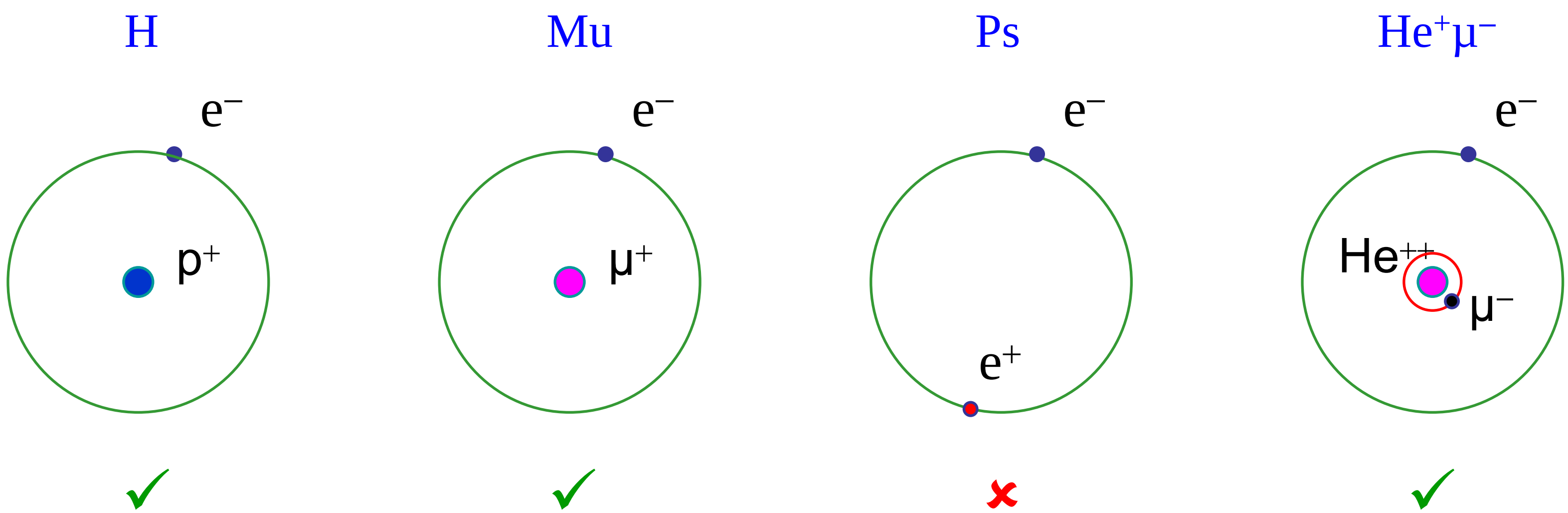
TRIUMF Summer Institute 2011

Lecture 9

Muonium

Paul Percival

Hydrogen-like Atoms



In the Bohr (planetary) model, the electrostatic attraction is balanced by the centrifugal acceleration of the orbiting electron

$$-\frac{(-Ze)e}{(4\pi\varepsilon_0)r^2} = \frac{m_e v^2}{r}$$

Assuming the orbital angular momentum is quantized, $L = mvr = n\hbar \qquad n = 1, 2, 3$

$$\Rightarrow \quad E_n = T + V = \tfrac{1}{2}mv^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{mZ^2e^4}{2n^2\hbar^2(4\pi\varepsilon_0)^2} = -\frac{\mathbb{R}}{n^2}$$

← Rydberg constant

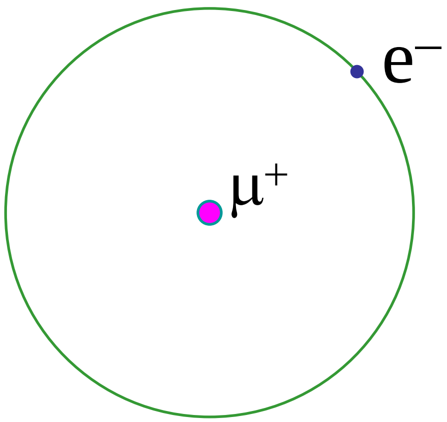
Muonium — a light isotope of hydrogen

Quantum mechanics gives the same result as the Bohr model

$$E_n = -\frac{Z^2 m_r e^4}{2\hbar^2 (4\pi\varepsilon_0)^2} \cdot \frac{1}{n^2} \qquad a_0 = \frac{\hbar^2 (4\pi\varepsilon_0)}{m_r e^2}$$

but if the coordinate system is defined by the centre of mass we need the reduced mass m_r

$$\frac{1}{m_r} = \frac{1}{m_N} + \frac{1}{m_e} \approx \frac{1}{m_e}$$



The properties of a single electron atom are determined by m_r

$$m_\mu = \tfrac{1}{9} m_p$$

reduced mass of Mu = 0.995 m_r(H)

ionization potential = 13.539 eV

Bohr radius = 0.532 Å

Muonium Isotope Effects

The chemistry of an atom depends primarily on

- the ionization potential — How easy is it to remove an electron?
- the radius — How are the electrons distributed?

For Mu these are almost the same as for H

However, for molecular vibrations involving Mu,

Mu—X

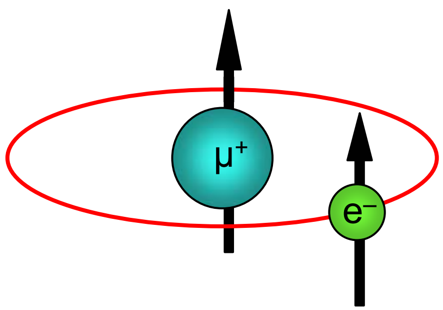
$$m_r = \frac{m_\mu m_X}{m_\mu + m_X} \approx m_\mu$$

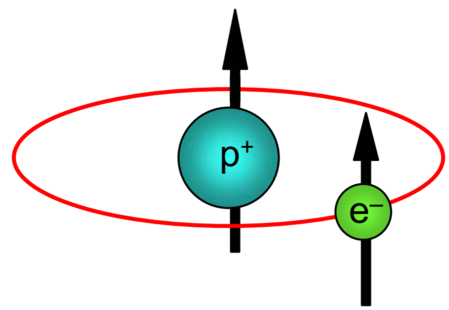
if $m_X >> m_\mu$

$$\therefore \upsilon_{MuX} = \sqrt{\frac{m_{HX}}{m_{MuX}}}\,\upsilon_{HX} \approx 3\upsilon_{HX}$$

$\Rightarrow$ Vibrational frequencies involving Mu are higher than for H

Muonium is a two-spin system like Hydrogen





The muon (proton) and the electron have spins and magnetic moments.

The interaction between them is termed the hyperfine interaction.

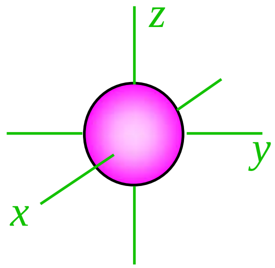
The H atom has no net dipolar interaction

(in its ground state)

$$E_{\mathrm{dipolar}} = \frac{(1-3\cos^2\theta)}{r^3}\mu_{\mathrm{I}}\mu_{\mathrm{S}}$$

Averaging over the spherical distribution of an electron in an *s* orbital

$$\left\langle \cos^2\theta \right\rangle = \frac{\int_0^{2\pi}\int_0^{\pi}\cos^2\theta\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi}{\int_0^{2\pi}\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi} = \frac{1}{3}$$



$$E_{\mathrm{dipolar}} = 0$$

The dipolar interaction determines the anisotropic part of the hyperfine interaction (off-diagonal components of the hyperfine tensor.

Isotropic hf constants are due to the "contact" interaction

Fermi (1930)

For a single electron

$$a = \frac{8\pi}{3} g\beta g_N \beta_N \left|\psi(0)\right|^2$$

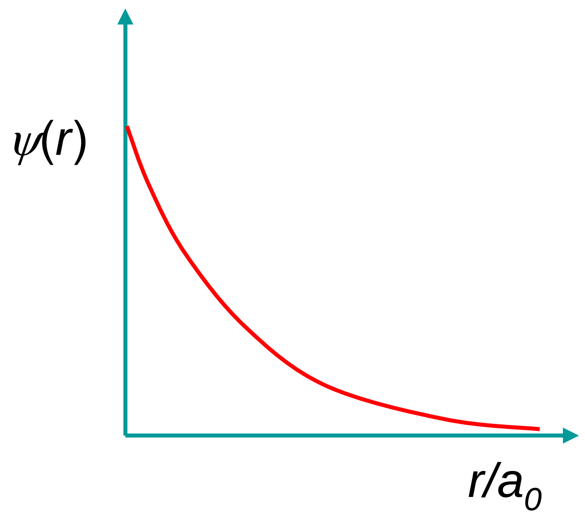
Only s electrons have density at the nucleus.

For the H atom

$$\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \qquad \psi(0)^2 = \frac{1}{\pi a_0^3}$$

A_H = 1420 MHz

A_{Mu} = 4463 MHz



Matrix Representation of Spin Operators

Consider a simple spin-½ system, such as an electron, a proton, or a muon.

Take as basis set, the eigenfunctions of $\hat{S}_z$: $\hat{S}_z|\alpha\rangle = \tfrac{1}{2}|\alpha\rangle$ $\hat{S}_z|\beta\rangle = -\tfrac{1}{2}|\beta\rangle$

The matrix elements are $\langle\alpha|\hat{S}_z|\alpha\rangle = \tfrac{1}{2}$ $\langle\beta|\hat{S}_z|\beta\rangle = -\tfrac{1}{2}$

$$\langle\alpha|\hat{S}_z|\beta\rangle = \tfrac{1}{2}\langle\alpha|\beta\rangle = 0 \qquad \langle\beta|\hat{S}_z|\alpha\rangle = 0$$

$$\Rightarrow \quad \hat{S}_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Similarly, $\hat{S}^2|\alpha\rangle = s(s+1)|\alpha\rangle = \tfrac{3}{4}|\alpha\rangle$

$$\hat{S}^2|\beta\rangle = \tfrac{3}{4}|\beta\rangle$$

$$\Rightarrow \quad \hat{S}^2 = \tfrac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \hat{S}^2\hat{S}_z = \tfrac{3}{8}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{S}_z\hat{S}^2$$

$$\left[\hat{S}^2, \hat{S}_z\right] = 0$$

$$\hat{S}_x|\alpha\rangle = \tfrac{1}{2}|\beta\rangle \qquad \hat{S}_x|\beta\rangle = \tfrac{1}{2}|\alpha\rangle$$

$$\hat{S}_y|\alpha\rangle = \tfrac{1}{2}i|\beta\rangle \qquad \hat{S}_y|\beta\rangle = -\tfrac{1}{2}i|\alpha\rangle$$

$$\hat{S}_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{S}_y = \tfrac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

α and β are not eigenfunctions of $\hat{S}_x$ and $\hat{S}_y$

$$\hat{S}_x\hat{S}_y = \tfrac{1}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \tfrac{1}{4}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\hat{S}_y\hat{S}_x = \tfrac{1}{4}i\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\Rightarrow \quad \left[\hat{S}_x, \hat{S}_y\right] = \tfrac{1}{2}i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\hat{S}_z$$

Matrix Diagonalization of a Spin Operator

$\hat{S}_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$ Set up the secular equation: $\det\begin{pmatrix} 0-\lambda & \frac{1}{2} \\ \frac{1}{2} & 0-\lambda \end{pmatrix} = \lambda^2 - \frac{1}{4} = 0$ and solve:

$$\lambda = \pm\tfrac{1}{2}$$

To find the coefficients of the eigenvectors, write out the simultaneous equations for each eigenvalue. Solve for coefficients and normalize

For $\lambda = -\frac{1}{2}$

$$\left(0+\tfrac{1}{2}\right)c_{11} + \tfrac{1}{2}c_{12} = 0 \qquad \tfrac{1}{2}c_{11} + \left(0+\tfrac{1}{2}\right)c_{12} = 0$$

$$c_{11} = -c_{12} \qquad c_{11}^2 + c_{12}^2 = 1 \qquad c_{11} = \tfrac{1}{\sqrt{2}} = -c_{12}$$

For $\lambda = \frac{1}{2}$

$$\left(0-\tfrac{1}{2}\right)c_{21} + \tfrac{1}{2}c_{22} = 0 \qquad \tfrac{1}{2}c_{21} + \left(0-\tfrac{1}{2}\right)c_{22} = 0$$

$$c_{21} = c_{22} \qquad c_{21}^2 + c_{22}^2 = 1 \qquad c_{21} = \tfrac{1}{\sqrt{2}} = c_{22}$$

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \qquad \frac{1}{4}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

or

$$\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \qquad \frac{1}{4}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

arbitrary labelling of wave functions

↑ $\hat{S}_x$ is diagonal in the new basis

H Atom Spin States – 1

also muonium!

