Applications of μSR - Charge transport

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Overview

- Introduction
- Hyperfine coupling in muonium
- Charge carrier dynamics probed with muonium
- Muon diffusion
- Li diffusion

Introduction

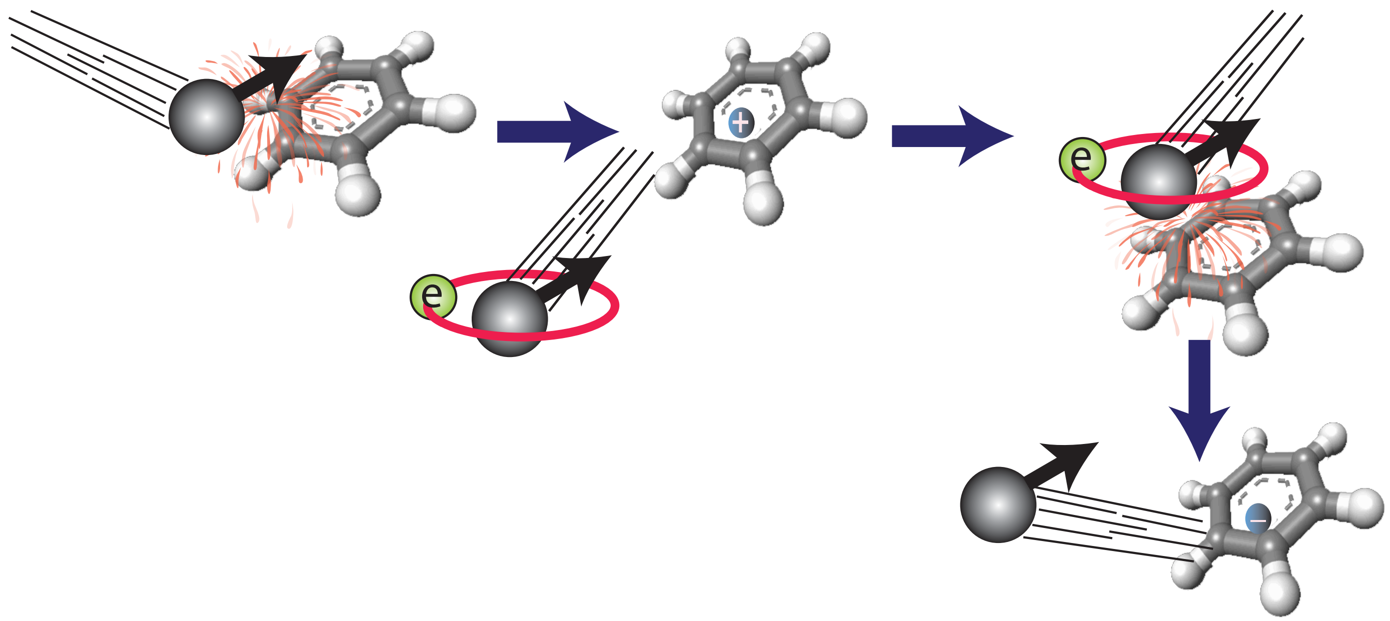
- In a very large number of processes in biology, chemistry, solid state physics, soft matter physics, nuclear physics..... one has to deal with diffusion phenomena and particle dynamics

- Invariably these are limited by potential barriers.

- If the diffusion process alters the magnetic environment of the muon, then the muon can measure it.

Hyperfine coupling in muonium

Muonium



Isolated isotropic muonium serves as a simple example to demonstrate the interaction between the electron spin, *Se,* and the muon spin, *Sμ,* in an external magnetic field.

Interaction of muon spin with B

Interaction between both spins

$$H_0 = -\gamma_\mu \vec{S}_\mu \cdot \vec{B} + \gamma_e \vec{S}_e \cdot \vec{B} + A\vec{S}_\mu \cdot \vec{S}_e$$

Interaction of muon spin with B

Isotropic HF coupling constant.

Muonium

$$H_0 = -\gamma_\mu \vec{S}_\mu \cdot \vec{B} + \gamma_e \vec{S}_e \cdot \vec{B} + A\vec{S}_\mu \cdot \vec{S}_e$$

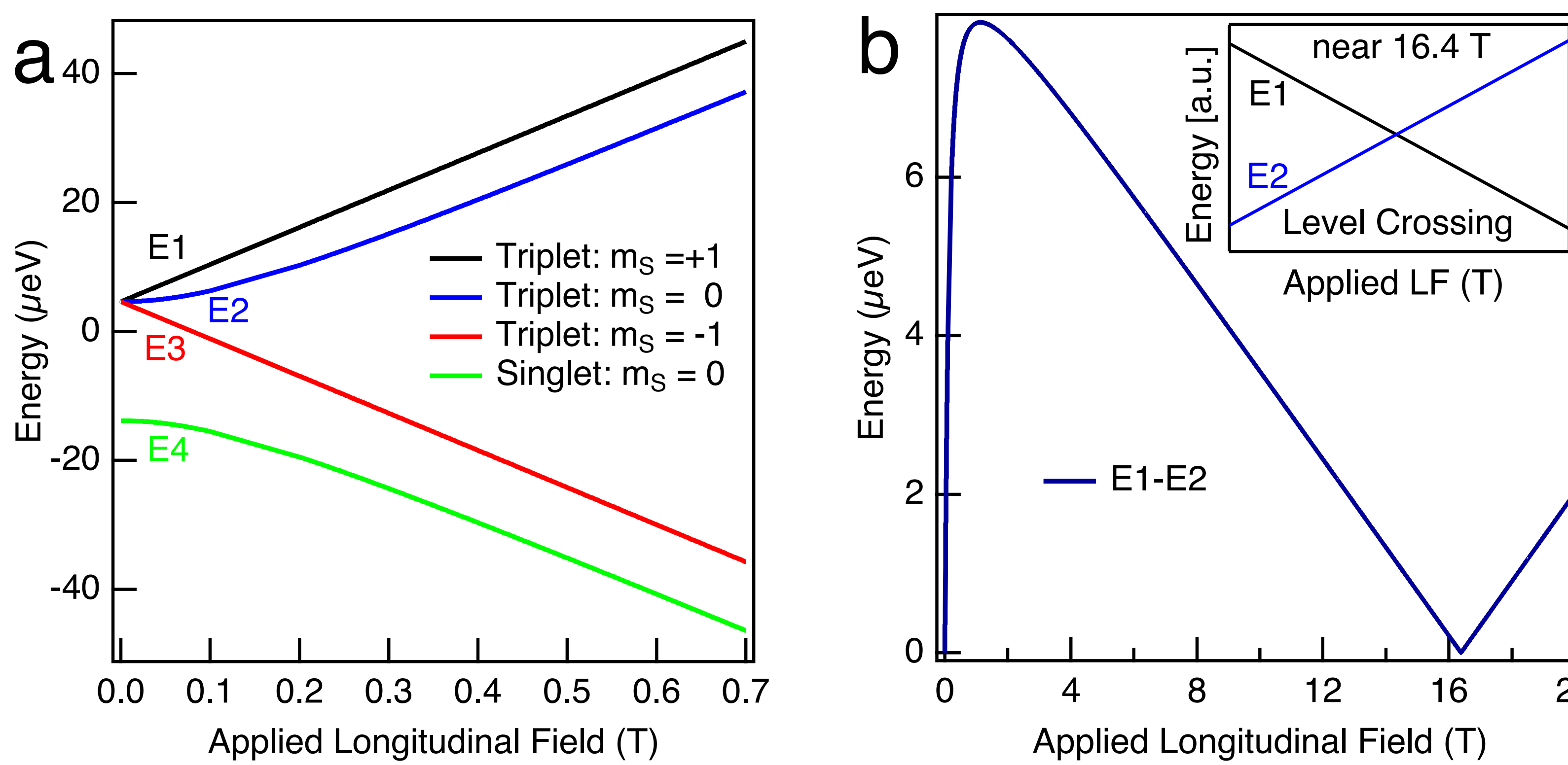
Se and *Sμ* are defined by the four-dimensional Pauli spin matrices, which are used to calculate the energy levels of the coupled two-spin system:

$$E_1 = \frac{\hbar}{4}\left[A + 2B\left(\gamma_e - \gamma_\mu\right)\right]$$

$$E_2 = -\frac{\hbar}{4}\left[A - 2\sqrt{A^2 + B^2\left(\gamma_e + \gamma_\mu\right)^2}\right]$$

$$E_3 = \frac{\hbar}{4}\left[A - 2B\left(\gamma_e - \gamma_\mu\right)\right]$$

$$E_4 = -\frac{\hbar}{4}\left[A + 2\sqrt{A^2 + B^2\left(\gamma_e + \gamma_\mu\right)^2}\right]$$



S Blundell, Chemical Review, 104:5717–5735, 2004.

