TRIUMF Summer Institute 2011

Lecture 4

Introduction to Magnetic Resonance

Paul Percival

Spin

Just what does that 4th quantum number represent?

- Introduced empirically to explain certain features of atomic spectra (1925).
- Theory developed by Pauli and shown to be a consequence of the Dirac equation.
- It is the intrinsic, characteristic and irremovable angular momentum of a particle.
  You can visualize it as the rotation of a body about its own axis, but…
  what about point particles?
- It is a non-classical phenomenon!
  In contrast, orbital angular momentum → classical behaviour at high enough l values.
- All matter can be classified according to spin:

  Fermions have half-integral spins and satisfy Fermi-Dirac statistics.

  Bosons have integral spin (0, 1, 2, …) and satisfy Bose-Einstein statistics.

Magnetic Moments in Atoms and Molecules

In addition to rotation of molecules, angular momentum can arise from:

- orbital motion of electrons $\vec{L}$
- electron spin $\vec{S}$
- nuclear spin $\vec{I}$

In general, for an angular momentum quantum number j

magnitude $= \left[j(j+1) \right]^{1/2} \hbar$ z-component $= m_j \hbar$ $m_j = j, j-1, \ldots -j$

The interaction of the orbital or spin angular momentum with a magnetic field is characterized by the magnetic moment. $E = -\vec{\mu} \cdot \vec{B} = -\mu_z \cdot B_z$ $\vec{B} = (0,\ 0,\ B_z)$

orbital $\mu_z = \gamma_e m_l \hbar = -\beta m_l$

magnetogryric ratio $\gamma_e = -\dfrac{e}{2m_e}$

electron spin $\mu_z = g_e \gamma_e m_S \hbar = -g_e \beta m_S$

g-value $= 2.0023$

$\gamma_S = g_e \gamma_e$

Bohr magneton $\beta = \dfrac{e\hbar}{2m_e}$

nuclear spin $\mu_z = \gamma_N m_I \hbar = g_N \beta_N m_I$

nuclear magneton $\beta_N = \dfrac{e\hbar}{2m_p}$

Rotational/Orbital (and Spin) Angular Momentum

The energy is quantized. $E_{lm} = \frac{\hbar^2}{2I} l(l+1)$ $\begin{cases} l = 0,1,2,\ldots \\ m = 0,\pm1,\pm2,\ldots,\pm l \end{cases}$ for orbital (l) and rotation (J)

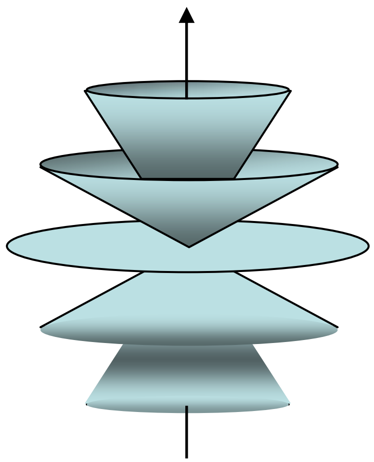
There are ($2l$+1) degenerate states with energy determined by the quantum number l.

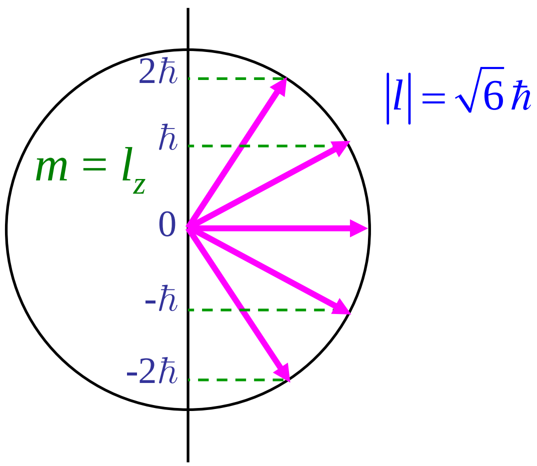
Electron spin (S) and nuclear spin (I) have fixed values, either integral or half-integral.