Spin Hamiltonian

in units of $\hbar$

$$\hat{\mathbf{H}} = \omega_e \hat{\mathbf{S}}_z - \omega_p \hat{\mathbf{I}}_z + \omega_0 \hat{\mathbf{S}} \bullet \hat{\mathbf{I}}$$

electron nuclear
Zeeman interactions

hyperfine interaction
(isotropic case)

$$\hat{\mathbf{S}} \bullet \hat{\mathbf{I}} = \hat{\mathbf{S}}_x \hat{\mathbf{I}}_x + \hat{\mathbf{S}}_y \hat{\mathbf{I}}_y + \hat{\mathbf{S}}_z \hat{\mathbf{I}}_z$$

$$\left. \begin{aligned} \hat{\mathbf{S}}_+ &= \hat{\mathbf{S}}_x + i\hat{\mathbf{S}}_y \\ \hat{\mathbf{S}}_- &= \hat{\mathbf{S}}_x - i\hat{\mathbf{S}}_y \end{aligned} \right\} \Leftrightarrow \left\{ \begin{aligned} \hat{\mathbf{S}}_x &= \tfrac{1}{2}\left(\hat{\mathbf{S}}_+ + \hat{\mathbf{S}}_-\right) \\ \hat{\mathbf{S}}_y &= \tfrac{1}{2i}\left(\hat{\mathbf{S}}_+ - \hat{\mathbf{S}}_-\right) \end{aligned} \right.$$

$$\hat{\mathbf{S}} \bullet \hat{\mathbf{I}} = \tfrac{1}{2}\left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+\right) + \hat{\mathbf{S}}_z \hat{\mathbf{I}}_z$$

$$\hat{\mathbf{S}}_x \hat{\mathbf{I}}_x = \tfrac{1}{4}\left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_+ + \hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+ + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_-\right)$$

$$\hat{\mathbf{S}}_y \hat{\mathbf{I}}_y = -\tfrac{1}{4}\left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_+ - \hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- - \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+ + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_-\right)$$

Consider a basis set of product spin functions

$$|\alpha\alpha\rangle,\ |\alpha\beta\rangle,\ |\beta\alpha\rangle \text{ and } |\beta\beta\rangle \qquad \equiv |m_S, m_I\rangle$$

$$\hat{\mathbf{H}}|\alpha\alpha\rangle = \omega_e \hat{\mathbf{S}}_z|\alpha\alpha\rangle - \omega_p \hat{\mathbf{I}}_z|\alpha\alpha\rangle + \tfrac{1}{2}\omega_0\left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+\right)|\alpha\alpha\rangle + \omega_0 \hat{\mathbf{S}}_z \hat{\mathbf{I}}_z|\alpha\alpha\rangle$$

$$= \tfrac{1}{2}\omega_e|\alpha\alpha\rangle - \tfrac{1}{2}\omega_p|\alpha\alpha\rangle + 0 + \tfrac{1}{4}\omega_0|\alpha\alpha\rangle$$

$|\alpha\alpha\rangle$ is an eigenfunction

$$\hat{\mathbf{H}}|\alpha\beta\rangle = \omega_e \hat{\mathbf{S}}_z|\alpha\beta\rangle - \omega_p \hat{\mathbf{I}}_z|\alpha\beta\rangle + \tfrac{1}{2}\omega_0\left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+\right)|\alpha\beta\rangle + \omega_0 \hat{\mathbf{S}}_z \hat{\mathbf{I}}_z|\alpha\beta\rangle$$

$$= \tfrac{1}{2}\omega_e|\alpha\beta\rangle + \tfrac{1}{2}\omega_p|\alpha\beta\rangle + \tfrac{1}{2}\omega_0\left(0 + |\beta\alpha\rangle\right) - \tfrac{1}{4}\omega_0|\alpha\beta\rangle$$

$|\alpha\beta\rangle$ is not an eigenfunction

H Atom Spin States – 2

Evaluating all matrix elements…

$$\hat{\mathbf{H}} = \begin{pmatrix} \tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 & 0 & 0 & 0 \\ 0 & \tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 & \tfrac{1}{2}\omega_0 & 0 \\ 0 & \tfrac{1}{2}\omega_0 & -\tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 & 0 \\ 0 & 0 & 0 & -\tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 \end{pmatrix} \begin{matrix} |\alpha\alpha\rangle \\ |\alpha\beta\rangle \\ |\beta\alpha\rangle \\ |\beta\beta\rangle \end{matrix}$$

$$E_1 = \tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 \qquad |1\rangle = |\alpha\alpha\rangle$$

$$E_4 = -\tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 \qquad |4\rangle = |\beta\beta\rangle$$

The central block must be diagonalized to find E_2 and E_3.

$$\left[\tfrac{1}{2}(\omega_e + \omega_p) - \tfrac{1}{4}\omega_0 - E\right]\left[-\tfrac{1}{2}(\omega_e + \omega_p) - \tfrac{1}{4}\omega_0 - E\right] - \tfrac{1}{4}\omega_0^2 = 0$$

$$E_2 = \tfrac{1}{2}\left[(\omega_e + \omega_p)^2 + \omega_0^2\right]^{1/2} - \tfrac{1}{4}\omega_0 \qquad |2\rangle = c|\alpha\beta\rangle + s|\beta\alpha\rangle$$

$$E_3 = -\tfrac{1}{2}\left[(\omega_e + \omega_p)^2 + \omega_0^2\right]^{1/2} - \tfrac{1}{4}\omega_0 \qquad |3\rangle = c|\beta\alpha\rangle - s|\alpha\beta\rangle$$

$$c^2 + s^2 = 1$$

Summary of Muonium Energies and States

$$E_1 = \tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_\mu + \tfrac{1}{4}\omega_0 \qquad |1\rangle = |\alpha\alpha\rangle$$

$$E_2 = \tfrac{1}{2}\left[\left(\omega_e + \omega_\mu\right)^2 + \omega_0^2\right]^{1/2} - \tfrac{1}{4}\omega_0 \qquad |2\rangle = c|\alpha\beta\rangle + s|\beta\alpha\rangle$$

$$E_3 = -\tfrac{1}{2}\left[\left(\omega_e + \omega_\mu\right)^2 + \omega_0^2\right]^{1/2} - \tfrac{1}{4}\omega_0 \qquad |3\rangle = c|\beta\alpha\rangle - s|\alpha\beta\rangle$$

$$E_4 = -\tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_\mu + \tfrac{1}{4}\omega_0 \qquad |4\rangle = |\beta\beta\rangle$$

Beware!

This is not the usual numbering of these two states

The mixing coefficients (c and s) govern the curvature in the Breit Rabi plot.

$$c = \frac{1}{\sqrt{2}}\left\{1 + \frac{\left(\omega_e + \omega_\mu\right)}{\left[\omega_0^2 + \left(\omega_e + \omega_\mu\right)^2\right]^{1/2}}\right\}^{1/2}$$

$$s = \frac{1}{\sqrt{2}}\left\{1 - \frac{\left(\omega_e + \omega_\mu\right)}{\left[\omega_0^2 + \left(\omega_e + \omega_\mu\right)^2\right]^{1/2}}\right\}^{1/2}$$

$$c^2 + s^2 = 1$$

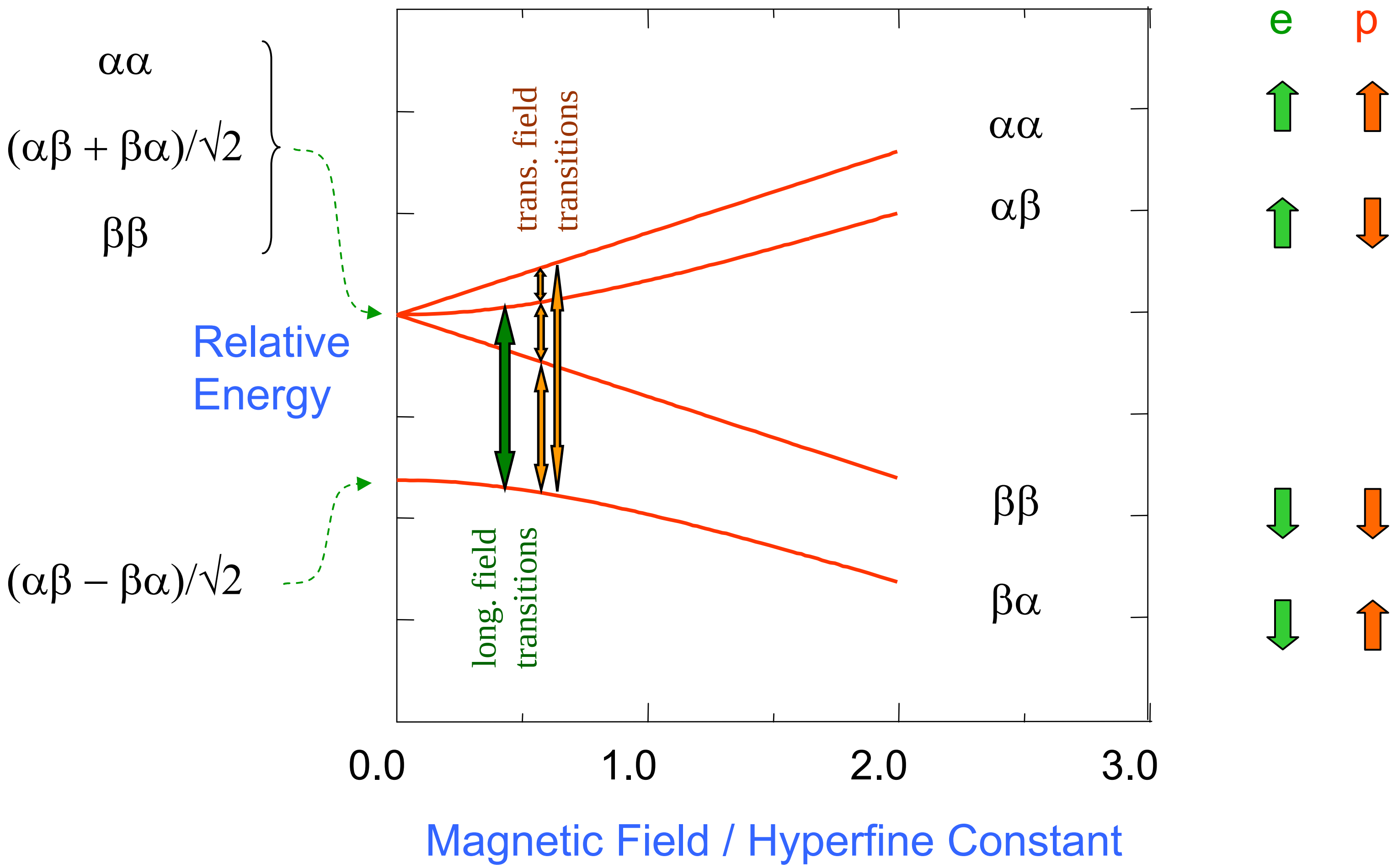
At zero field, $c = s = \dfrac{1}{\sqrt{2}}$

At low field, $c \rightarrow \dfrac{1}{\sqrt{2}} \leftarrow s$

At high field, $c \rightarrow 1,\ s \rightarrow 0$

Energy levels of a two spin-½ system

Breit-Rabi diagram



Muonium Energies and States

conventional numbering

$$|1\rangle = |\alpha\alpha\rangle \qquad E_1 = \tfrac{1}{4}\omega_0 + \omega_-$$

$$|2\rangle = c|\alpha\beta\rangle + s|\beta\alpha\rangle \qquad E_2 = -\tfrac{1}{4}\omega_0 + \left[\omega_+{}^2 + \tfrac{1}{4}\omega_0^2\right]^{1/2} = -\tfrac{1}{4}\omega_0 + \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$

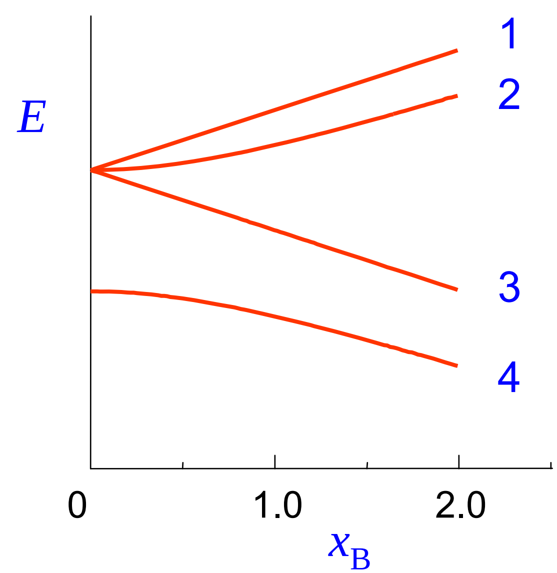
$$|3\rangle = |\beta\beta\rangle \qquad E_3 = \tfrac{1}{4}\omega_0 - \omega_-$$

$$|4\rangle = c|\beta\alpha\rangle - s|\alpha\beta\rangle \qquad E_4 = -\tfrac{1}{4}\omega_0 - \left[\omega_+{}^2 + \tfrac{1}{4}\omega_0^2\right]^{1/2} = -\tfrac{1}{4}\omega_0 - \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$

$$\omega_- = \tfrac{1}{2}\left(\omega_e - \omega_\mu\right) \qquad \omega_+ = \tfrac{1}{2}\left(\omega_e + \omega_\mu\right) \qquad x_B = \frac{\left(\omega_e + \omega_\mu\right)}{\omega_0}$$

$$c^2 = \frac{1}{2}\left(1 + \frac{x_B}{\left[1 + x_B^2\right]^{1/2}}\right)$$

$$s^2 = \frac{1}{2}\left(1 - \frac{x_B}{\left[1 + x_B^2\right]^{1/2}}\right)$$



Muonium in Zero and Longitudinal Field

If the muon ensemble is initially polarized, but the electrons not, the initial state of the system is $\tfrac{1}{2}|\alpha\alpha\rangle + \tfrac{1}{2}|\beta\alpha\rangle$.