Muonium

One can define the eigenvectors of this coupled spin system:

$$| \Psi_1\rangle = |\uparrow_\mu \uparrow_e\rangle$$

$$| \Psi_2\rangle = c_1\, |\uparrow_\mu \downarrow_e\rangle + c_2\, |\downarrow_\mu \uparrow_e\rangle$$

$$| \Psi_3\rangle = |\downarrow_\mu \downarrow_e\rangle$$

$$| \Psi_4\rangle = c_2\, |\uparrow_\mu \downarrow_e\rangle - c_1\, |\downarrow_\mu \uparrow_e\rangle,$$

Where

$$c_1 = \frac{1}{\sqrt{2}} \sqrt{1 - \frac{B}{\sqrt{B_0^2 + B^2}}}$$

$$c_2 = \frac{1}{\sqrt{2}} \sqrt{1 + \frac{B}{\sqrt{B_0^2 + B^2}}}.$$

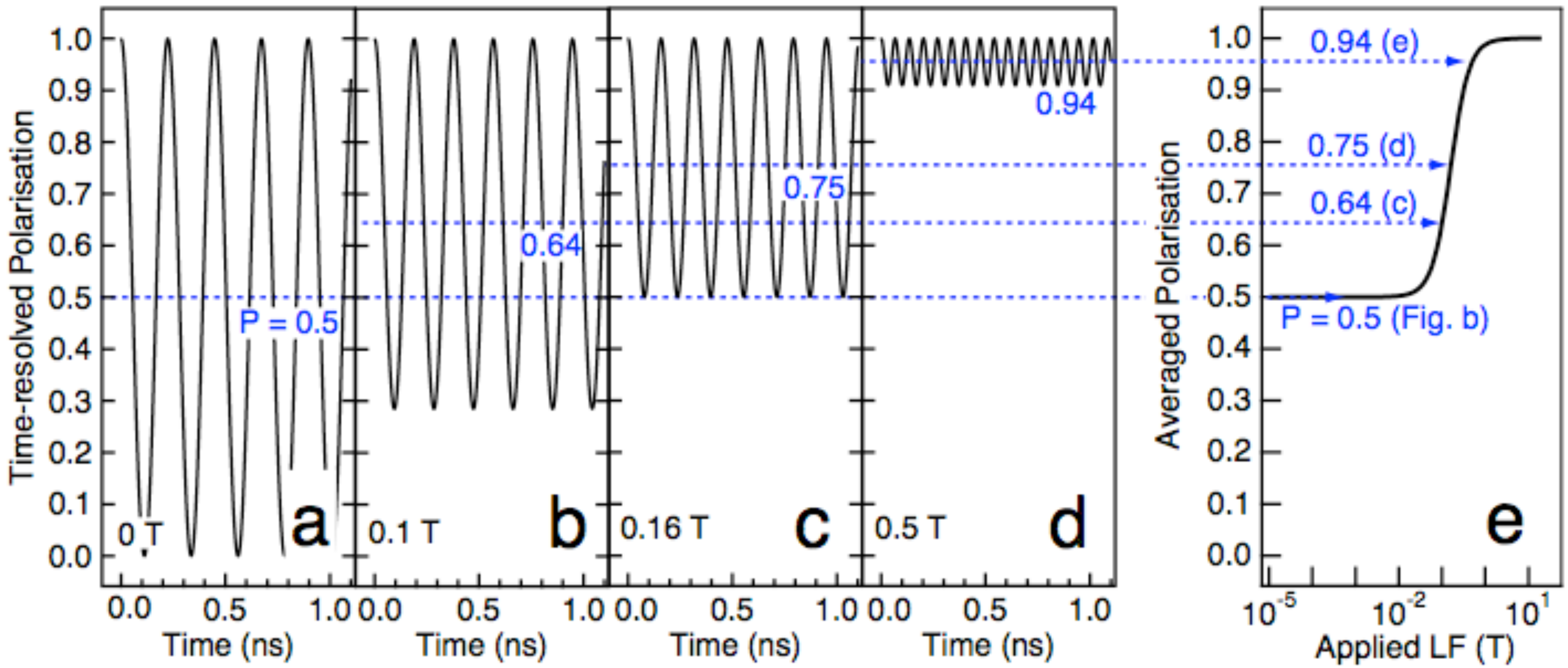
By using the spin density matrix formalism, it is possible to show that the polarisation of the muon's spin oscillates with respect to time:

$$P_\mu(t) = \underbrace{\frac{A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2}{2A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2}}_{\text{Non-oscillatory part}} + \underbrace{\frac{A^2}{2A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2} \cos\left(\omega_{24} t\right)}_{\text{Oscillatory part}}$$

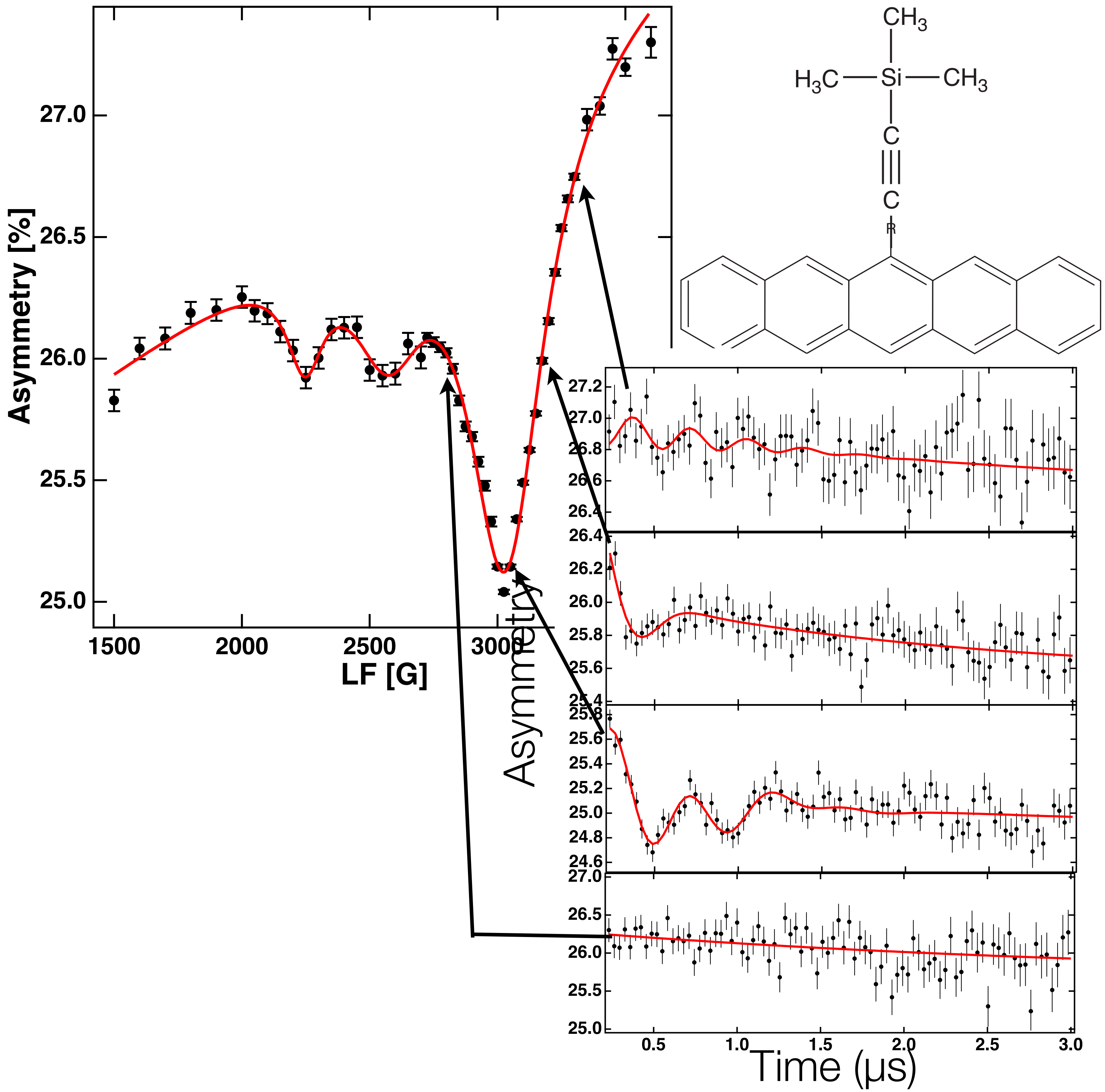
B. Patterson, Reviews of Modern Physics, 60(1):69, 1988.

Muonium

$$P_{\mu}(t) = \underbrace{\frac{A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2}{2A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2}}_{\text{Non-oscillatory part}} + \underbrace{\frac{A^2}{2A^2 + 2B^2\left(\gamma_e + \gamma_\mu\right)^2}\cos\left(\omega_{24} t\right)}_{\text{Oscillatory part}}$$



TIPS-Pentacene



Tangent..... Beware of protons.....

$$H_0 = -\gamma_\mu \vec{S}_\mu \cdot \vec{B} + \gamma_e \vec{S}_e \cdot \vec{B} + A\vec{S}_\mu \cdot \vec{S}_e$$

$$\begin{aligned}
H_{\mu,\mathrm{aniso}} = \frac{1}{2} A_\mu \left(S_e^+ S_\mu^- + S_e^- S_\mu^+\right) - D_{\mu,\perp}\Big[&\left(1 - 3\cos^2\theta\right) S_e S_\mu \\
&- \frac{1}{4}\left(1 - 3\cos^2\theta\right)\left(S_e^+ S_\mu^- + S_e^- S_\mu^+\right) && \Delta M = 0 \\
&- \frac{3}{2}\left(\sin\theta\cos\theta\exp(-i\phi)\right)\left(S_e S_\mu^+ + S_e^+ S_\mu\right) && \Delta M = 1 \\
&- \frac{3}{2}\left(\sin\theta\cos\theta\exp(+i\phi)\right)\left(S_e S_\mu^- + S_e^- S_\mu\right) && \Delta M = 1 \\
&- \frac{3}{4}\left(\sin^2\theta\exp(-2i\phi)\right)\left(S_e^+ S_\mu^+\right) && \Delta M = 2 \\
&- \frac{3}{4}\left(\sin^2\theta\exp(+2i\phi)\right)\left(S_e^- S_\mu^-\right)\Big] && \Delta M = 2
\end{aligned}$$

The addition of a single extra spin (muon-electron-proton) makes the maths considerably harder....