The different states, labelled by quantum numbers m, are related by simple symmetry transformations, i.e. they correspond to different orientations in space.

The orientation of the angular momentum vector is quantized.

Example for l = 2:





In QM language, the operator for the total angular momentum commutes with only one component. If l_z is known, l_x and l_y can not be specified.

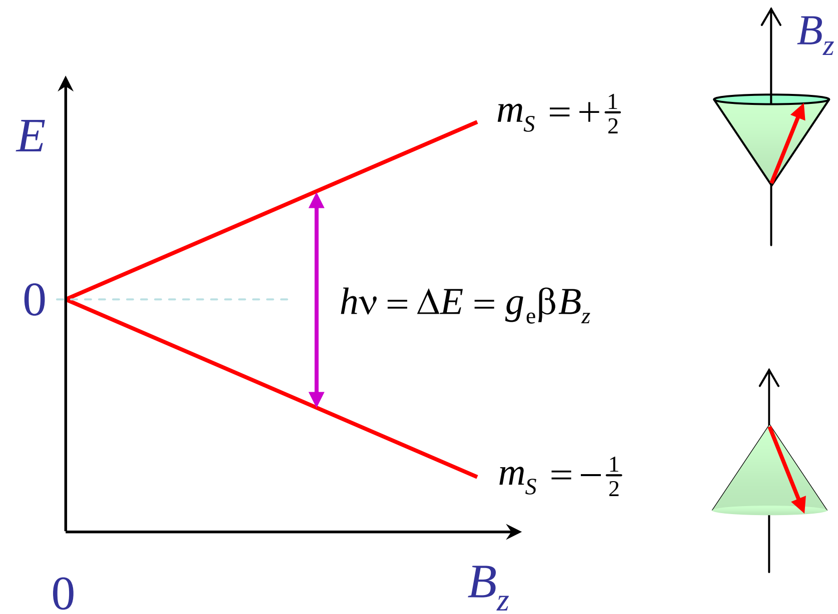
Electrons and Nuclei in a Magnetic Field

Electron spin $E_{m_S} = g_e \beta B_z m_S$

$m_S = \pm\frac{1}{2}$

selection rule $\Delta m_S = \pm 1$

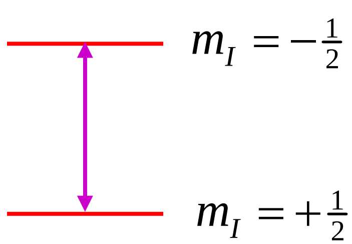
X band	9.5 GHz	⇔	3.4 kG	0.34 T
Q band	35 GHz	⇔	12.5 kG	1.25 T
W band	95 GHz	⇔	34 kG	3.4 T



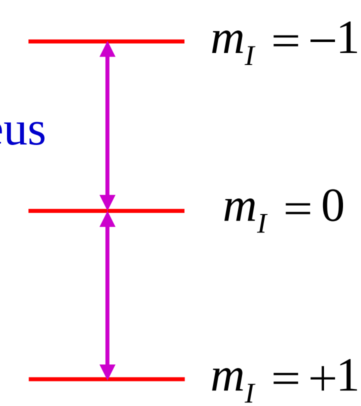
Nuclear spin $E_{m_I} = -\gamma_N \hbar B_z m_I$

selection rule $\Delta m_I = \pm 1$

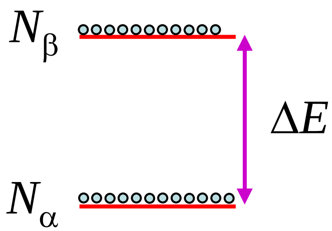
spin ½ nucleus



spin 1 nucleus



Spin Populations



At thermal equilibrium, the relative populations of the upper and lower spin states is given by the Boltzmann distribution.