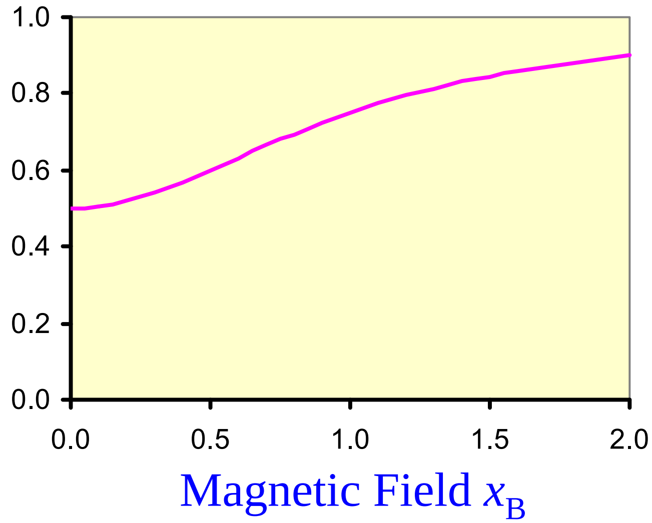
Half of the muon ensemble is static, in the eigenstate $|\alpha\alpha\rangle$, the other half oscillates between the mixed states $|2\rangle$ and $|4\rangle$ at frequency

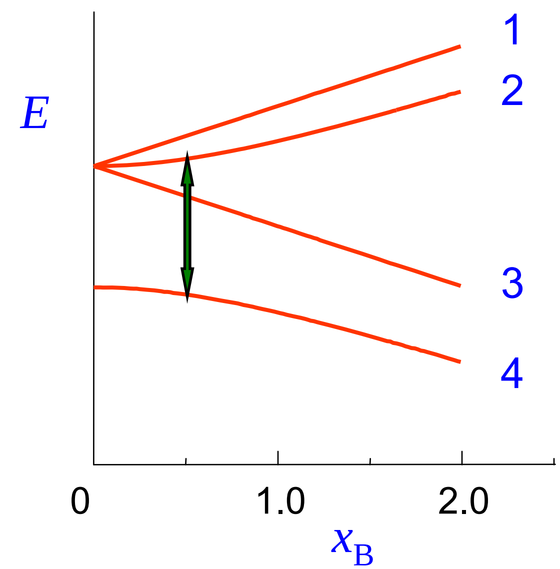
$$\omega_{24} = \omega_0 \left[1 + x_{\mathrm{B}}^2\right]^{1/2}$$

The muon polarization along the field direction is

$$P_z = \tfrac{1}{2}\left\{1 + \frac{x_{\mathrm{B}}^2 + \cos\omega_{24}t}{1 + x_{\mathrm{B}}^2}\right\}$$

non-osc. P_z

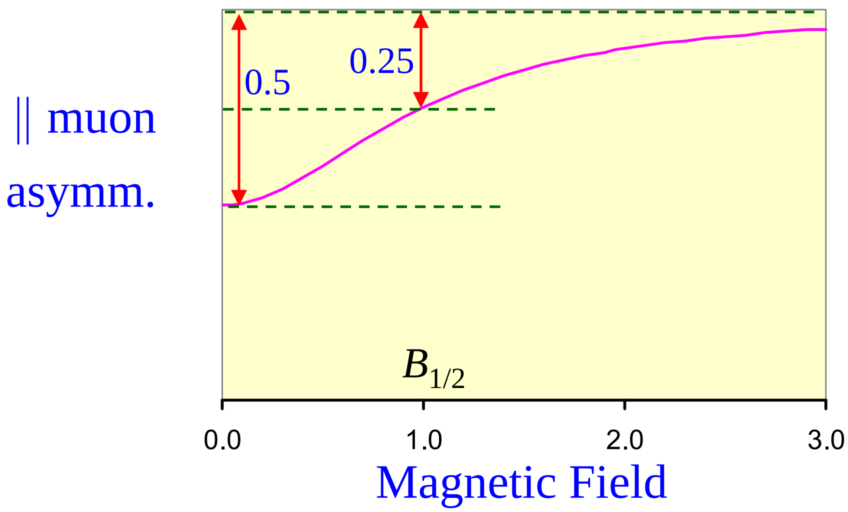




Repolarization Curves

sometimes described as decoupling curves

Contrary to common language in the field, the muon is never "decoupled" from the electron. As the external applied field increases, it surpasses the internal field from the hyperfine interaction. In energy terms, the Larmor term exceeds the hf term.



In principle, the hyperfine constant can be found from the field at which half of the polarization has been recovered (or better, by fitting the whole curve).

$$\omega_0 = \left(\gamma_e + \gamma_\mu\right) B_{1/2}$$

But...

- ❖ the high-field (maximum) polarization may not be easily determined.
- ❖ spin relaxation changes the shape of the repolarization curve.

Muonium in Transverse Field

$$P_\perp = \tfrac{1}{2}\left\{c^2\left(e^{i\omega_{12}t}+e^{i\omega_{43}t}\right)+s^2\left(e^{i\omega_{14}t}+e^{i\omega_{23}t}\right)\right\}$$

at low field

$$\omega_{12} = E_1 - E_2 = \omega_- + \tfrac{1}{2}\omega_0 - \tfrac{1}{2}\omega_0\left[1+x_B^2\right]^{1/2} \rightarrow \omega_-$$

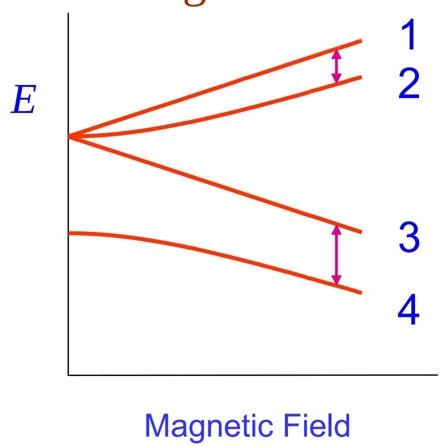
$$\omega_{43} = E_4 - E_3 = \omega_- - \tfrac{1}{2}\omega_0 - \tfrac{1}{2}\omega_0\left[1+x_B^2\right]^{1/2} \rightarrow \omega_- - \omega_0$$

$$\omega_{14} = E_1 - E_4 = \omega_- + \tfrac{1}{2}\omega_0 + \tfrac{1}{2}\omega_0\left[1+x_B^2\right]^{1/2} \rightarrow \omega_- + \omega_0$$

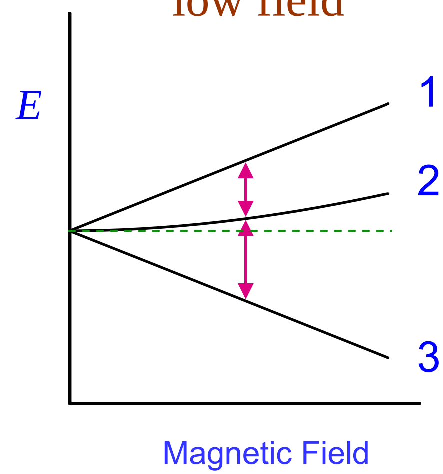
$$\omega_{23} = E_2 - E_3 = \omega_- - \tfrac{1}{2}\omega_0 + \tfrac{1}{2}\omega_0\left[1+x_B^2\right]^{1/2} \rightarrow \omega_-$$

