUMMING UP

$$G_z(t,\nu) = e^{-\nu t}\Big[ g_z(t) + \nu\int_0^t g_z(t_1)\, g_z(t-t_1)\, dt_1$$
$$+ \nu^2 \int_0^t\int_0^{t_2} g_z(t_1)\, g_z(t_2-t_1)\, g_z(t-t_2)\, dt_1 dt_2 + \ldots \Big]$$

Analytic solutions can be found by Laplace transforms.

BASIC IDEA: $G_z(t) = \sum_{n=0}^{\infty} g_z^{(n)}(t)$ with

$$g_z^{(n)}(t) = \nu^n \int_{t_n}^{t} \cdots \int_0^{t_2} dt_n \ldots dt_1\, e^{-\nu t} g_z(t-t_n) \ldots g_z(t_1)$$

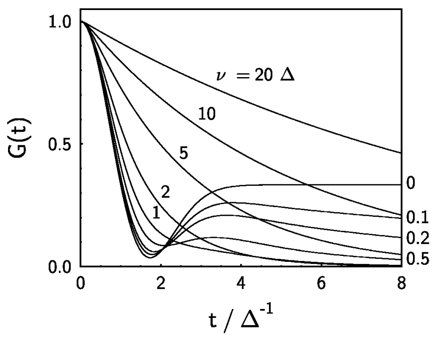
(a convolution!)

Write $f_z^{(n)}(s) = \int_0^\infty g_z^{(n)}(t)\, e^{-st}\, dt = \nu^n \left[f_z(s)\right]^{n+1}$

$$\Rightarrow F_z(s) = \int_0^\infty G_z(t)\, e^{-st}\, dt = \sum_{n=0}^{\infty} \nu^n \left[f_z(s)\right]^{n+1} = \frac{f_z(s)}{1-\nu f_z(s)}$$

Sum of an infinite geometric progression

## ZF Kubo-Toyabe with *dynamics*!




## ZF Kubo-Toyabe with *dynamics*!

A route to the dynamic Kubo-Toyabe function

$$g_z(t) = \frac{1}{3} + \frac{2}{3}(1+\Delta^2 t^2)\exp\left(-\tfrac{1}{2}\Delta^2 t^2\right)$$

$$\Rightarrow f_z(s) = \frac{1}{3s} + \frac{2s}{3\Delta^2}\left[1 - s\int_0^\infty \exp\left[-\tfrac{1}{2}\Delta^2 t^2 - st\right] dt\right]$$

$$\Rightarrow F_z(s) = \frac{f_z(s)}{1-\nu f_z(s)} \xrightarrow[\text{inverse Laplace transform}]{\text{numerically}} G_z(t)$$

In fact, numerically it's easier to work with

$$G_z(t,\nu) = g_z^{(0)}(t) + \nu\int_0^t dt_1\, g_z^{(0)}(t-t_1)\, G_z(t_1,\nu)$$

[though note that what you want is on the LHS and RHS!]

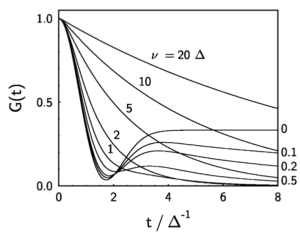
## Slow hopping

Main effect is in the tails!

The Kubo-Toyabe "$\frac{1}{3}$" becomes (at long times)

$$G_z(t) \rightarrow \frac{1}{3}\, e^{-\frac{2}{3}\nu t}$$

LOOKS THE RIGHT WAY ROUND



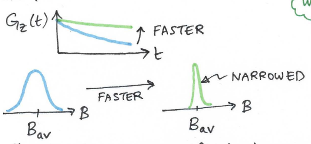
## Fast fluctuation limit

$G_z(t) \rightarrow e^{-\lambda t}$ EXPONENTIAL

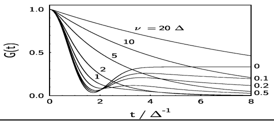
RELAXATION RATE $\hookrightarrow \lambda = \frac{2\Delta^2}{\nu}$ $\leftarrow$ FLUCTUATION RATE

LOOKS THE WRONG WAY ROUND

( TRICKY JARGON: MOTIONAL NARROWING

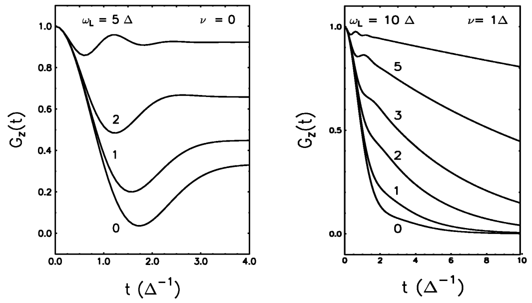



Muon "sees" more of an average field when moving fast – its effective field distribution narrows )