$$\frac{N_\beta}{N_\alpha} = \exp\left(\frac{-\Delta E}{k_B T}\right)$$

At room temperature, $k_B T = 4.1 \times 10^{-21}$ J

much larger than $\Delta E = h\nu = 6.3 \times 10^{-24}$ J for 9.5 GHz (X-band ESR)

4.0×10^{-25} J for 400 MHz (NMR)

The relative difference in populations

$$= \frac{N_\alpha - N_\beta}{N_\alpha + N_\beta} = \frac{1 - e^{-\Delta E/k_B T}}{1 + e^{-\Delta E/k_B T}} \approx \frac{\Delta E}{2 k_B T}$$

0.0008 for ESR

0.00005 for NMR

The ESR/NMR signal is proportional to the population difference.

Too much microwave/rf power equalizes the populations, known as saturation.

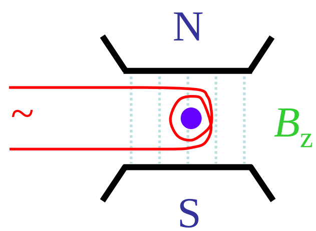
Thermal equilibrium is regained by spin-lattice relaxation.

NMR – Experimental Aspects

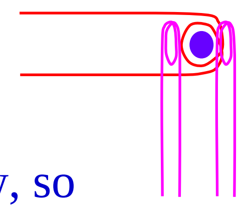
$h\nu = g_N \beta_N B_z$ For ^{1}H

100 MHz ⇔ 23.5 kG	electromagnet possible
300 MHz ⇔ 70.5 kG	superconducting magnet essential
600 MHz ⇔ 141 kG	typical high resolution work

- Resonance can be achieved by: sweeping magnetic field, sweeping r.f. frequency, pulsing r.f. } but always recorded in Hz



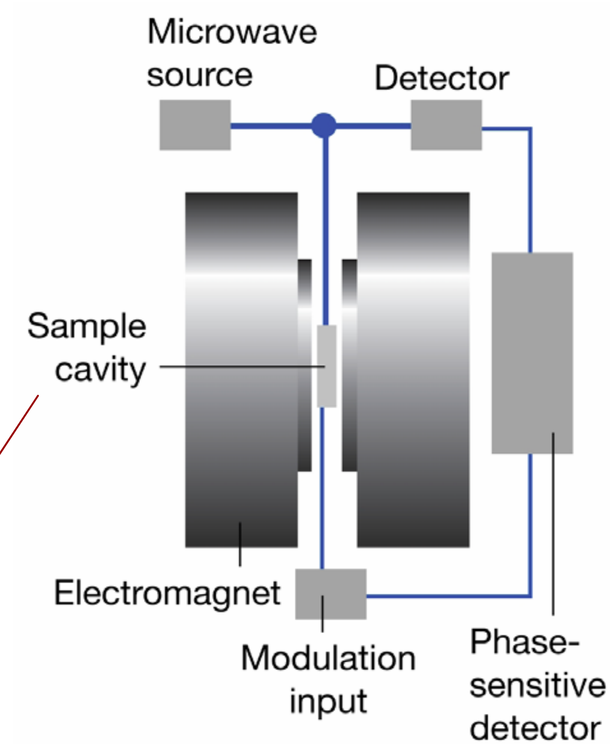
- The r.f. oscillating magnetic field is oriented perpendicular to the static field (B_z). At resonance, energy is absorbed by the sample from the coil, unbalancing the r.f. bridge circuit. Alternatively, an r.f. signal is induced in a second coil perpendicular to the exciting coil.



- The field sweep is usually very small ($\lesssim$ 1 in 10^4) and the lines very narrow, so both r.f. and magnetic field must be very stable. The field must also be very homogeneous (up to 1 in 10^9), so special sample tubes, sample spinning and field shimming coils are used.