} usually (?) too high to detect

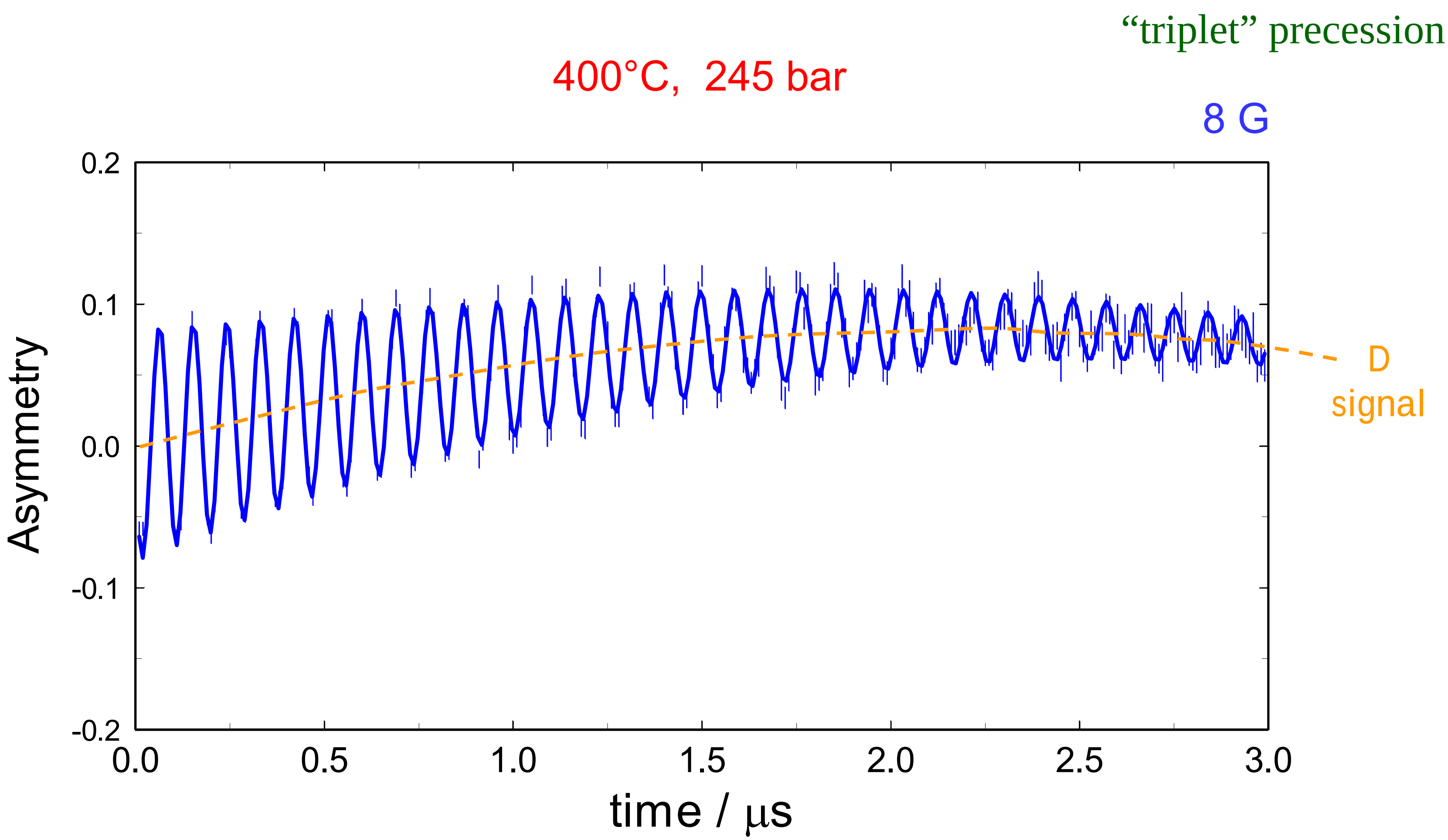
high field



low field



Muonium in supercritical water

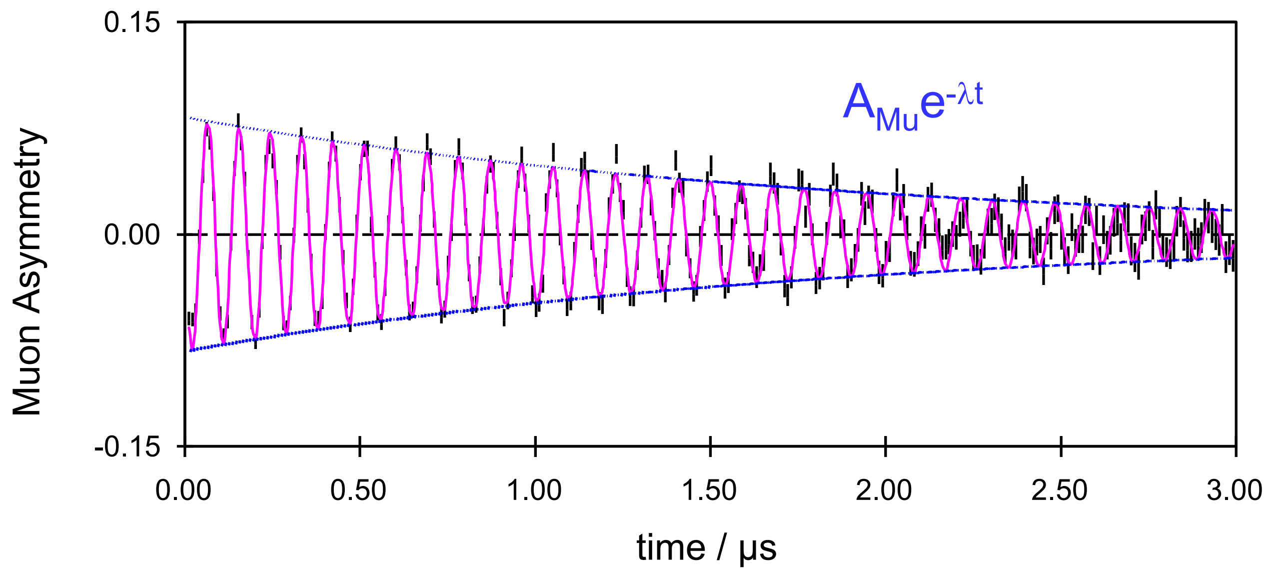


Percival, Brodovitch, Ghandi et al., Phys. Chem. Chem. Phys. 1 (1999) 4999

Muonium in supercritical water

400°C, 245 bar, 8 G

Diamagnetic signal subtracted



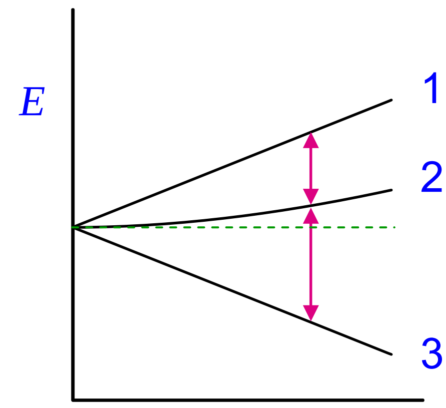
Muonium in Moderate Transverse Field

$$\omega_{12} = E_1 - E_2 = \omega_- + \tfrac{1}{2}\omega_0 - \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$

$$\omega_{43} = E_4 - E_3 = \omega_- - \tfrac{1}{2}\omega_0 - \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$

$$\omega_{14} = E_1 - E_4 = \omega_- + \tfrac{1}{2}\omega_0 + \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$

$$\omega_{23} = E_2 - E_3 = \omega_- - \tfrac{1}{2}\omega_0 + \tfrac{1}{2}\omega_0\left[1 + x_B^2\right]^{1/2}$$



Defining $\Omega = \tfrac{1}{2}\omega_0\left[\left(1 + x_B^2\right)^{1/2} - 1\right]$

$$\omega_{12} = \omega_- - \Omega$$

$$\omega_{43} = \omega_- - \Omega - \omega_0$$

$$\omega_{14} = \omega_- + \Omega + \omega_0$$

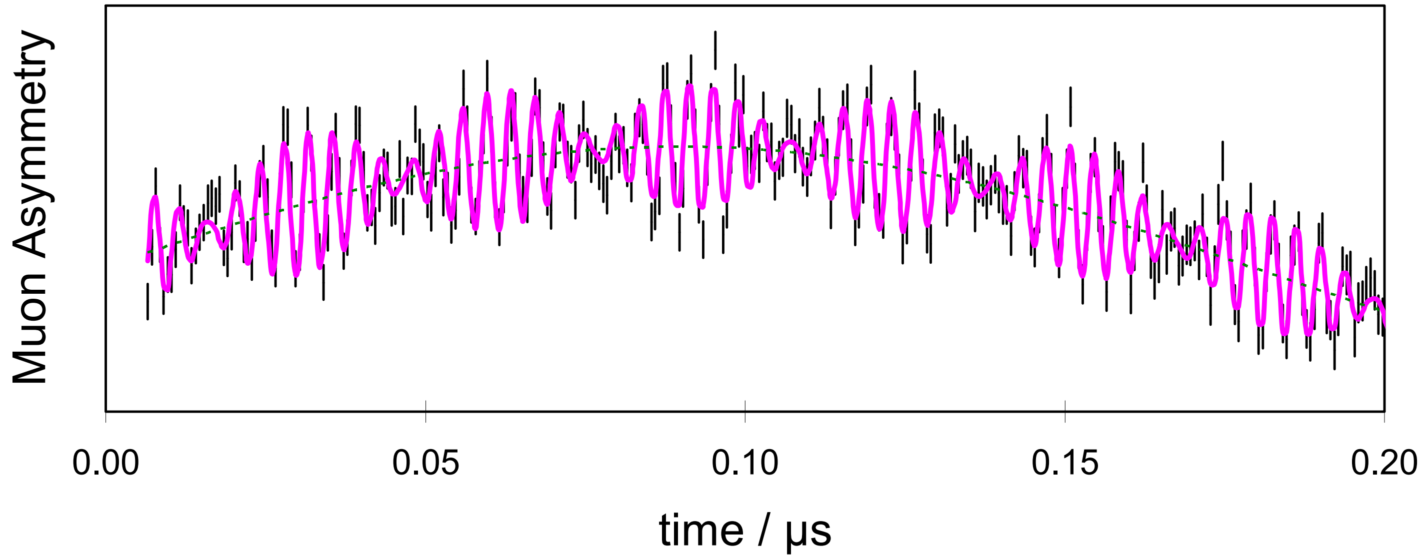
$$\omega_{23} = \omega_- + \Omega$$

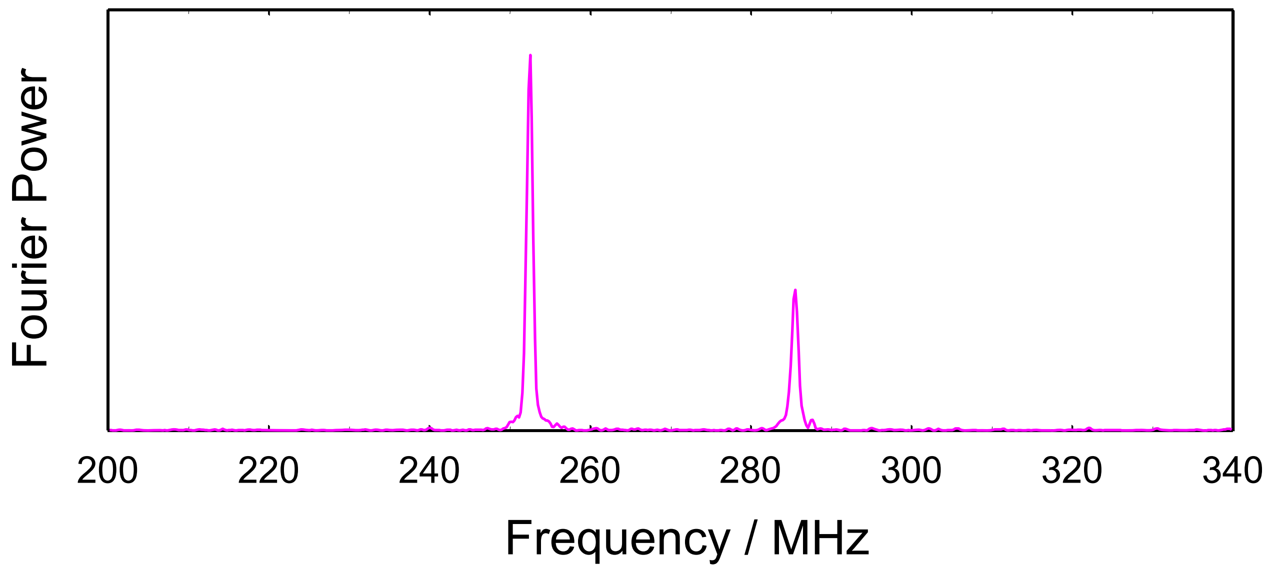
a pair of frequencies "split" about ω_-

The splitting can be used to determine ω_0

$$\omega_0 = \tfrac{1}{2}\left[\frac{\left(\omega_{23} + \omega_{12} + 2\omega_\mu\right)^2 - \left(\omega_{23} - \omega_{12}\right)^2}{\omega_{23} - \omega_{12}}\right]$$