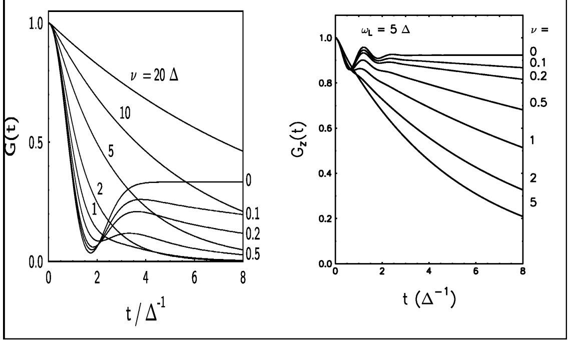

## The effect of longitudinal-field

Static Dynamic




## The effect of dynamics

Zero-field Longitudinal-field




## The stretched exponential

$e^{-(\lambda t)^{\beta}}$

stretch parameter

STRETCHED EXPONENTIALS FIT EVERYTHING

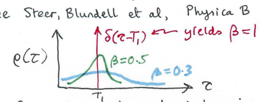
## Distribution of RELAXATION TIMES

$$e^{-t/\tau} \longrightarrow \int_0^\infty \rho(\tau)\, e^{-t/\tau}$$

This yields a STRETCHED EXPONENTIAL $e^{-(t/T_1)^{\beta}}$

if $\rho(\tau) = -\frac{1}{\pi\tau} \sum_{\ell=1}^{\infty} \frac{(-1)^{\ell}\,\Gamma(1+\ell\beta)}{\ell!} \left(\frac{\tau}{T_1}\right)^{\beta\ell} \sin(\pi\beta\ell)$

[see Steer, Blundell et al, Physica B 326, 513 '03 ]




The form of $\rho(\tau)$ is hard to justify physically in most cases, but broad distributions of $\tau$ lead to smaller $\beta$.

The $\beta = \frac{1}{2}$ case is worth looking at in more detail.

## Muons and spin glasses

Muons that stop closer to magnetic ions "see" a wider local field distribution (which extends to higher fields) than muons which stop at a greater distance

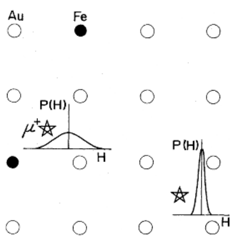



FIG. 3. Schematic view of different variable ranges of random local fields at different muon sites in dilute-alloy spin glasses. When Fe (or Mn) moments fluctuate, the local field at muon sites closer to the magnetic ions will be modulated in a wider range.

Y.J. Uemura et al, PRB **31**, 546 (1985)

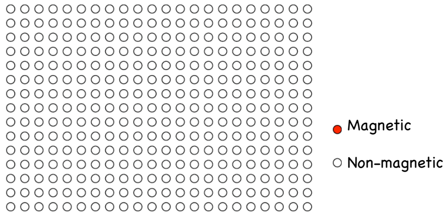
## Muons and spin glasses

The correct relaxation function must therefore be an average over distribution widths $\Delta$.

This leads to a root-exponential relaxation function: $G(t) = G(0)\exp(-(\lambda t)^{1/2})$

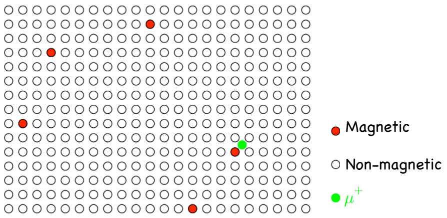
where the relaxation rate $\lambda$ is inversely proportional to the fluctuation rate $\nu$.

## Non-magnetic host



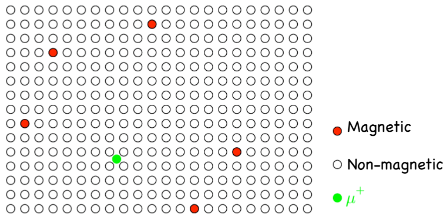

## Spin glass

Muon stops close to magnetic ion




## Spin glass

Muon stops well away from magnetic ion

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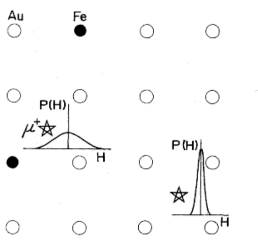


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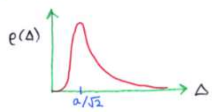
## Range of coupling strengths

i.e. distribution of $\Delta$

PRB 31 546 '85
PRB 50 10039 '94

$$\rho(\Delta) = \sqrt{\frac{2}{\pi}}\,\frac{a}{\Delta^2}\,e^{-a^2/2\Delta^2}$$

$\langle\Delta\rangle \sim a$




so that

$$P(t) = \int_0^\infty e^{-\Gamma t}\rho(\Delta)\,d\Delta$$

$$= \exp\left[-(\lambda t)^{1/2}\right] \quad \text{where } \lambda = \frac{2a^2\Gamma}{\Delta^2}$$