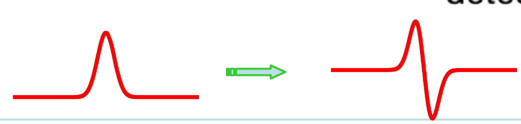
Components of an ESR Spectrometer

9.5 GHz X-band
35 GHz Q-band
95 GHz W-band



3 x 1 cm
cross-section
for X-band

waveguide



resonant cavity
in a tuned circuit

NMR in Liquids

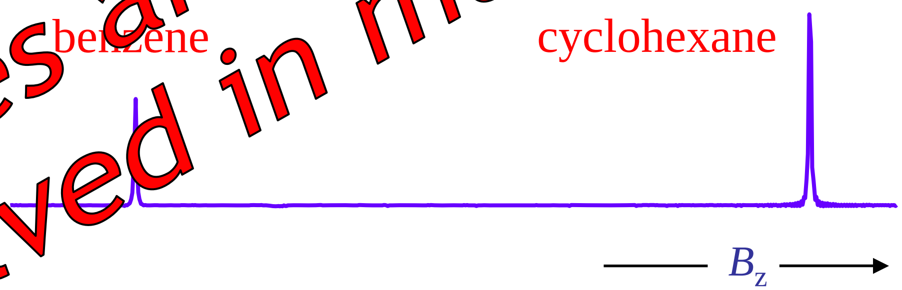
Spin-½ nuclei in molecules tumbling in liquids usually have very narrow lines ~ 1 Hz

MHz for ESR!

This is high resolution NMR, most commonly [1]H and [13]C.

The resonant frequency of each nucleus is determined by its electronic environment, described in terms of chemical shift.

e.g. equimolar mixture of



The spectrum is displayed as if for an increase in field, *but* differences in line positions are always quoted in frequency units.

Splitting of lines can arise from spin-spin coupling, characterized by the coupling constant *J*.

e.g. acetaldehyde

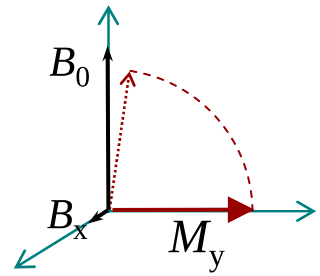
These features are too fine to be resolved in muSR

Paul Percival

Pulsed NMR (and ESR)

Apply a short rf pulse to tip M into the xy plane

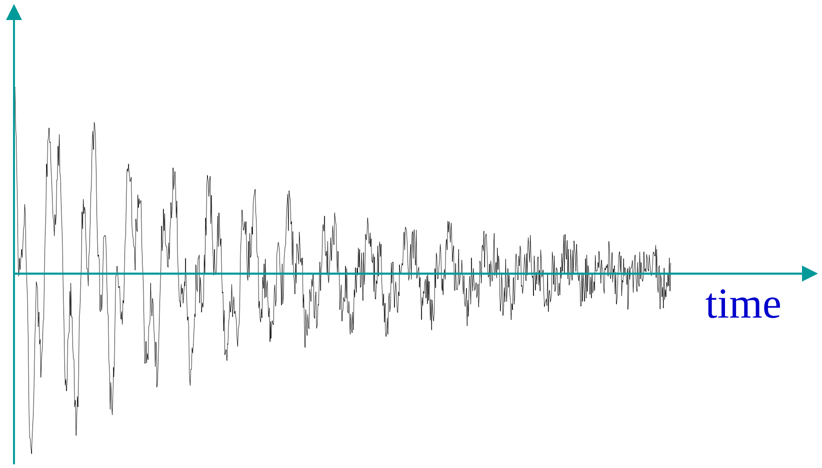
– a 90° pulse

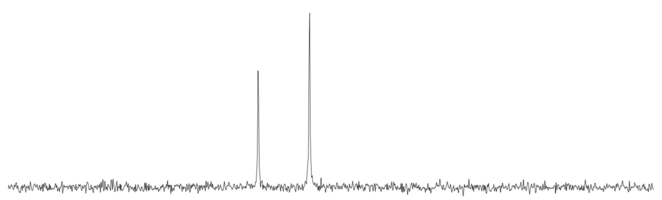


This gives a strong signal as M precesses.