Muonium in supercritical water at 196 G

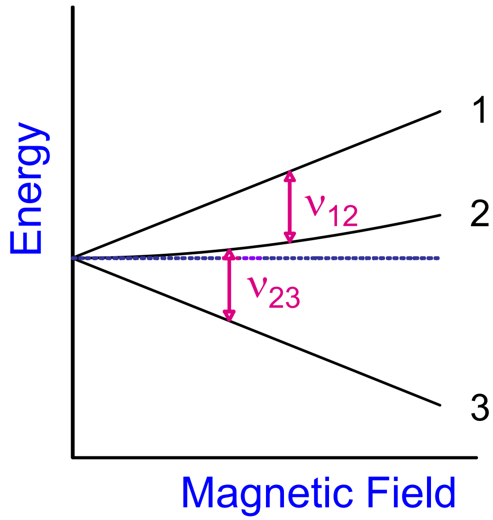


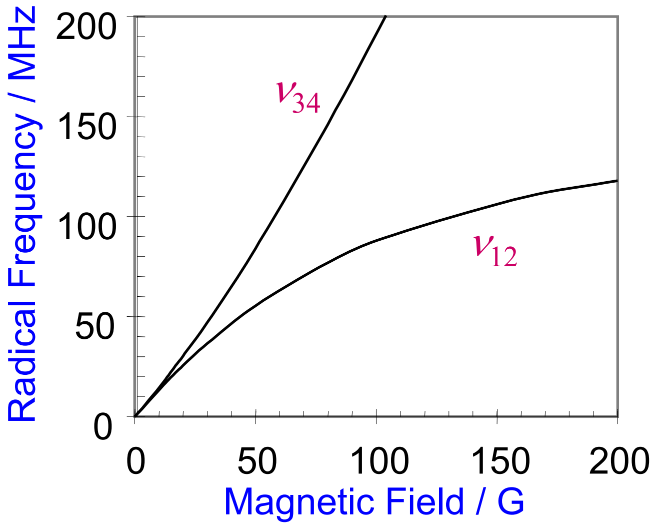


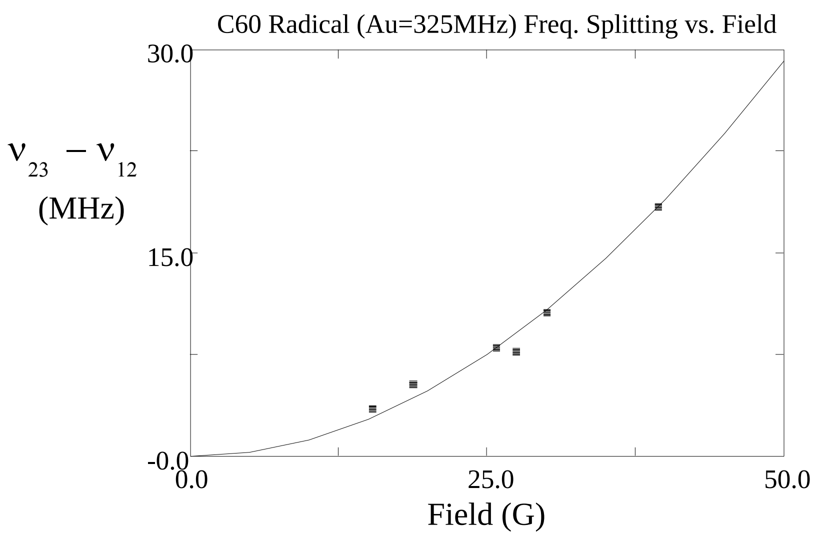
400°C

245 bar

C_{60}Mu Radical Precession Frequencies in Low Magnetic Field

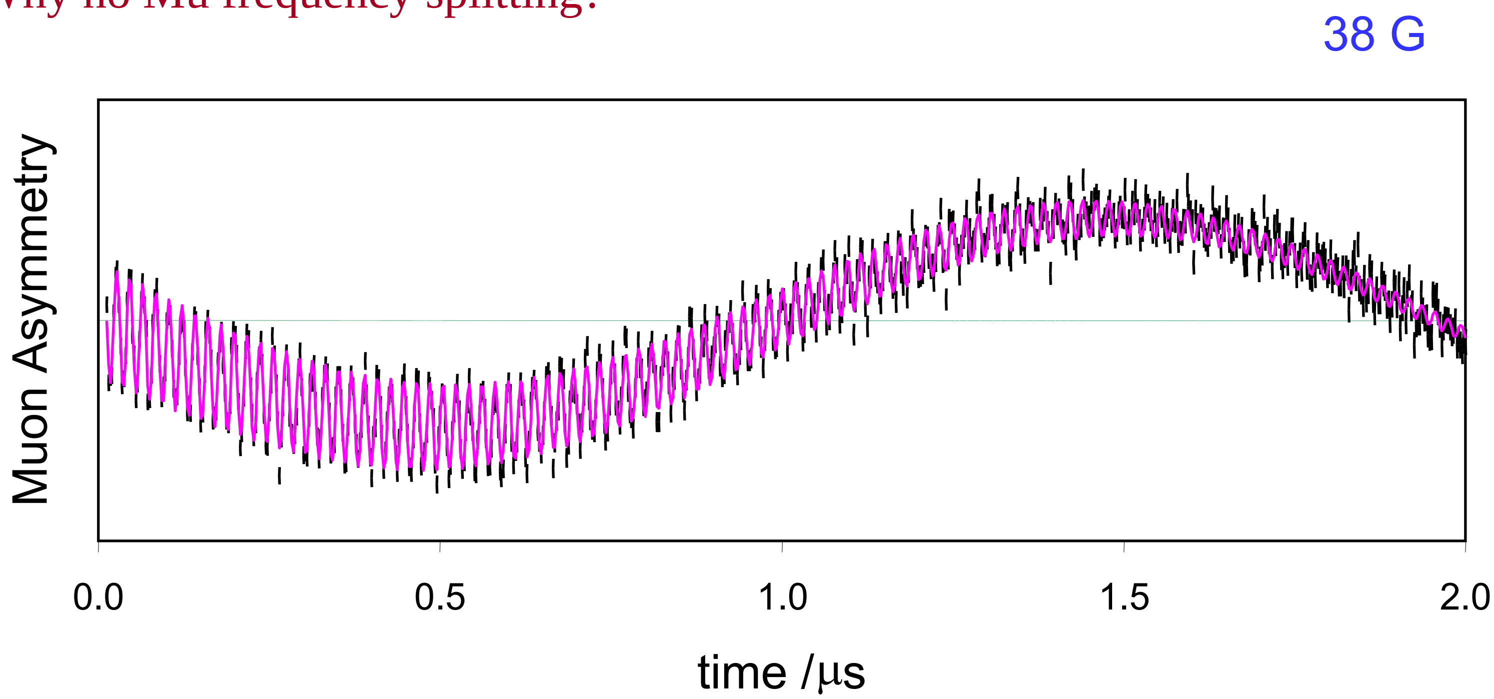






Muon spin precession in D_2O crystal at 227 K

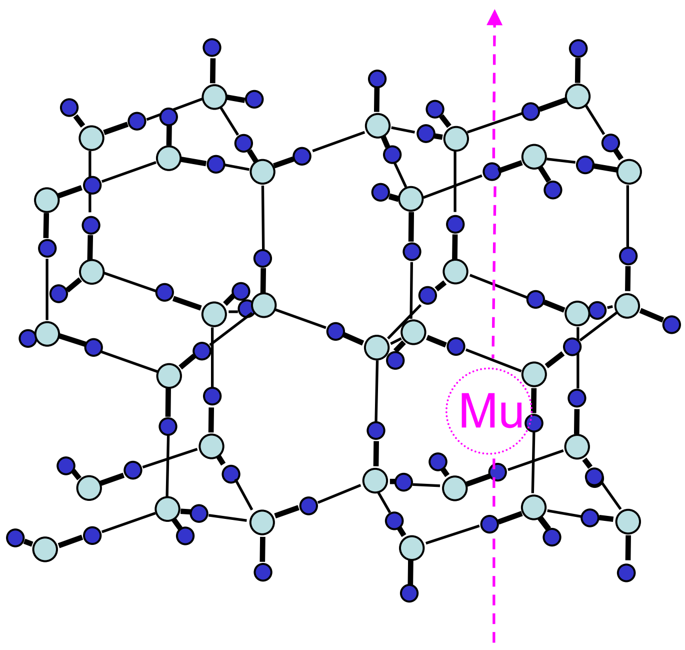
Why no Mu frequency splitting?



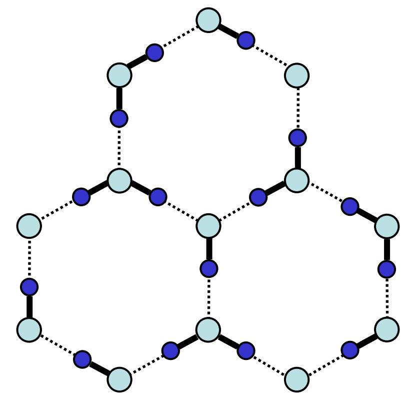
The high frequency precession is due to "triplet" (F=1) muonium.

The low frequency is due to muons in diamagnetic environments, such as MuOD and $MuOD_2^+$