Anything more complicated needs to be solved numerically (or by a theoretician).

$$H_{\mathrm{nuclei}} = \underbrace{\sum_{k=1}^{n} -\gamma_k I_k \cdot B_z}_{\text{Zeeman term}} + \frac{1}{2}\sum_{k=1}^{n} A_k \left(S_e^+ I_k^- + S_e^- I_k^+\right)$$

$$\begin{aligned}
- \sum_{k=1}^{n} D_{k,\perp}\Big[&\left(1 - 3\cos^2\theta\right) S_e I_k \\
&- \frac{1}{4}\left(1 - 3\cos^2\theta\right)\left(S_e^+ I_k^- + S_e^- I_k^+\right) && \Delta M = 0 \\
&- \frac{3}{2}\left(\sin\theta\cos\theta\exp(-i\phi)\right)\left(S_e I_k^+ + S_e^+ I_k\right) && \Delta M = 1 \\
&- \frac{3}{2}\left(\sin\theta\cos\theta\exp(+i\phi)\right)\left(S_e I_k^- + S_e^- I_k\right) && \Delta M = 1 \\
&- \frac{3}{4}\left(\sin^2\theta\exp(-2i\phi)\right)\left(S_e^+ I_k^+\right) && \Delta M = 2 \\
&- \frac{3}{4}\left(\sin^2\theta\exp(+2i\phi)\right)\left(S_e^- I_k^-\right)\Big]. && \Delta M = 2
\end{aligned}$$

Tangent..... Beware of protons.....

Hyperfine Interactions 32 (1986) 727-731 727

AVOIDED LEVEL CROSSING μSR OF ORGANIC FREE RADICALS

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2.2. T_1^e-processes

The relaxing influence of elctron spin flips in muonated organic radicals may be accounted for by extending the phenomenological theory of Ivanter and Smilga /12/ for Muonium in solids to a three-spin-1/2 system.

Following /15/ we define a 63-dimensional polarization vector:

Tangent..... Beware of protons.....

$$P(t) = (P^i_e(t), P^i_\mu(t), P^i_k(t), P^{ij}_{e\mu}(t), P^{ij}_{ek}(t), P^{ij}_{k\mu}(t), P^{ijk}_{e\mu k}(t)) \qquad (13)$$

where the polarizations are defined via:

$$P^{ijk}_{e\mu k}(t) = \mathrm{Tr}(\rho\sigma^i\tau^j\gamma^k) \qquad (14)$$

and related expressions. ρ is the density matrix of the system and σ, τ, γ are Pauli spin matrices. Via the equation of motion for the density matrix it is possible to define a set of coupled linear differential equations

$$\dot{P} = \Sigma_j\, M_{ij}P_j \quad , \quad 1 \leq i,j \leq 63 \qquad (15)$$

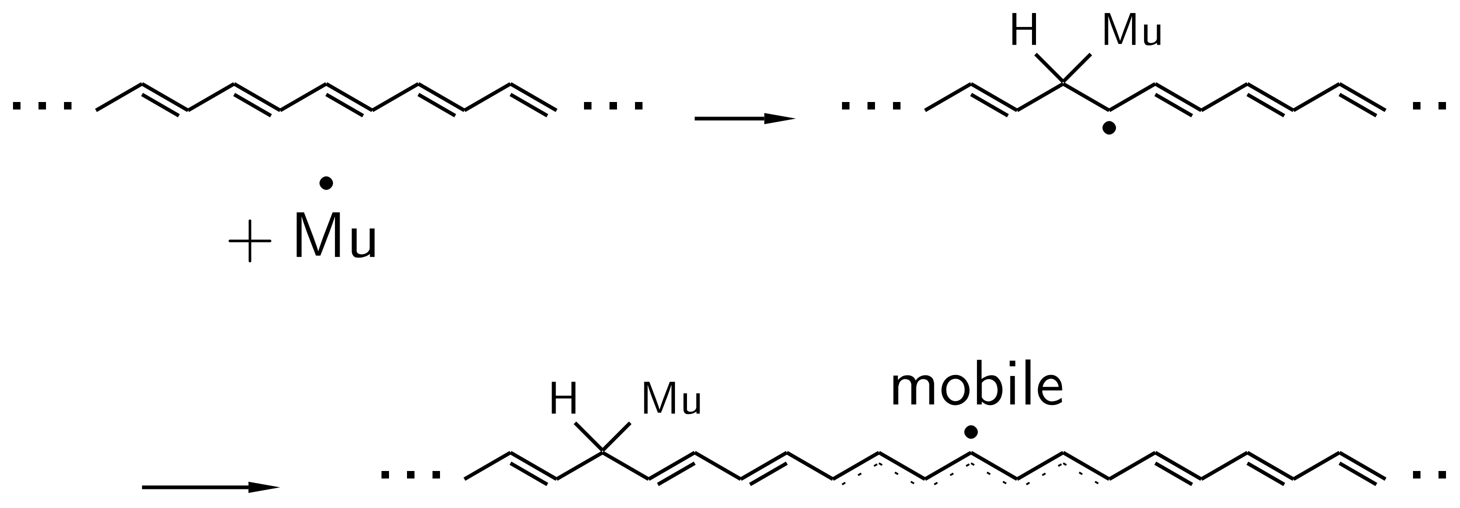
For longitudinal magnetic fields the number of coupled equations reduces to 30. Relaxation processes, which lead to an electron spin flip, can be accounted for by introducing a phenomenological electron spin flip rate λ_{ex}:

$$\dot{P}^i_e = \ldots - 2\lambda_{ex}P^i_e \qquad \dot{P}^{ij}_{e\mu} = \ldots - 2\lambda_{ex}P^{ij}_{e\mu}$$
$$\dot{P}^{ij}_{ek} = \ldots - 2\lambda_{ex}P^{ij}_{ek} \qquad \dot{P}^{ijk}_{e\mu k} = \ldots - 2\lambda_{ex}P^{ijk}_{e\mu k} \qquad (16)$$

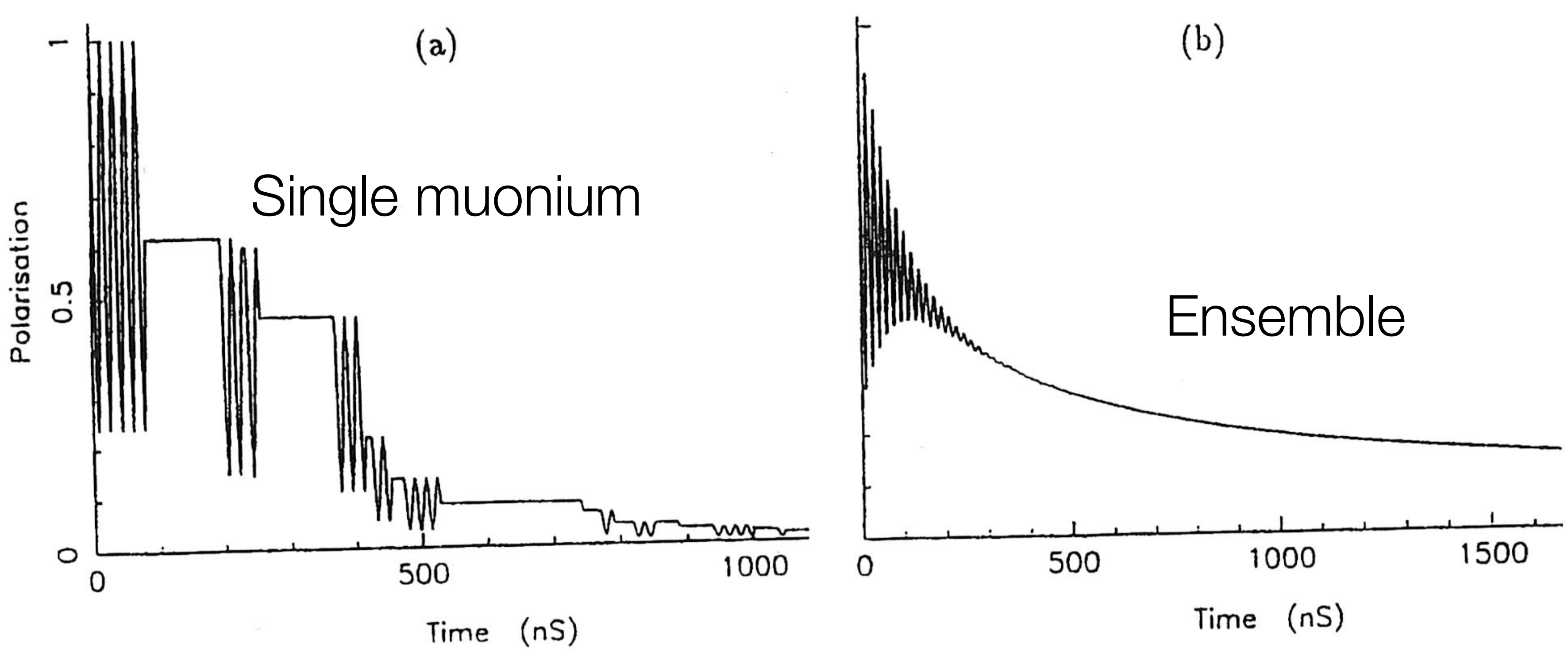
Charge carrier dynamics probed with muonium

Relaxation effects

- If the muonium electron is mobile, the it results in a modulation of the HFC



- Qualitatively, the modulation of HF interactions result in a relaxation of the muon’s spin. How?