A short pulse of duration Δt centred at frequency ω_0 contains all frequencies in the range $(\omega_0 - 1/\Delta t)$ to $(\omega_0 + 1/\Delta t)$ so that nuclei of all chemical shifts are excited.

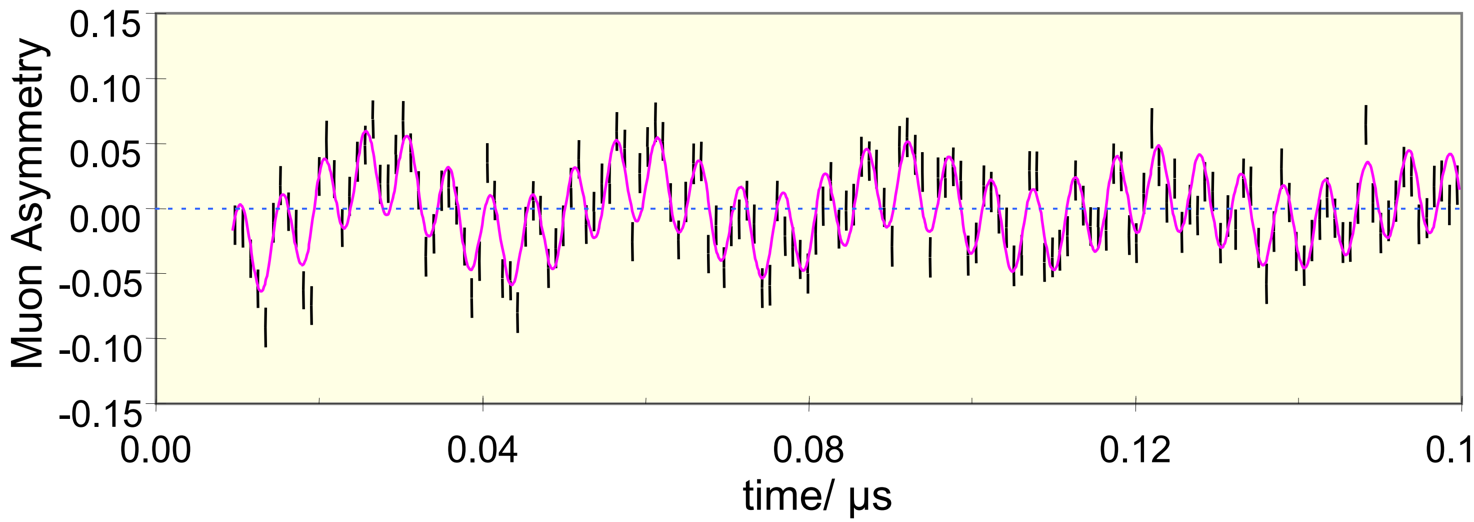
The resulting free induction decay signal is processed by Fourier Transform to give a frequency spectrum.



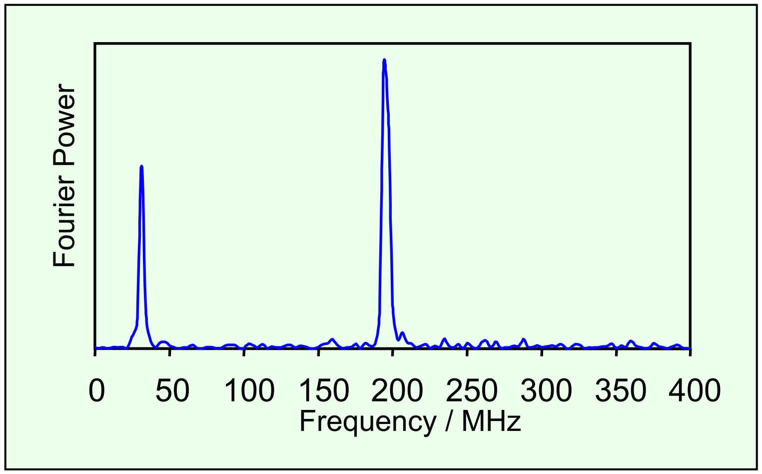


"Free Induction Decay" in Muon Spin Spectroscopy

In TF-μSR *M* is already in the xy plane, and precesses in applied and local magnetic fields.