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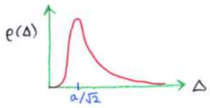


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……**but is the dogma correct?**

## Monte-Carlo calculation of distribution of Δ

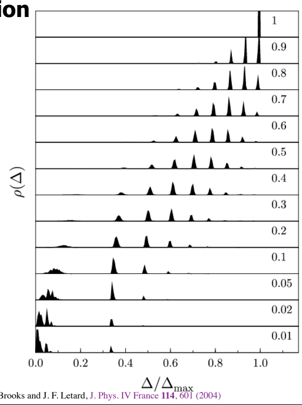
$$\Delta^2 = \tfrac{2}{3} S^2 \hbar^2 \gamma_\mu^2 \gamma_e^2 \sum_k \tfrac{1}{r_k^6}$$

$r_k$ is the distance from the muon to the $k^{\rm th}$ spin

the sum is taken over sites occupied with probability $c$

- If $c = 1$, $\rho(\Delta) = \delta(\Delta - \Delta_{\max})$.
- For $c = 0.01$, substantial departures from

$$\rho(\Delta) = \sqrt{\frac{2}{\pi}} \left(\frac{a}{\Delta^2}\right) e^{-a^2/2\Delta^2}.$$

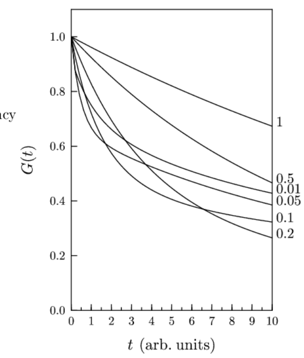



S. J. Blundell, T. Lancaster, F. L. Pratt, C. A. Steer, M. L. Brooks and J. F. Letard, J. Phys. IV France **114**, 601 (2004)

The $\mu$SR function can be obtained from $\rho(\Delta)$ using

$$G(t) = \int_0^\infty \exp(-2\Delta^2 t/\nu)\rho(\Delta)\, d\Delta.$$

- Adjust the fluctuation frequency as $\nu \propto c^2$ to crudely simulate the effect of the slowing down of the remaining spins as $c$ decreases.
- If $c = 1$, simple exponential relaxation results.
- If $c \ll 1$, the relaxation is similar to the observed root exponential behaviour.

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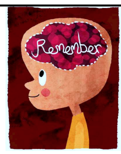
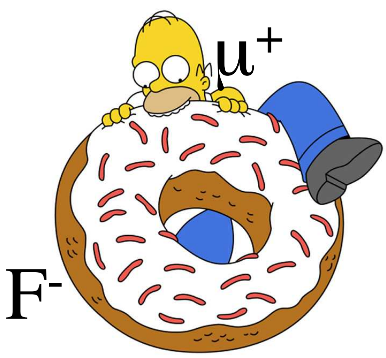


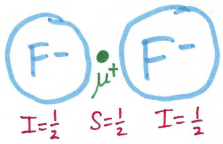

## Some things to REMEMBER.

1. The standard fit functions (particularly $e^{-(\lambda t)^\beta}$) may "work" – but what does it mean?
2. Fluctuations in magnets are often CORRELATED i.e. not Markov!
3. Beware the hints of quantum coherence! (see work of Celio & Meier.)

see Keren et al. PRB 64 054403 '01 (beautiful paper)



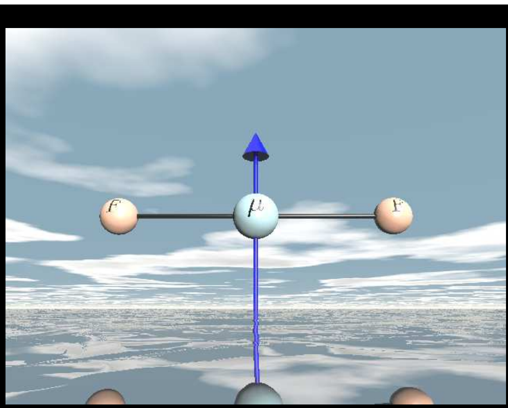

## The F-μ-F state




COHERENT OSCILLATIONS

∵ magnetic dipolar interaction

$$P_z(t) = \frac{1}{6}\left(3 + \cos\sqrt{3}\,\omega t + \left(1-\frac{1}{\sqrt{3}}\right)\cos\left[\frac{3-\sqrt{3}}{2}\,\omega t\right] + \left(1+\frac{1}{\sqrt{3}}\right)\cos\left[\frac{3+\sqrt{3}}{2}\,\omega t\right]\right)$$