Relaxation mechanism....

From Fermi's Golden Rule, the transition probability between two spin states is

$$W = (\gamma_\mu B)^2 f(\omega_\mu) \propto \lambda$$

Typically, it is proportional to the relaxation rate of the muon

Spectral density function of the field fluctuation - contains full information about dimensionality of charge carrier motion

How to calculate for charge carrier diffusion?

For an anisotropic random walk, it can be shown that:

$$f(\tau) = e^{-2\tau(D_1+D_2+D_3)}[I_o(2D_1\tau)\cdot I_o(2D_2\tau)\cdot I_o(2D_3\tau)]$$

Bessel functions

Diffusion rates along 3 dimensions

$$I_o(x) = \frac{1}{\pi}\int_0^\pi e^{x\cos\theta}\, d\theta \rightarrow \begin{cases} 1 & (x \to 0) \\ \dfrac{e^x}{\sqrt{2\pi x}} & (x \to \infty) \end{cases}$$

In other words $\lambda \propto \exp^{-2\tau(D_1+D_2+D_3)}$

Pratt et al., Hyp. Int. 106, 33 (1997); Pratt et al., Phys. Rev. Lett. 96, 247203 (2006); Mizoguchi, Makr. Chem. Macr. Symp. 37, 53 (1990)

Exponential relaxation

$F(t)$ contains all the information about the mechanisms and dimensionality of the diffusion and could in principle include such additional factors as interchain hopping, reflection at chain ends and trapping sites or the presence of an initial activation barrier at the muon site.

For uniaxial anisotropic muonium, the actual relaxation rate is:

$$\lambda(B) = 1/20[3D^2 f(\omega_\mu) + (5A^2 + 7D^2) f(\omega_e)]$$

3D	$f(\omega) = f(0) - A\omega^{1/2}$
2D	$f(\omega) = B - C\ln(\omega)$
Fractal dimension $d(d < 2)$	$f(\omega) = D + E\omega^{-1+d/2}$
1D	$f(\omega) = F\omega^{-1/2}$
$\omega > D_\parallel$ (above diffusive limit)	$f(\omega) = G\omega^{-2}$

A bit of a mess... only solved via numerical method (difficult to write a fit function)

However, can empirically fit to the following:

$$f(\omega) = \frac{1}{\sqrt{2D_\parallel D_\perp}} \left(\frac{1 + \sqrt{1 + (\omega/2D_\perp)^2}}{2[1 + (\omega/2D_\perp)^2]} \right)^n$$

Pratt et al., Hyp. Int. 106, 33 (1997); Pratt et al., Phys. Rev. Lett. 96, 247203 (2006)

1D relaxation function

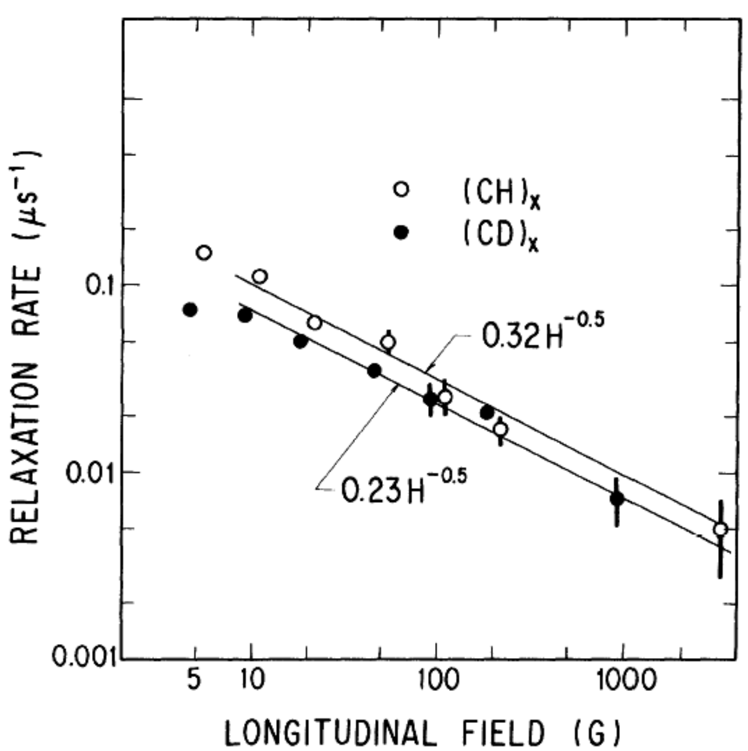
$$f(\omega)_{Q1D} = \frac{1}{\sqrt{4D_{//}D_{\perp}}}\sqrt{\frac{1+\sqrt{1+(\omega/2D_{\perp})^2}}{1+(\omega/2D_{\perp})^2}}$$

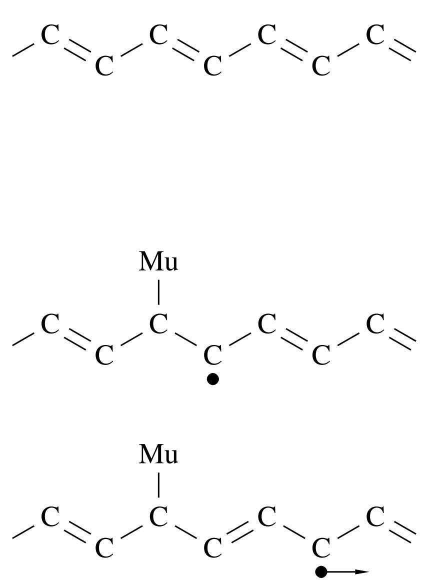
For 1D motion (on the muon's timescale) →

$\lambda \propto B^{-0.5}$

$$= \frac{1}{\sqrt{2D_{//}\omega}}, \quad \text{at the medium frequencies } D_{\perp} << \omega << D_{//}$$

$$= \frac{1}{\sqrt{2D_{//}D_{\perp}}}, \quad \text{at the low frequencies } \omega << D_{\perp}$$



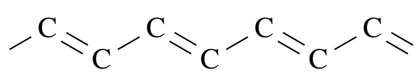


Good review: FL Pratt J. Phys.: Condens. Matter 16 (2004) S4779–S4796

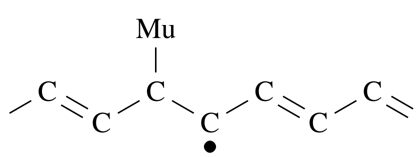
But.....

Fundamental assumption of the standard relaxation theory:

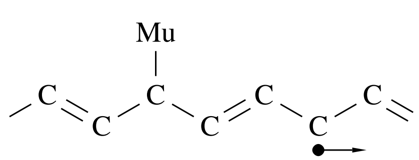
Assumes the existence of a correlation time of the fluctuations that produce the relaxation.... in other words, they always return to origin.



For a 1D process, this correlation time diverges



i.e the electron can escape the muon, never returning to its origin.



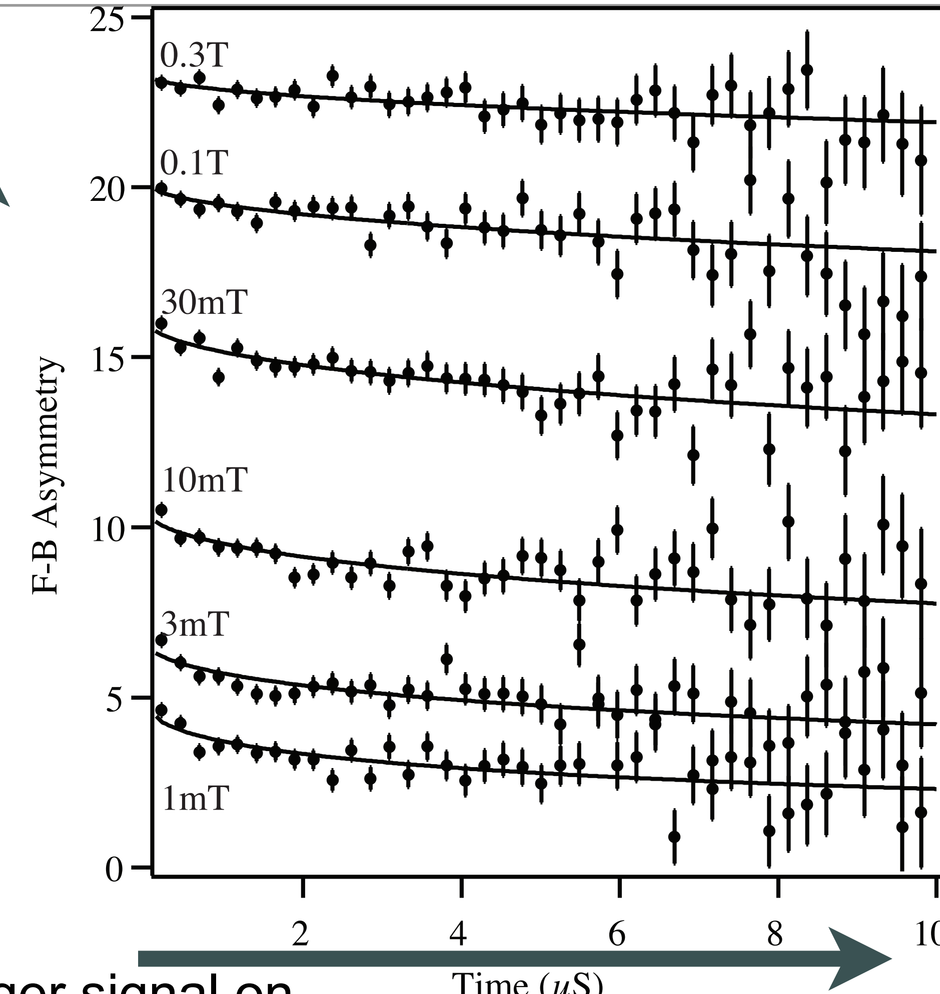
This fundamental assumption is invalid.....