Mu diffuses along the c-axis channels of ice-Ih

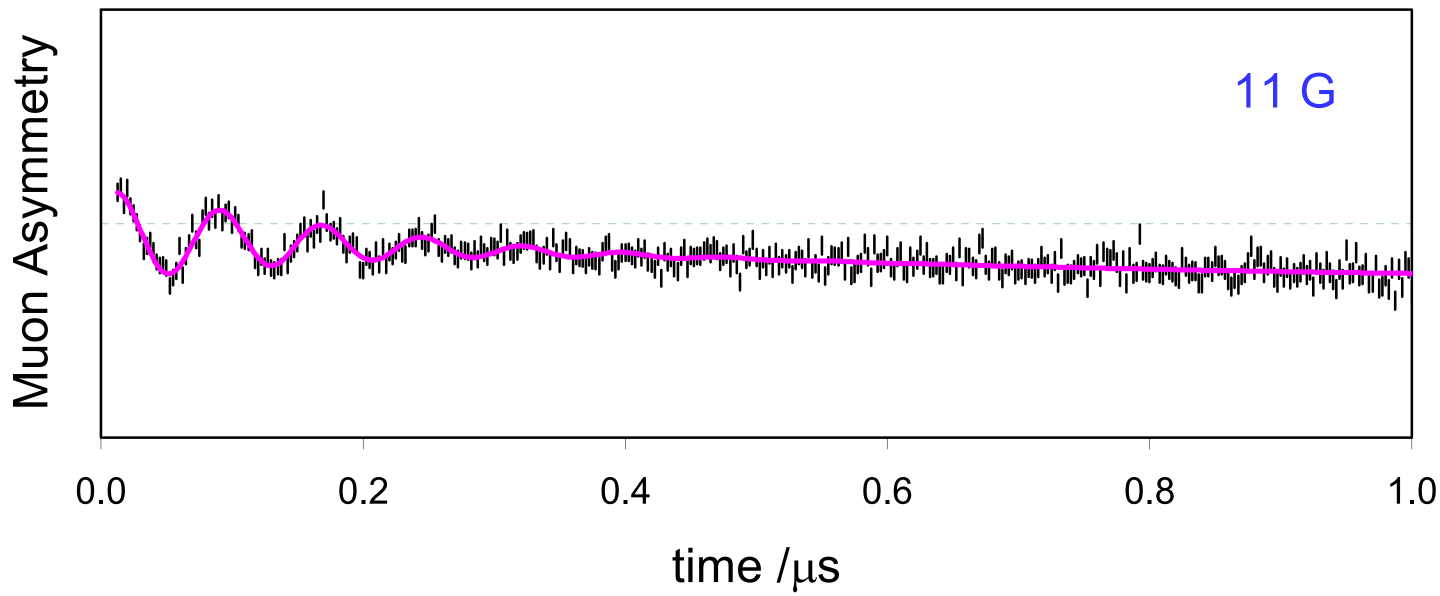


side view



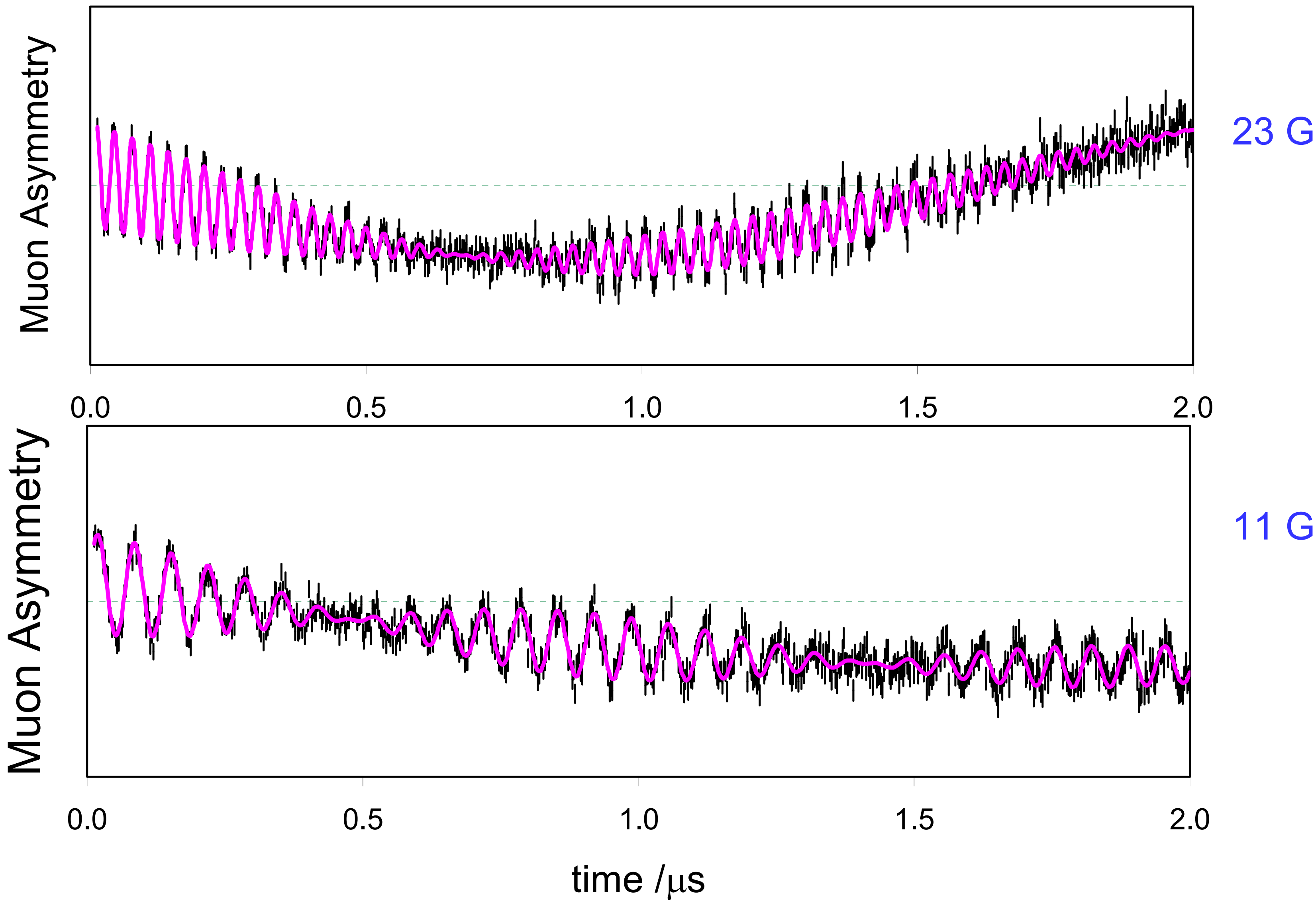
view along *c* channel

Muon spin precession in D_2O crystal at 27 K

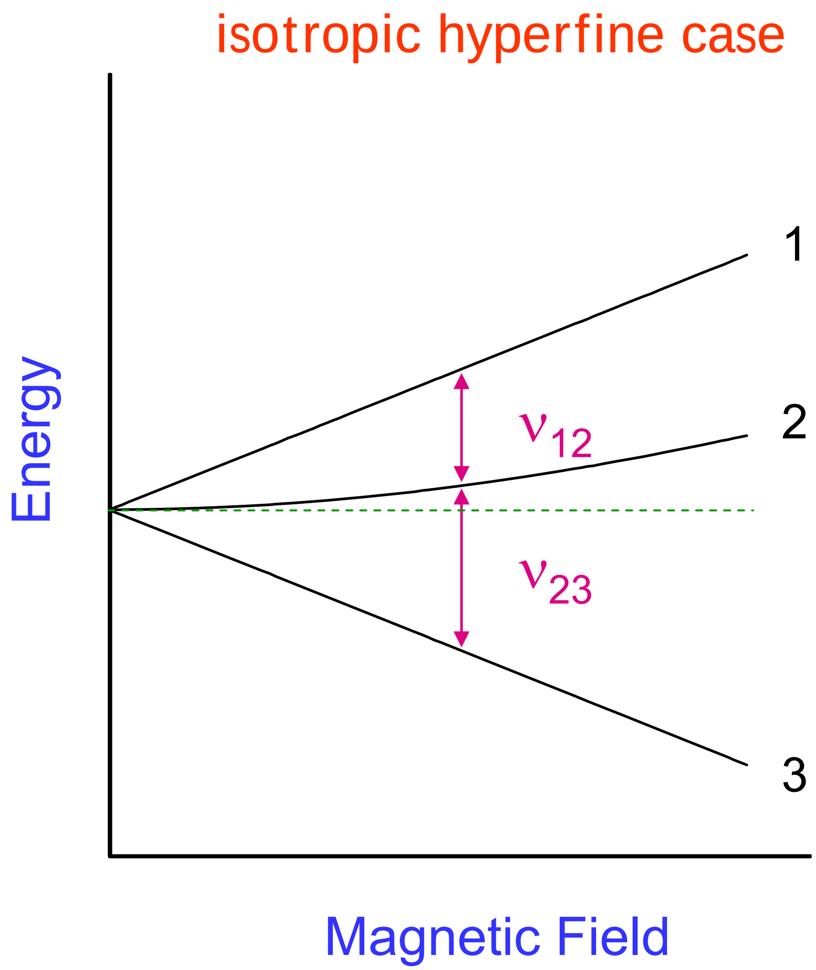


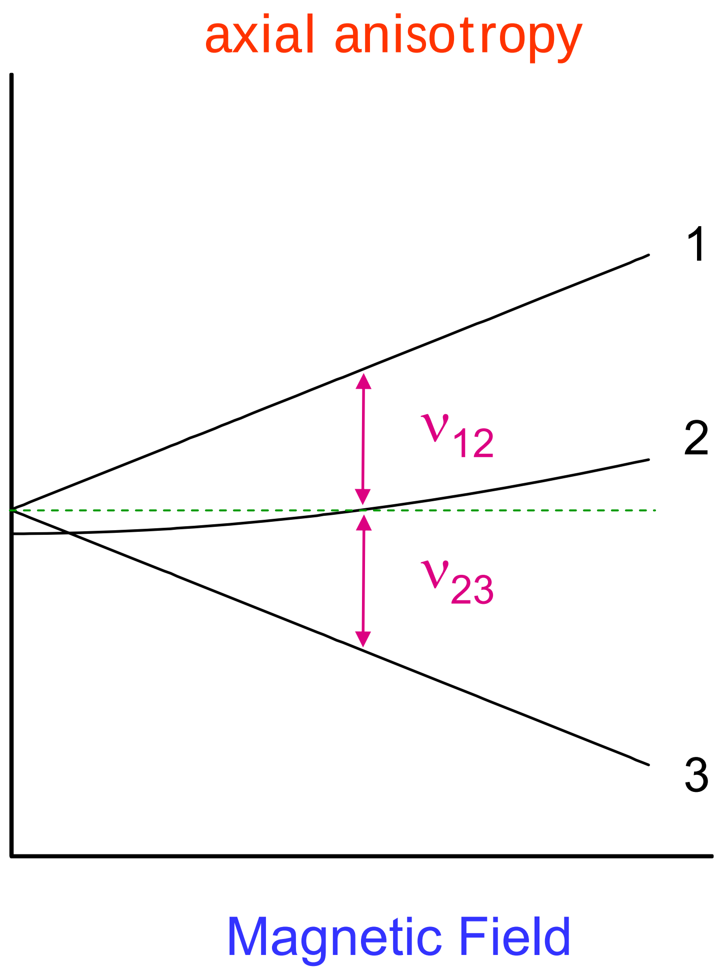
At lower temperature the muonium atom diffuses more slowly. The dipolar interaction between the muonium electron and the lattice nuclei results in spin relaxation.

Muon spin precession in D_2O crystal at 230 K

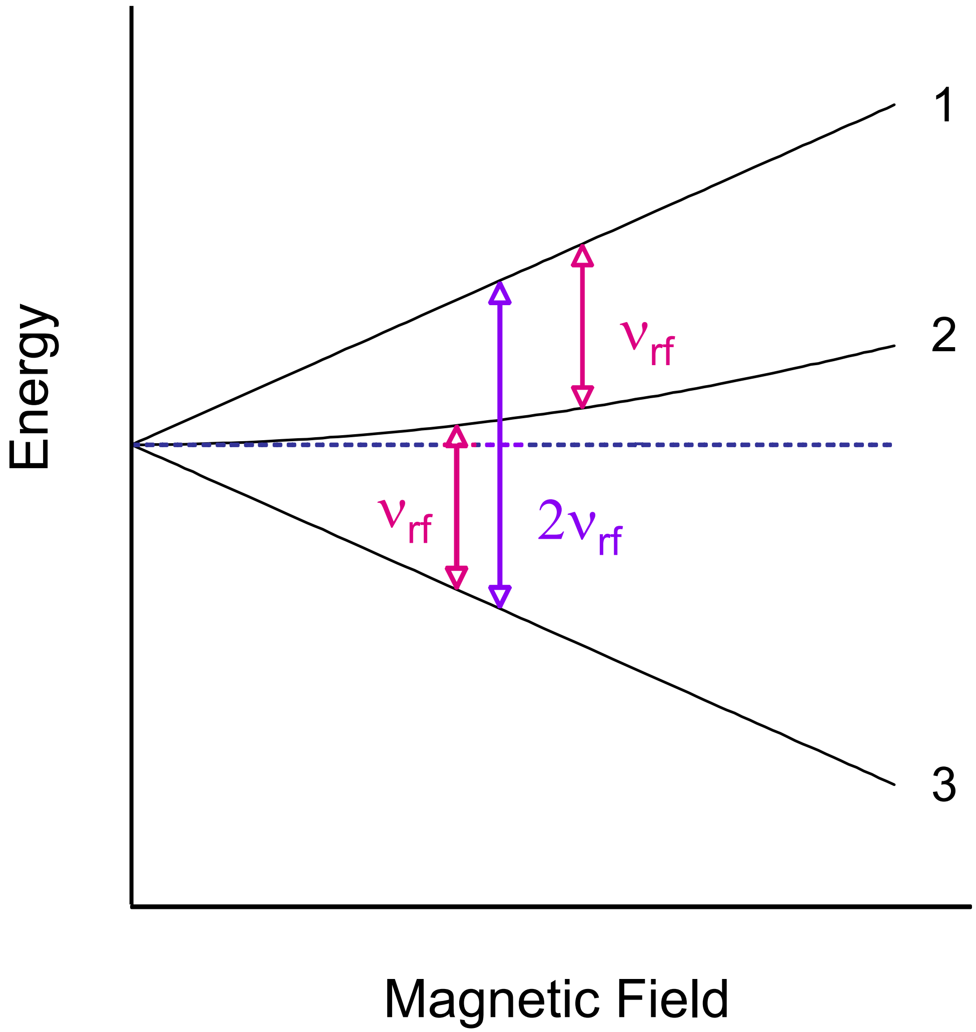


Mu precession frequencies in low magnetic field

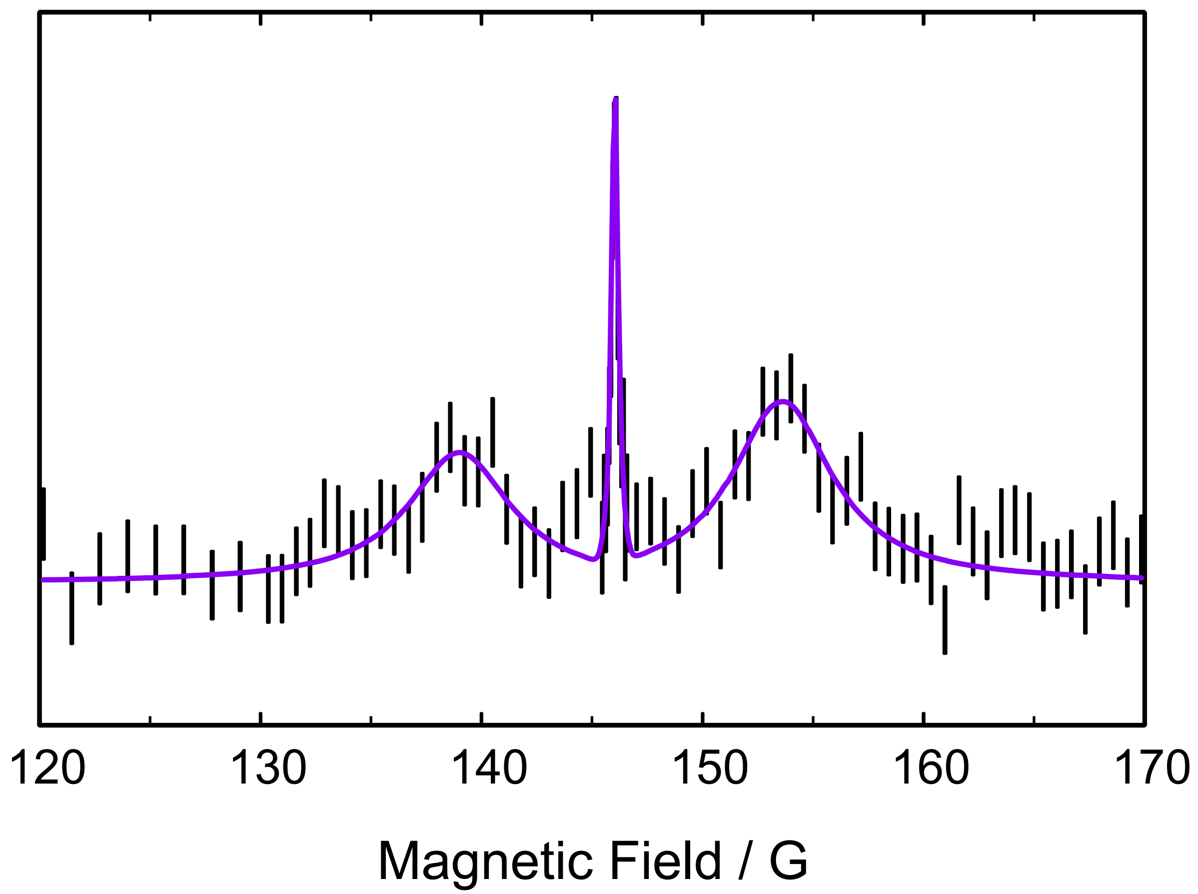




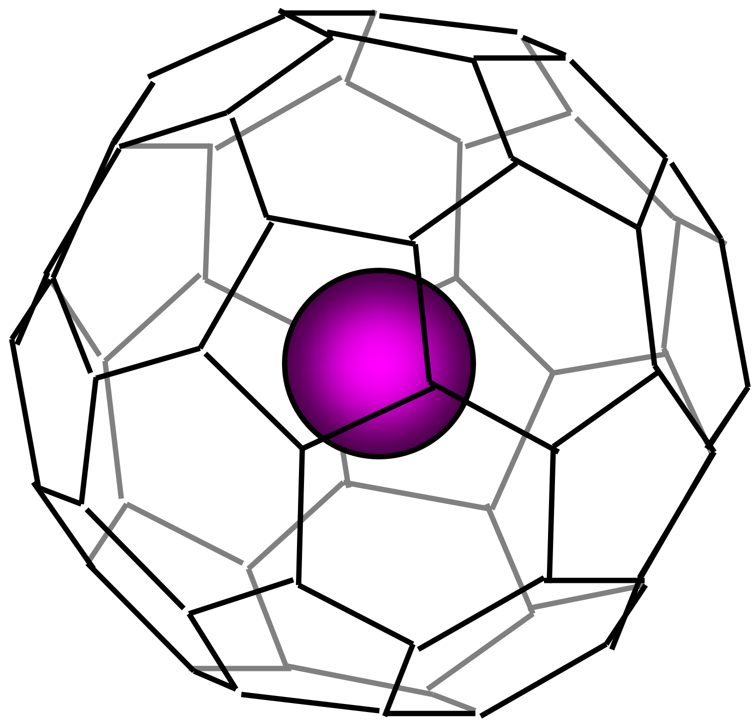
RF Transitions in Muonium at Low Magnetic Field



RFμSR Spectrum of $Mu@C_{60}$ in C_{60} Powder



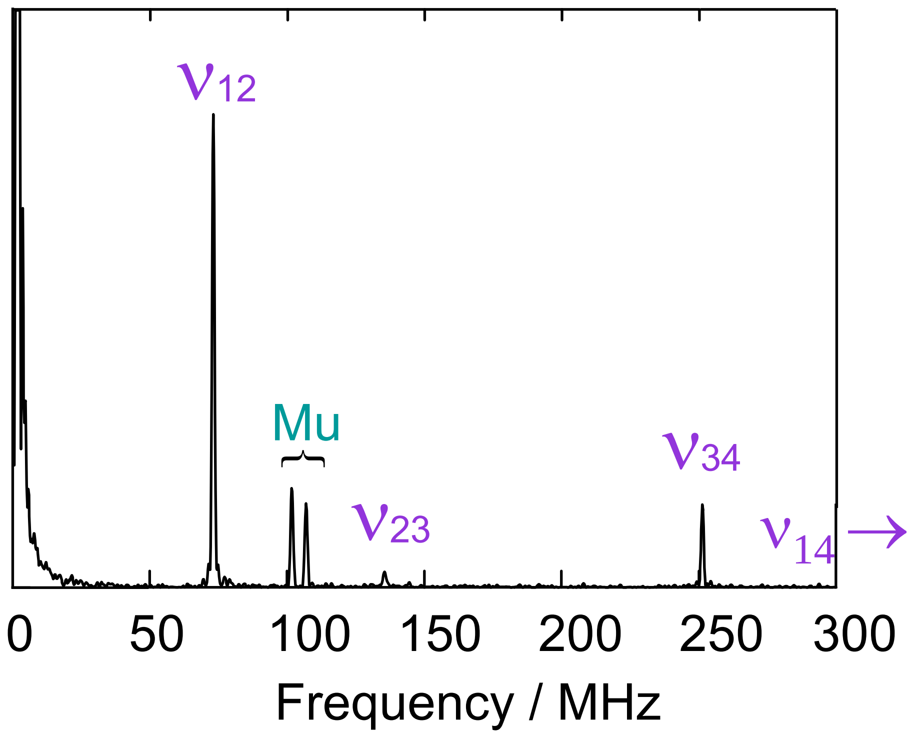
Endohedral Muonium Mu@C_{60}



Muonium in a universe of its own

The Curious Case of C_{60} (as studied by μSR)

Is it a bird? is it a plane?