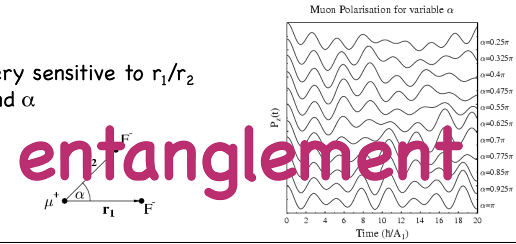


## F-μ-F state

F=small, high nuclear moment abundant species

| Anion | Abundance | Spin | Ionic radius (pm) | Magnetic moment ($\mu_N$) |
|---|---|---|---|---|
| $^{19}F$ | 100% | 1/2 | 119 | 2.6 |
| $^{35}Cl$ | ~ 75% | 3/2 | 167 | 0.82 |
| $^{37}Cl$ | ~ 25% | 3/2 | 167 | 0.68 |
| $^{79}Br$ | ~ 50% | 3/2 | 182 | 2.1 |
| $^{81}Br$ | ~ 50% | 3/2 | 182 | 2.3 |
| $^{127}I$ | 100% | 5/2 | 206 | 2.8 |
| $^{17}O$ | 0.04% | 5/2 | 126 | -1.9 |
| $^{33}S$ | 0.76% | 3/2 | 170 | 0.64 |
| $^{77}Se$ | 7.6% | 1/2 | 184 | 0.53 |
| $^{123}Te$ | 0.89% | 1/2 | 207 | -0.73 |
| $^{125}Te$ | 7.1% | 1/2 | 207 | -0.89 |

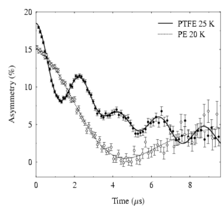
very sensitive to $r_1/r_2$ and $\alpha$

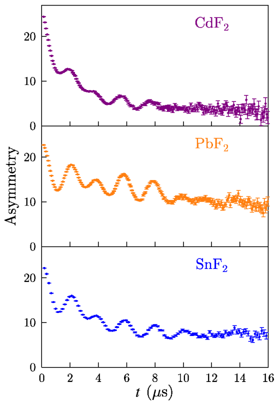


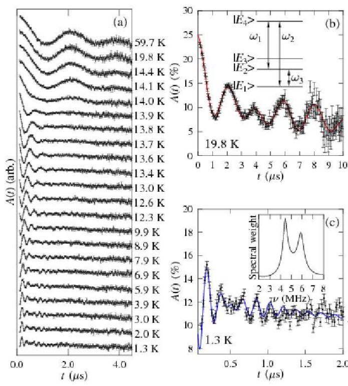

entanglement

## F-μ-F state

state found in many ionic fluorides, and also teflon (PTFE)




## $Cs_2AgF_4$

$\omega_d = 2\pi \times 0.211(1)$ MHz

F-μ separation 1.19(1) Å.

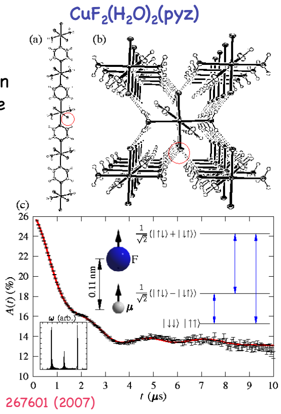
$T_c$=13.95(3) K

T. Lancaster, S. J. Blundell, et al.

Phys. Rev. B **75**, R220408 (2007)

## $CuF_2(H_2O)_2(pyz)$

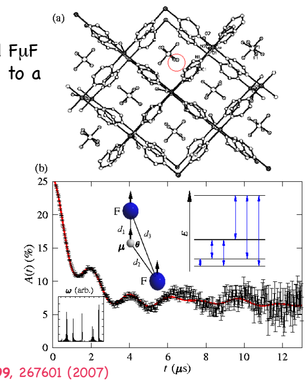
1. Interaction with a single fluorine ion




Phys. Rev. Lett. **99**, 267601 (2007)

## $[CuNO_3(pyz)_2]PF_6$

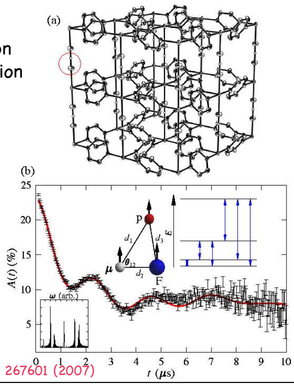
2. Crooked FμF bond close to a $PF_6$ ion




Phys. Rev. Lett. **99**, 267601 (2007)

## $[Cu(HF_2)(pyz)_2]X$

3. Interaction with a $HF_2^-$ ion




Phys. Rev. Lett. **99**, 267601 (2007)