Risch-Kehr model

Increase field:

1. Repolarise nuclear spins and impurities: reduced electron spin flip = reduced relaxation rate

2. Repolarise muon's spin (i.e quench muon-electron hyperfine coupling)



At t=0, larger signal on Front detector: no time for relaxation

At higher times, signal reduces: more counts on Back detector because of relaxation

Relxation rate fit function:

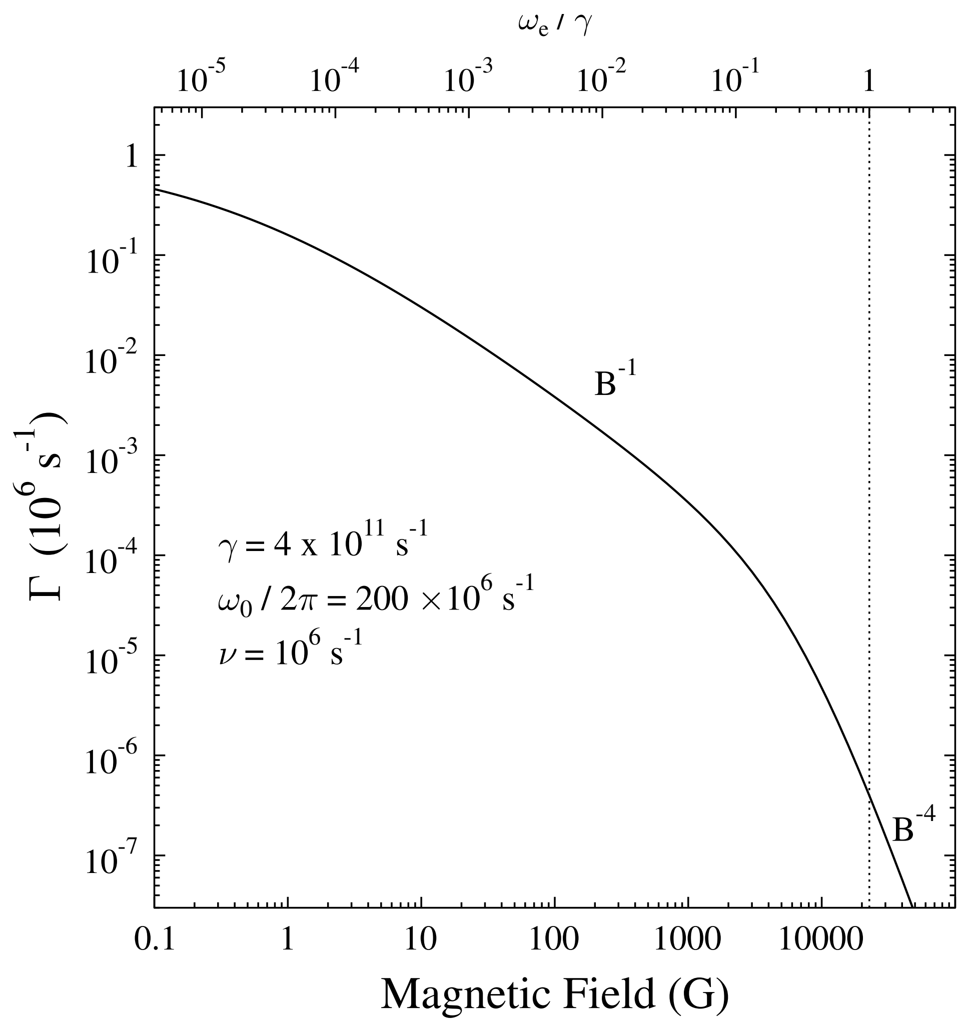
Risch-Kerr model - Stochastic 1D model for charge carrier diffusion.

Parameters:
1. Hyperfine coupling constant
2. Electron hopping rate
3. Electron spin flip rate
4. Electron precession

$$\mathrm{A}(t) \propto \mathrm{G}_Z(t) = \mathrm{e}^{\Gamma t}\mathrm{erfc}(\Gamma t)$$

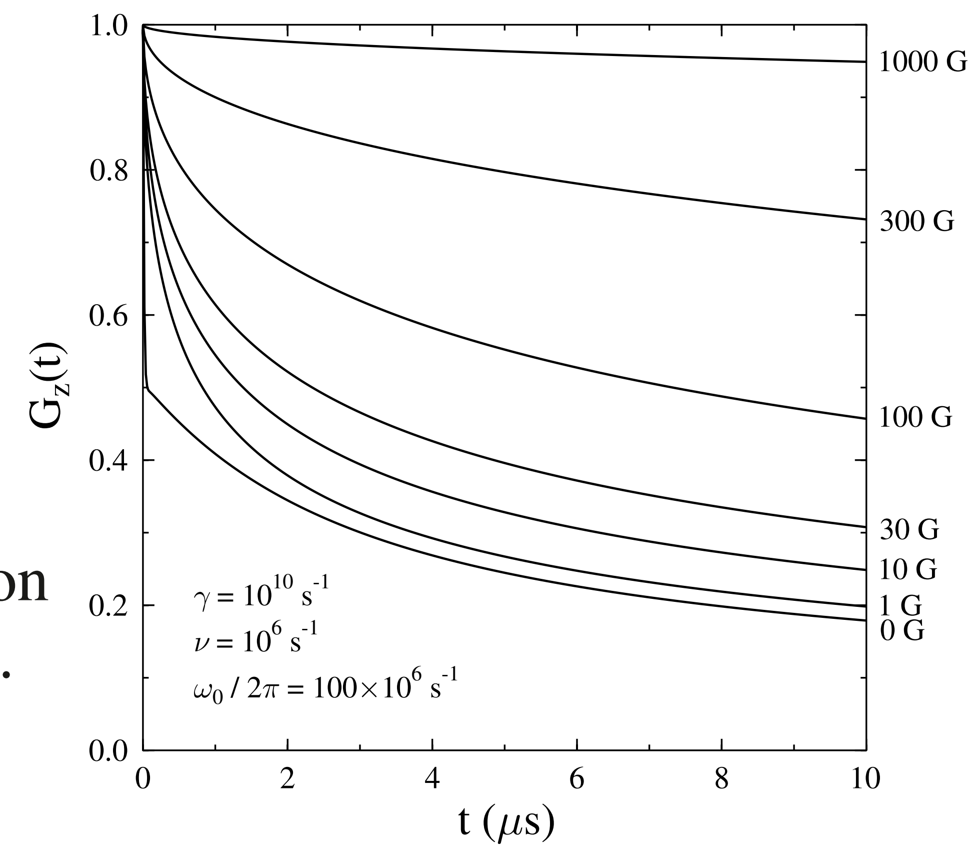
R. Risch & W. Kehr, *Phys. Rev.* **B 46**, 5246 (1992)

Risch-Kehr model



The field dependence of the RK relaxation rate in the fast diffusion limit ($\gamma > \omega_0$), where a broad region of 1D behaviour is apparent. A high field cut-off is seen when $\omega_e > \gamma$ and at high fields follows a B^{-4} law.