The signals are characteristic of *both* muonium and a free radical. No other single phase material had shown such behaviour.

First report: Ansaldo, Niedermayer *et al.*, 1991.

Muonium and Diamagnetic Fractions

		P_M	P_D
Helium	gas	0	1.0
Hydrogen	gas	0.6	0.4
Nitrogen	gas	0.8	0.2
Water	liquid	0.2	0.6
Water ice	solid	0.5	0.5
Cyclohexane	liquid	0.2	0.7
CCl_4	liquid	0	1.0

approximate values; they depend on temperature, pressure, …

Why are the values so different? Do we care?

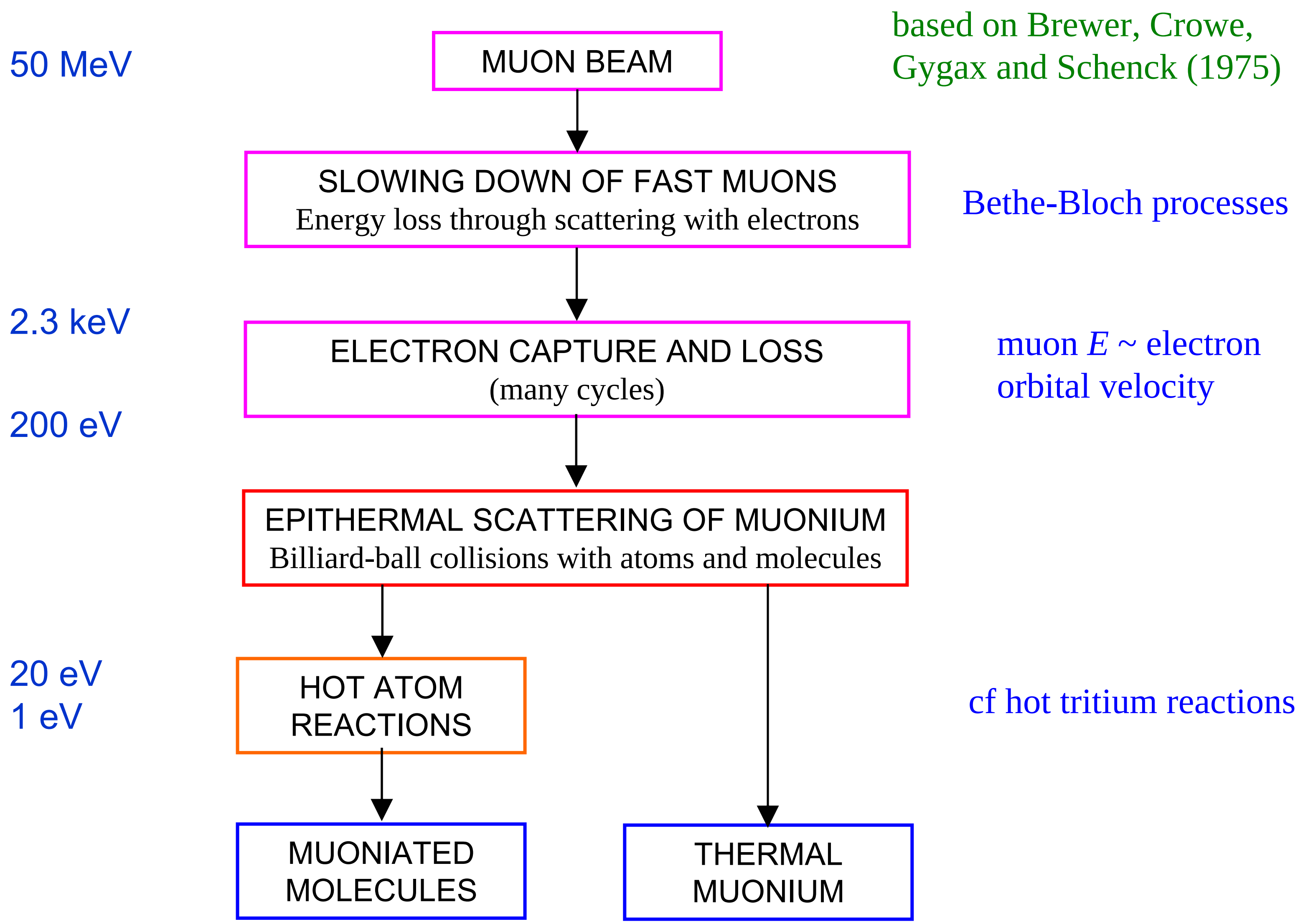
We start with high energy muons (MeV) but we measure these values after the muons have thermalized.

History

- 1975 “final formation of stable, neutral muonium” by about 200 eV
  Brewer et al.
- 1978 Radiolysis effects
  Percival et al.
- 1981 Arguments against a spur model for muonium formation
  Walker et al.
- 1988 Cyclic charge-exchange and Mu formation in gases
  Senba et al.
- 1988 The reaction of muonium with hydrated electrons
  Leung, Percival et al.
- 1988 “…we conclude that the muon has no direct, persistent interaction with its ionization cloud on the time scale of a μSR experiment
  Patterson
- 1994 Electric field dependence of muonium formation
  Storchak, Brewer et al.
- 2009 Magnetic polaron (muon bound spin polaron) controversy
  Storchak, Brewer et al.

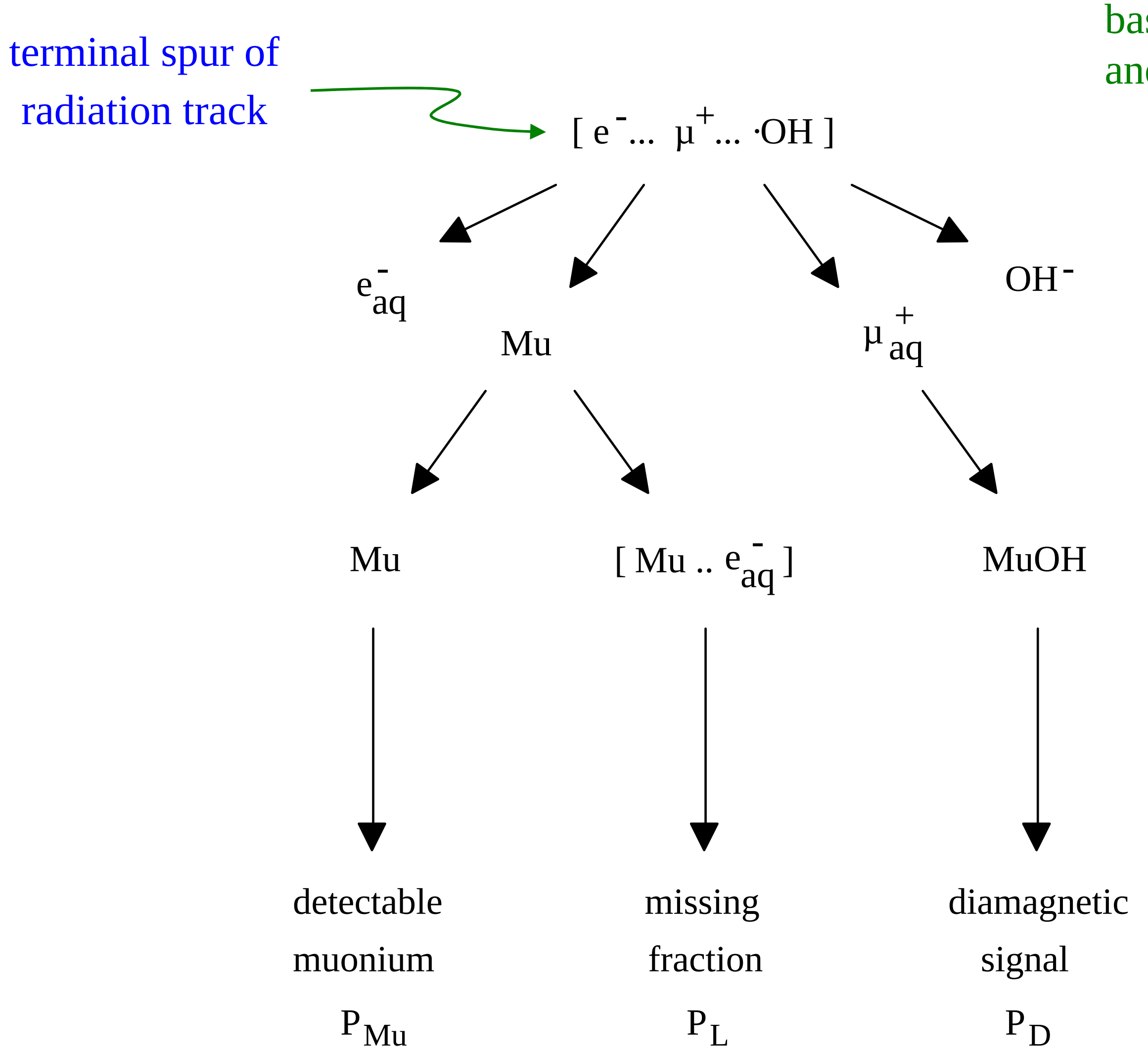
⇒ The muon is *not* in general an innocent probe of material

Muon Thermalization circa 1975



The Spur Model for Mu Formation (in water) circa 1978

based on Percival, Roduner and Fischer (1978)



Muons are Peculiar

compared to conventional radiation chemistry

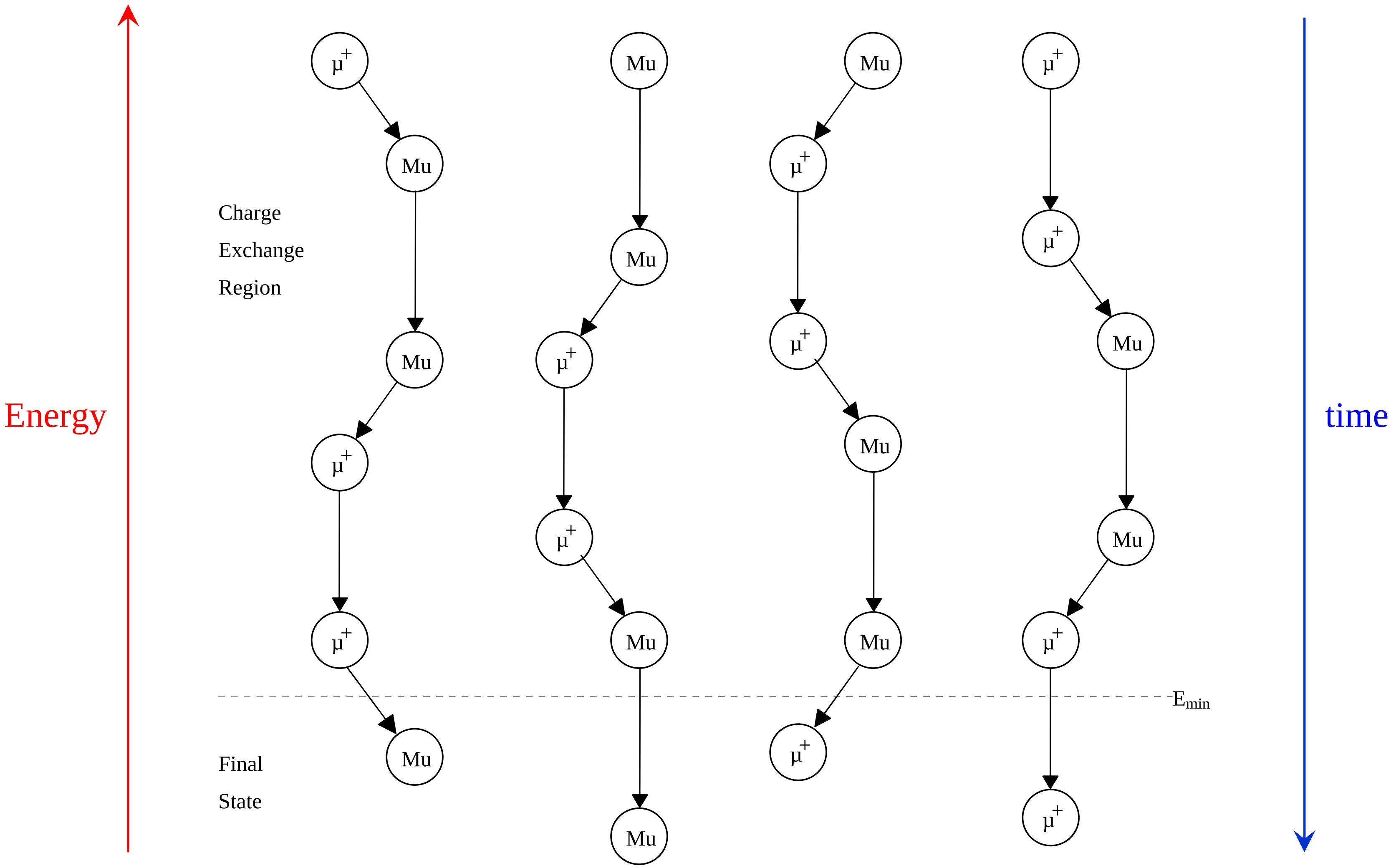
Walker et al published many papers arguing why the spur model must be wrong.