$$A(t) \propto G_Z(t) = e^{\Gamma t} \mathrm{erfc}(\Gamma t)$$

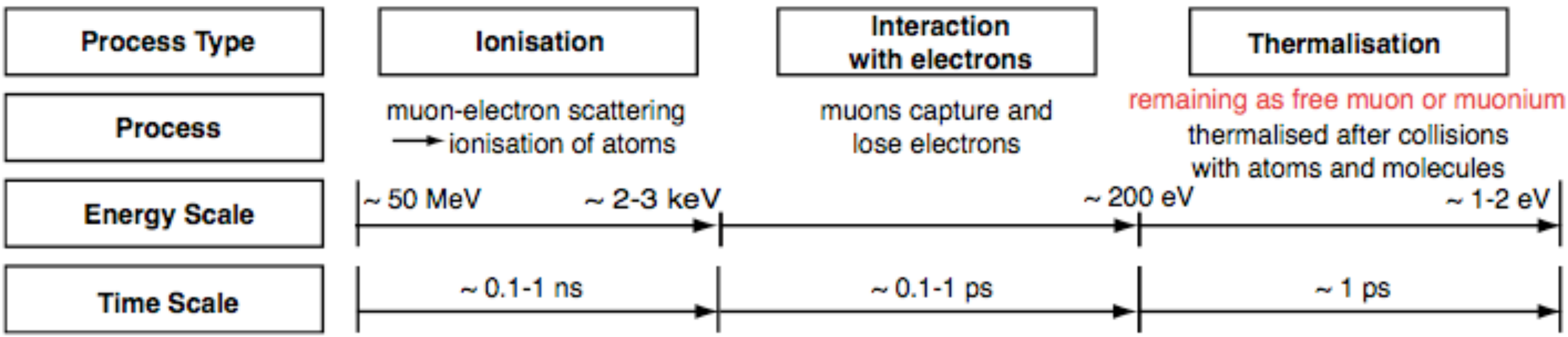


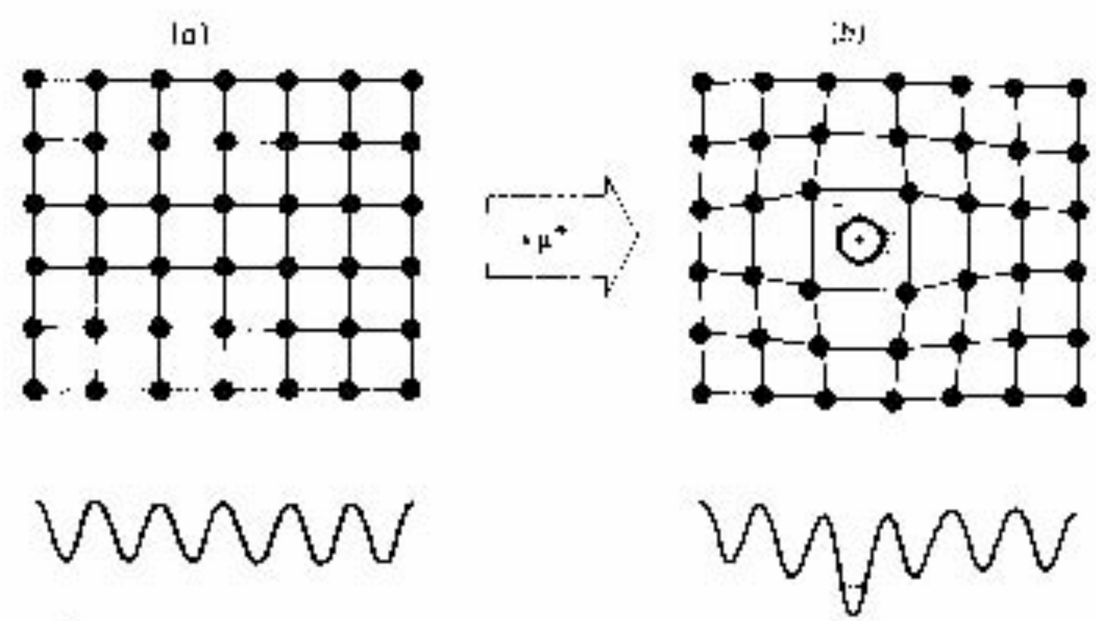
The field dependence of the muon spin relaxation in the RK model.

R. Risch & W. Kehr, *Phys. Rev.* **B 46**, 5246 (1992), FL Pratt J. Phys.: Condens. Matter 16 (2004) S4779–S4796

Muon diffusion

Thermalisation of muons





There is a local accumulation of charge density which screens the muon potential, and a small elastic distortion of the lattice.

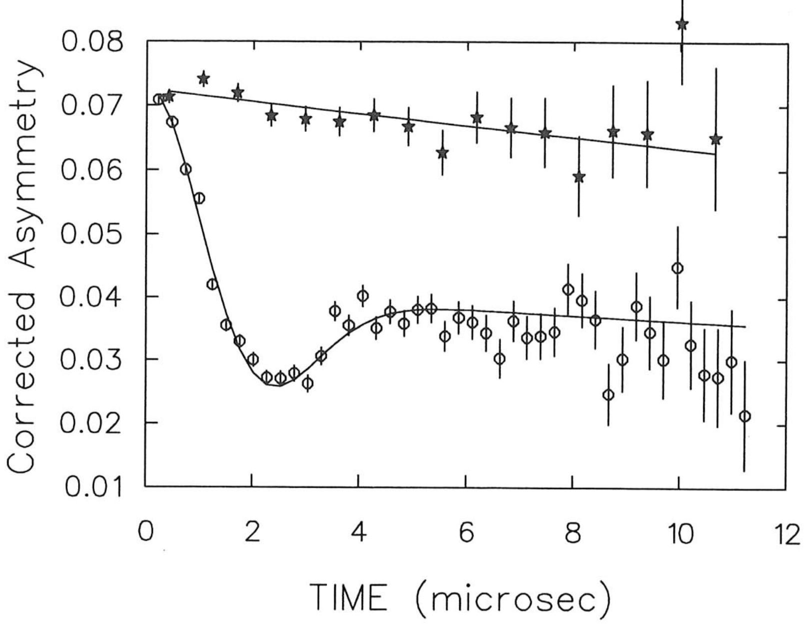
The muon's are effectively "self trapped" - they cause a lattice distortion, which creates a potential to "bind" the muon in place.

Kubo Toyabe

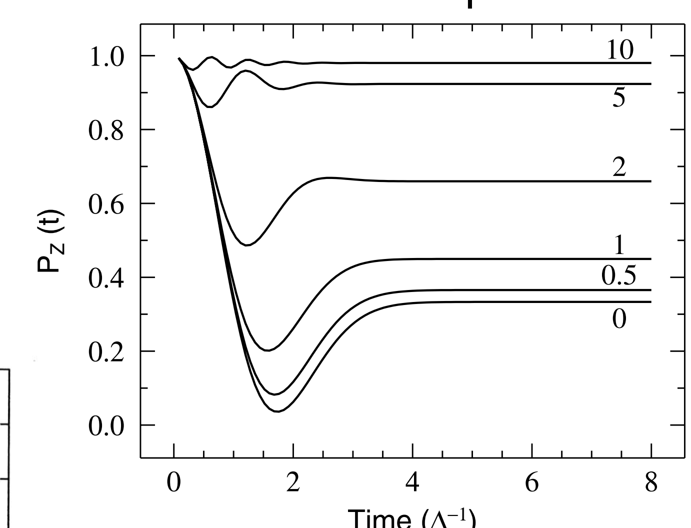
For a Gaussian distribution of static local fields, the polarisation is:

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

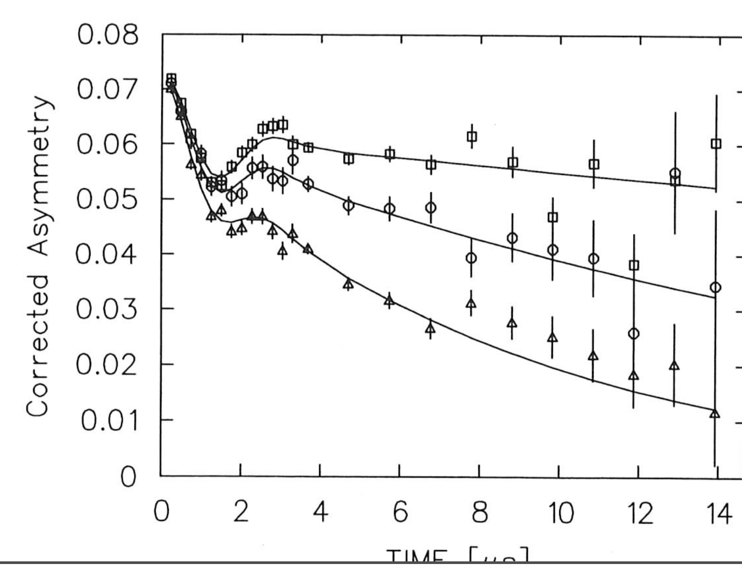
1/3 tail reflects that 1/3 of the muon polarisation is, on average, parallel to the local field (see Youanc & De Routier’s book for more details)



KT function has an LF-field dependence

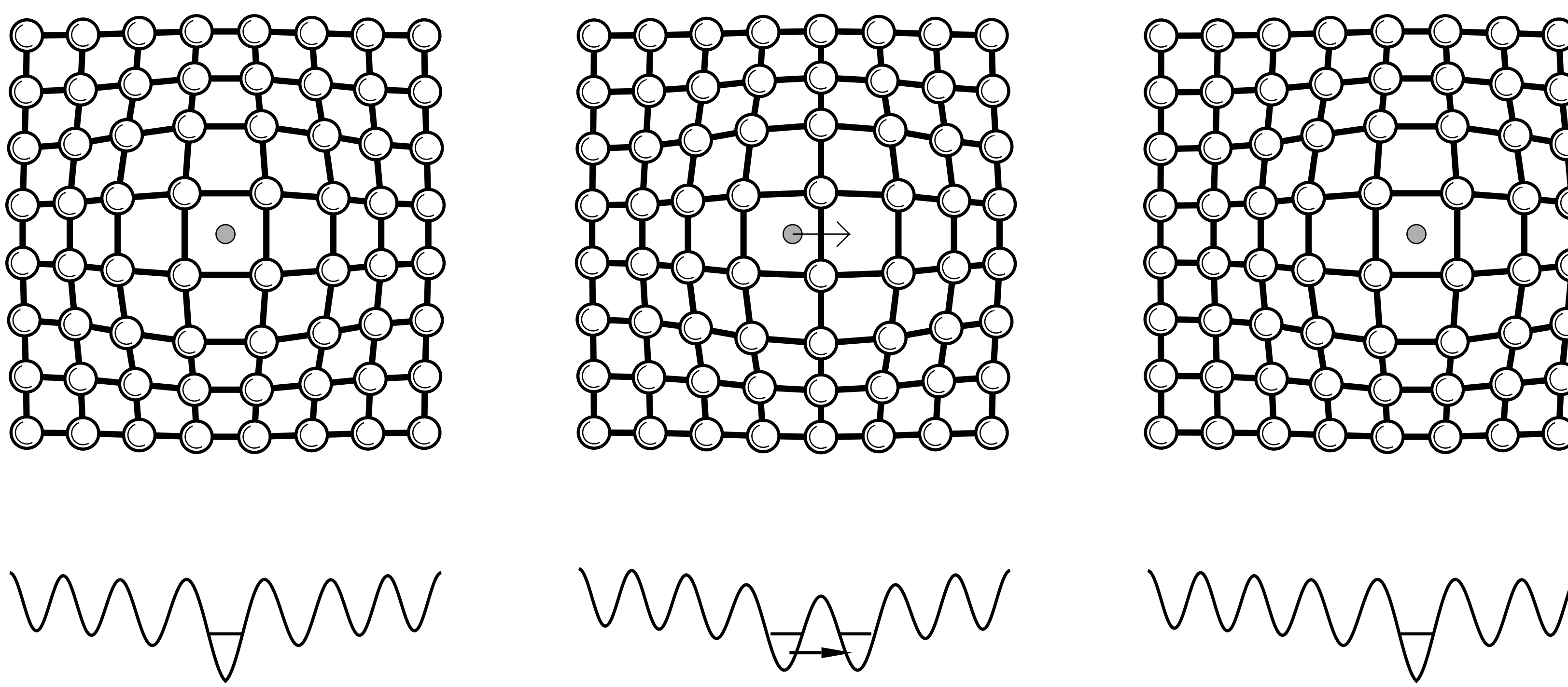


Slow dynamics leads to the function being “relaxed”. One is able to measure muonium hopping rates (analogous to hydrogen hopping).



Muon diffusion - how?

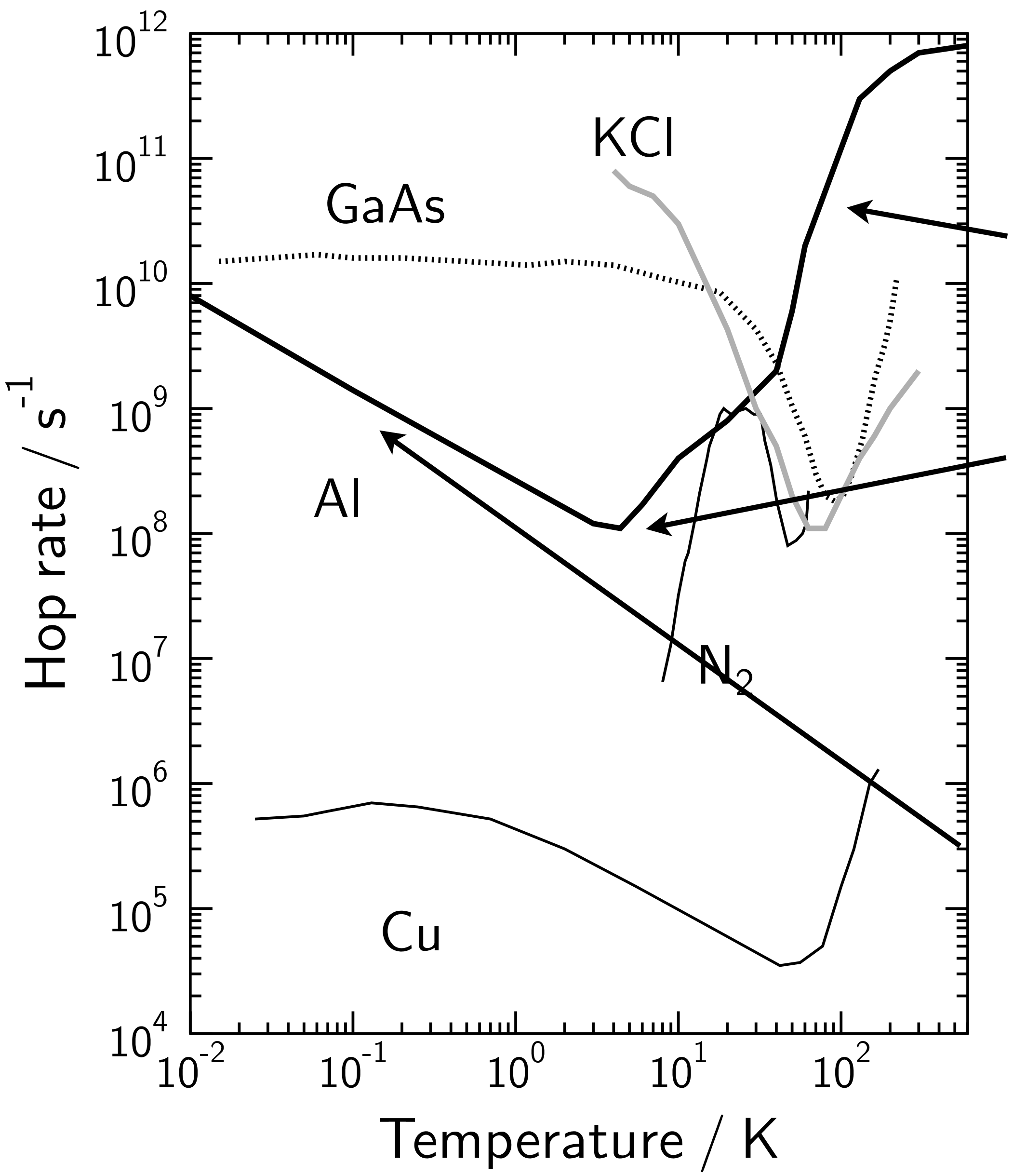
However, they can be mobile, depending on temperature.... Of interest is how hydrogen diffuses so rapidly from one interstitial site to the next.



At high temperatures, muons move between sites via phonon-assisted hopping.

Hopping rate proportional to $T^{1/2} \exp^{-E_a/kT}$

Temperature dependent muon hopping



As sample is cooled, diffusion drops due to phonon-assisted hopping.

A minima is reached

Then diffusion rate increases, due to tunnelling between states.

S. Blundell, Contemp. Phys. (2001)

Dynamic Kubo-Toyabe

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 + ...

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

no jumps

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

the static relaxation function

fraction of muons not hopped up to time t

one jump at t_1

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

$\boxed{\text{Sum up all single jumps between 0 and } t}$

two jumps

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

SUMMING UP

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

Analytic solutions can be found by Laplace transforms.

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

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

(a convolution!)

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

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

Sum of an infinite geometric progression

So not going into the details.....

Dynamic Kubo Toyabe

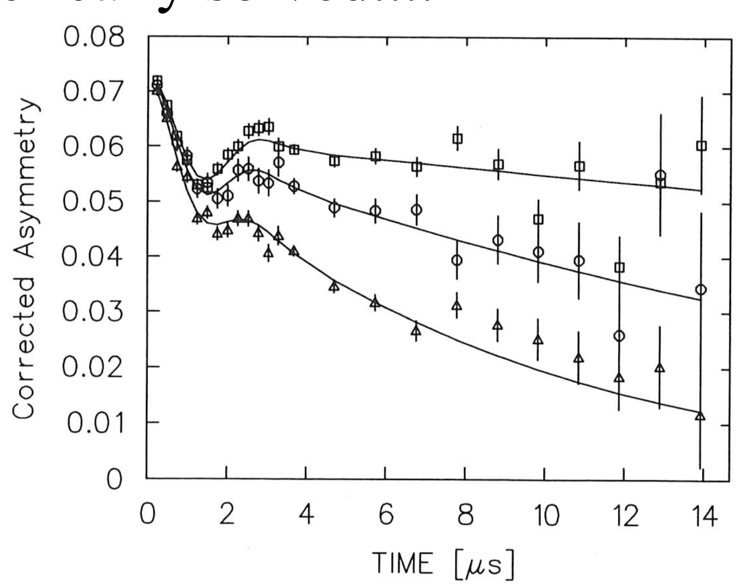
For a Gaussian distribution of static local fields, the polarisation is:

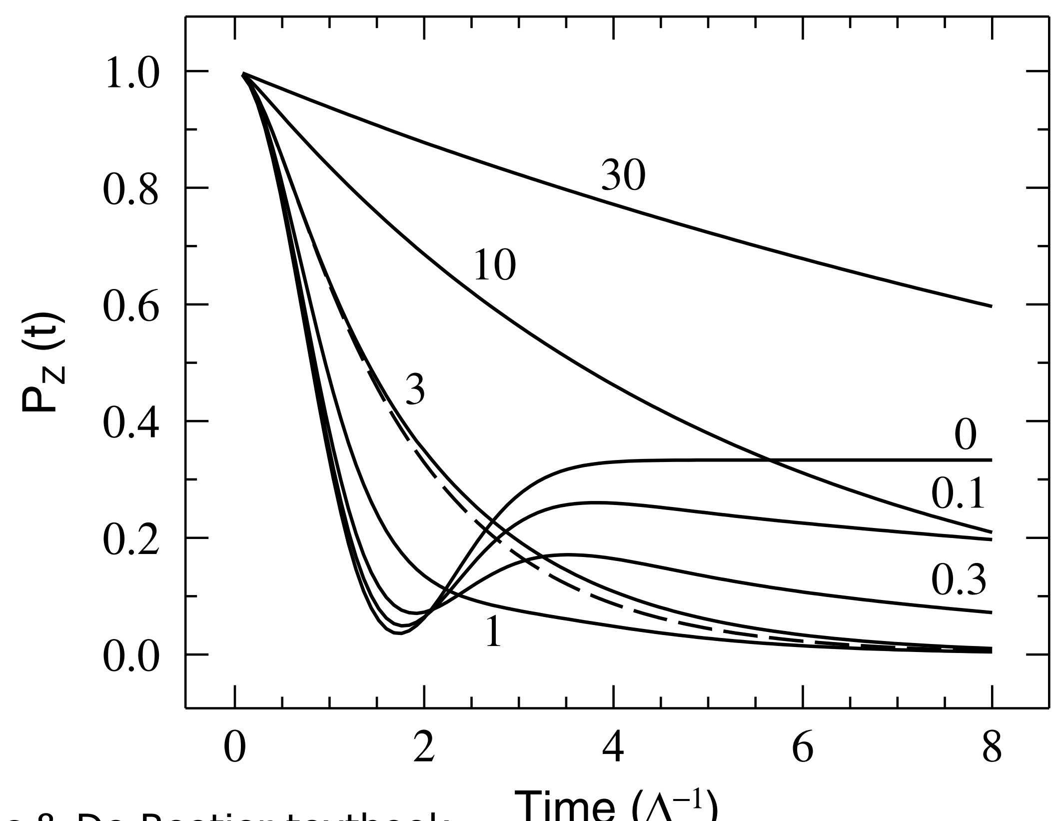
$$P(t) = \frac{1}{3} + \frac{2}{3}\left(1 - \Delta^2 t^2\right) \exp\left(-\frac{1}{2}\Delta^2 t^2\right) \ .$$

When the muon move, it averages over differences of the local field at different sites and a reduction of the linewidth is apparent (motional narrowing).

Equivalently, the lineshape goes over from Gaussian, when the muon is static in the lattice, to lorentzian, when the muon is diffusing rapidly.

This results in a dynamic Kubo-Toyabe function and must be numerically solved....

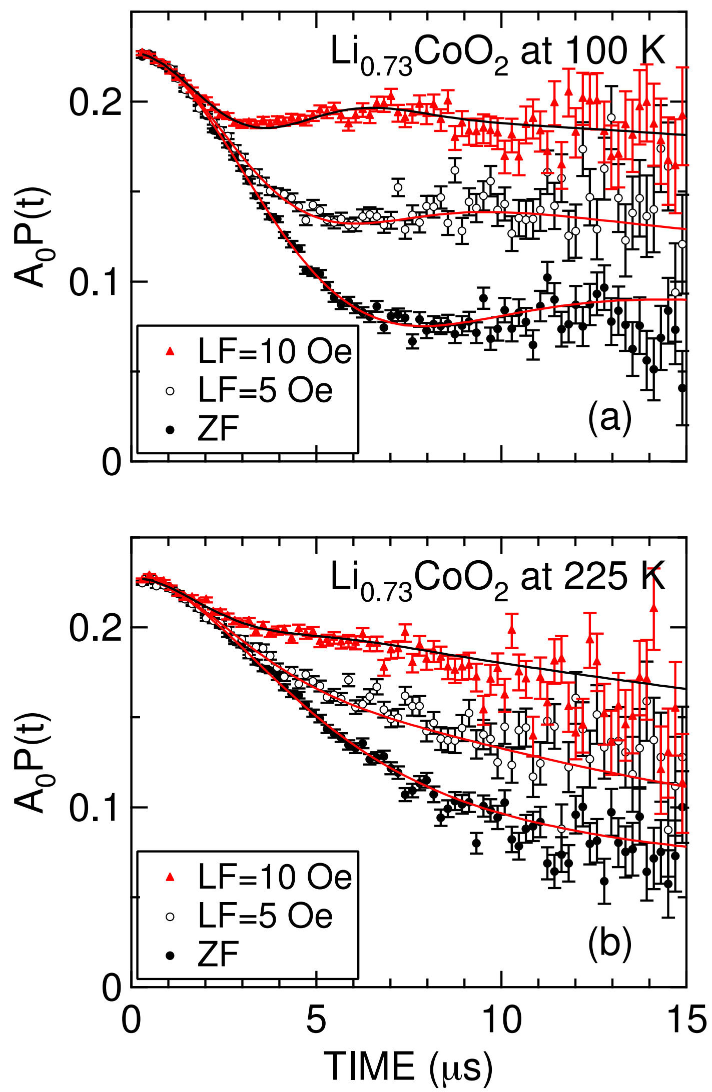




S. Cox, J. Phys. C: Solid State Phys. 20, 3187 (1987); Yaouanc & De Reotier textbook

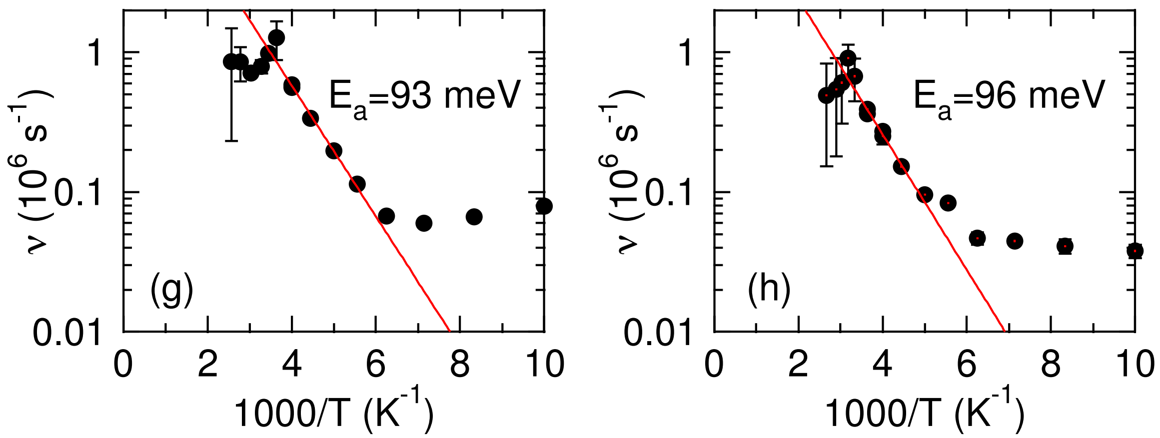
Li diffusion

Li diffusion in Li_xCoO_2



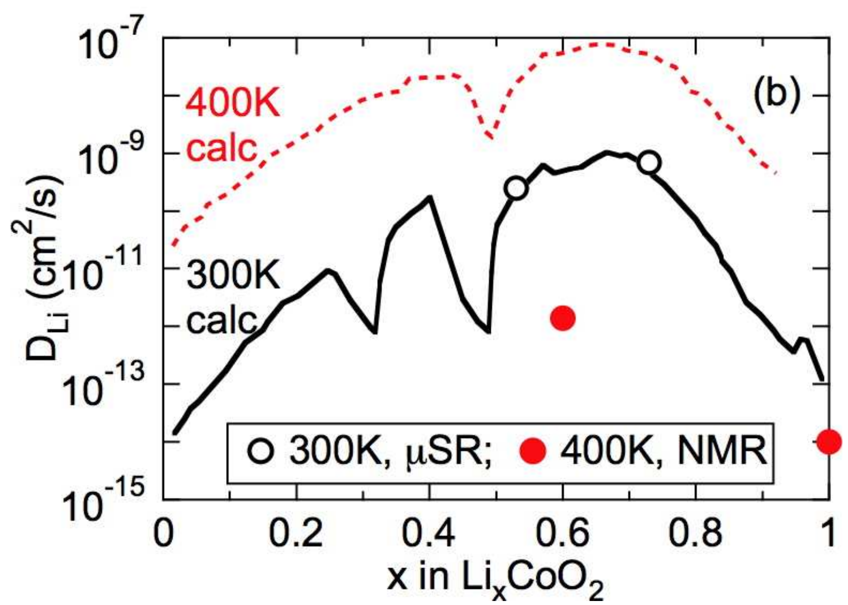
Fit to a dynamic Gaussian KT function

$$A_0\,P_{\rm LF}(t) \;=\; A_{\rm KT}G^{\rm DGKT}(\Delta,\nu,t,H_{\rm LF})+A_{\rm BG}$$



Li diffusion constant determined from the fluctuation rate

$$D_{\rm Li} \;=\; \sum_{i=1}^{n}\frac{1}{N_i}Z_{v,i}s_i^2\nu,$$



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