However…

- We detect *stopped* muons.
  In gas-phase beam studies the mean free path between collisions is long.
- The stopped muon is at the *end* of the radiation track.
  The extensive literature of radiation chemistry deals almost exclusively with radiolysis of the medium not the fate of the ionizing particle itself.
- We detect muon spin polarization, *not* chemical fractions of muon species.
  We need to understand how muon spin polarization can be lost.

What Determines the Muonium Fraction? in a gas

based on Senba (1988)



Where does the Diamagnetic Signal come from?

Muonium has an ionization potential of 13.5 eV, greater than most molecules

⇒ electron capture should occur down to thermal energy...? ??

Experimental evidence contradicts this.

The "hot fraction h has been a source of annoyance in the history of muonium chemistry, ...

J.H. Brewer et al (1975)

There are two routes to stable diamagnetic compounds:

- Muon attachment (molecular ion formation, followed by transfer)

$$\mu^+ + RH \rightarrow RHMu^+$$

$$RHMu^+ + RH \rightarrow RMu + RH_2^+$$

- Hot atom reactions

$$Mu^* + RH \rightarrow \begin{cases} MuH + R \\ MuR + H \end{cases}$$

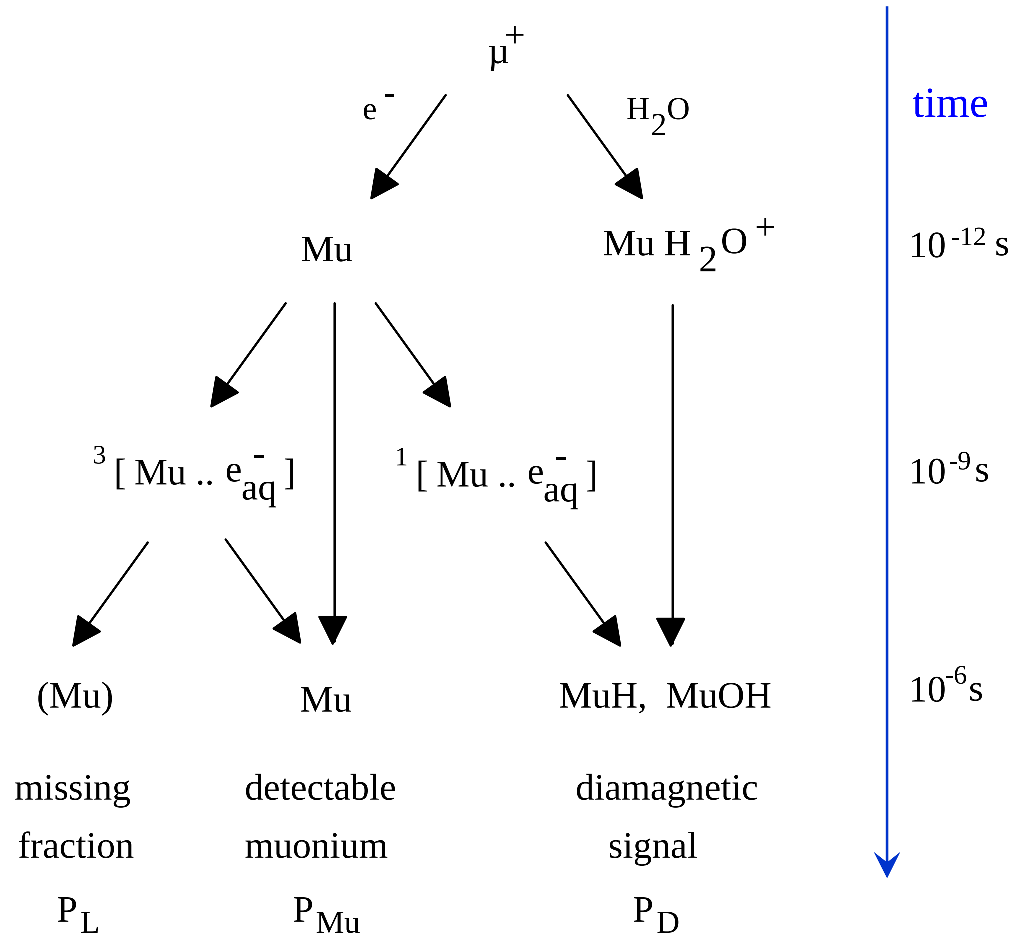
Complications, complications, complications

In condensed matter the model of successive two-body collisions no longer holds. Consider the *epithermal* muon with a few eV kinetic energy:

- The mean free path has the same order of magnitude as molecular dimensions.
- Does the charge state of the muon have any meaning if the muon is travelling through the overlapping electron clouds of molecules?
- The muon velocity is comparable to *nuclear* motion in molecules
  – a 3 eV muon takes 4 fs to traverse a molecular diameter of 3 Å, half the vibrational period of a typical C-H or O-H stretch.

Mu Formation in Water with Spin-dependent Chemistry

based on Leung, Brodovitch, Percival, et al. (1987)



History

- 1975 “final formation of stable, neutral muonium” by about 200 eV
  Brewer et al.
- 1978 Radiolysis effects
  Percival et al.
- 1981 Arguments against a spur model for muonium formation
  Walker et al.
- 1988 Cyclic charge-exchange and Mu formation in gases
  Senba et al.
- 1988 The reaction of muonium with hydrated electrons
  Leung, Percival et al.
- 1988 “…we conclude that the muon has no direct, persistent interaction with its ionization cloud on the time scale of a μSR experiment
  Patterson
- 1994 Electric field dependence of muonium formation
  Storchak, Brewer et al.
- 2009 Magnetic polaron (muon bound spin polaron) controversy
  Storchak, Brewer et al.

The muon is *not* in general an innocent probe of material

Perturbation Theory

time-independent theory for non-degenerate states

Used if the Schrödinger equation cannot be solved exactly, but the problem is similar to another whose solution is known.

If $\hat{\mathbf{H}} = \hat{\mathbf{H}}_0 + \hat{\mathbf{h}}$ where $\hat{\mathbf{H}}_0 \psi_n^0 = E_n^0 \psi_n^0$

Approximate energies

$$E_j = E_j^0 + \langle \psi_j^0 | \hat{\mathrm{h}} | \psi_j^0 \rangle + \sum_{k \neq j} \frac{\langle \psi_j^0 | \hat{\mathrm{h}} | \psi_k^0 \rangle \langle \psi_k^0 | \hat{\mathrm{h}} | \psi_j^0 \rangle}{E_j^0 - E_k^0}$$

zero order

1st-order correction

2nd-order correction

Approximate wave functions

$$\psi_j = \psi_j^0 + \sum_{k \neq j} c_k \psi_k^0 \quad \text{where} \quad c_k = \frac{\langle \psi_k^0 | \hat{\mathrm{h}} | \psi_j^0 \rangle}{E_j^0 - E_k^0}$$

Does not work for $E_j^0 = E_k^0$!

The perturbed wave function has *other* eigenfunctions admixed.

The mixing coefficients c_k depend on the strength of the perturbation relative to the energy separation $E_j^0 - E_k^0$

If necessary, use linear combinations to avoid this problem.

Perturbation Theory – Example of H spin states

$$\hat{\mathbf{H}}^0 = \omega_e \hat{\mathbf{S}}_z - \omega_p \hat{\mathbf{I}}_z + \omega_0 \hat{\mathbf{S}}_z \hat{\mathbf{I}}_z \qquad \hat{\mathbf{H}}^1 = \tfrac{1}{2}\omega_0 \left(\hat{\mathbf{S}}_+ \hat{\mathbf{I}}_- + \hat{\mathbf{S}}_- \hat{\mathbf{I}}_+ \right)$$

0th order:

$$E_1^0 = \hat{\mathbf{H}}_{11}^0 = \tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 \qquad |1\rangle^0 = |\alpha\alpha\rangle$$

$$E_2^0 = \hat{\mathbf{H}}_{22}^0 = \tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 \qquad |2\rangle^0 = |\alpha\beta\rangle$$

$$E_3^0 = \hat{\mathbf{H}}_{33}^0 = -\tfrac{1}{2}\omega_e - \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 \qquad |3\rangle^0 = |\beta\alpha\rangle$$

$$E_4^0 = \hat{\mathbf{H}}_{44}^0 = -\tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p + \tfrac{1}{4}\omega_0 \qquad |4\rangle^0 = |\beta\beta\rangle$$

1st order:

$$\hat{\mathbf{H}}_{11}^1 = 0 \qquad \hat{\mathbf{H}}_{22}^1 = 0 \qquad \hat{\mathbf{H}}_{33}^1 = 0 \qquad \hat{\mathbf{H}}_{44}^1 = 0$$

2nd order:

$$\hat{\mathbf{H}}_{12}^1 = 0, \quad \hat{\mathbf{H}}_{13}^1 = 0, \quad \hat{\mathbf{H}}_{14}^1 = 0, \quad \hat{\mathbf{H}}_{24}^1 = 0, \quad \hat{\mathbf{H}}_{34}^1 = 0, \quad \hat{\mathbf{H}}_{23}^1 = \tfrac{1}{2}\omega_0$$

$$\hat{\mathbf{H}}_{21}^1 = 0, \quad \hat{\mathbf{H}}_{31}^1 = 0, \quad \hat{\mathbf{H}}_{41}^1 = 0, \quad \hat{\mathbf{H}}_{42}^1 = 0, \quad \hat{\mathbf{H}}_{43}^1 = 0, \quad \hat{\mathbf{H}}_{32}^1 = \tfrac{1}{2}\omega_0$$

$$E_2^0 - E_3^0 = \omega_e + \omega_p - \tfrac{1}{2}\omega_0 \qquad E_3^0 - E_2^0 = -\omega_e - \omega_p + \tfrac{1}{2}\omega_0$$

Perturbation: $$E_2 = \tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 + \frac{\tfrac{1}{4}\omega_0^2}{\omega_e + \omega_p - \tfrac{1}{2}\omega_0}$$ to 2nd order

Exact: $$E_2 \to \tfrac{1}{2}\omega_e + \tfrac{1}{2}\omega_p - \tfrac{1}{4}\omega_0 + \frac{\tfrac{1}{4}\omega_0^2}{\omega_e + \omega_p}$$ for $\omega_0^2 \ll \left(\omega_e + \omega_p\right)^2$ high field

Spin Symmetry and Selection Rules

The intensity of a stimulated electric dipole transition is proportional to the square of the transition dipole moment:

$$I \propto |\mu_{mn}|^2 = |\mu^x_{mn}|^2 + |\mu^y_{mn}|^2 + |\mu^z_{mn}|^2 \qquad \text{where} \quad \mu^x_{mn} = \langle m|\hat{\mu}^x|n\rangle \quad \text{etc.}$$

In magnetic resonance the relevant operator is the magnetic dipole.

For TF-μSR this involves muon-spin-flipping operators.

$$\langle \psi'_e\psi'_\mu\psi'_p|\hat{P}_\mu|\psi''_e\psi''_\mu\psi''_p\rangle = \langle\psi'_e|\psi''_e\rangle\langle\psi'_\mu|\hat{P}_\mu|\psi''_\mu\rangle\langle\psi'_p|\psi''_p\rangle$$

$$= \langle\psi'_\mu|\hat{P}_\mu|\psi''_\mu\rangle \quad \text{if} \quad \psi'_e = \psi''_e \quad \text{and} \quad \psi'_p = \psi''_p$$

$$\text{i.e.} \quad \langle m'_S|m''_S\rangle = 1 \quad \text{and} \quad \langle m'_I|m''_I\rangle = 1$$

$$\Delta m_S = 0 \quad \text{and} \quad \Delta m_I = 0$$

The transition moment is zero (“forbidden” transition) if the electronic (or nuclear) spin states (α, β) are orthogonal: $\langle\alpha|\beta\rangle = 0$

The simple rule breaks down when eigenstates have mixed spin functions.