$MuCH_2\dot{C}H_2$ from ethene gas at 10 bar, 25°C, 14.4 kG.

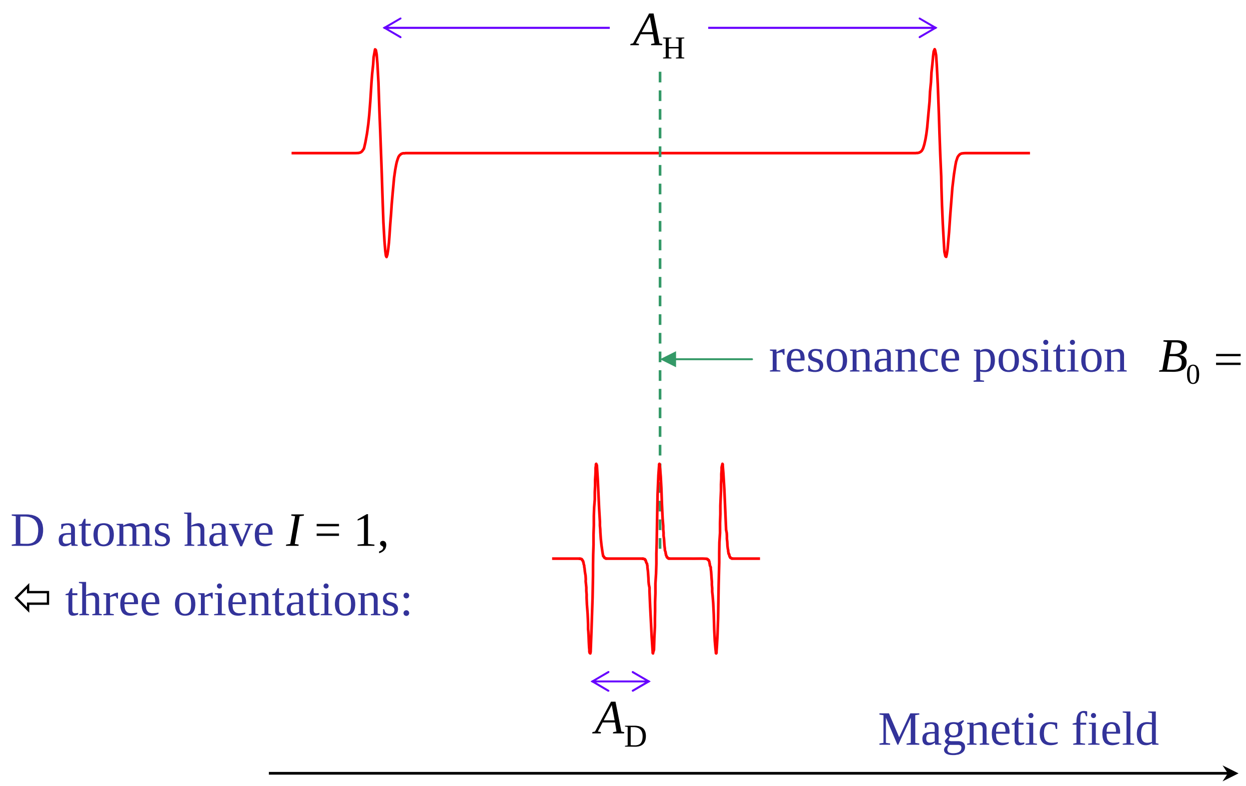


The Fourier Transform conveniently reveals the precession frequencies.

ESR Hyperfine Splitting

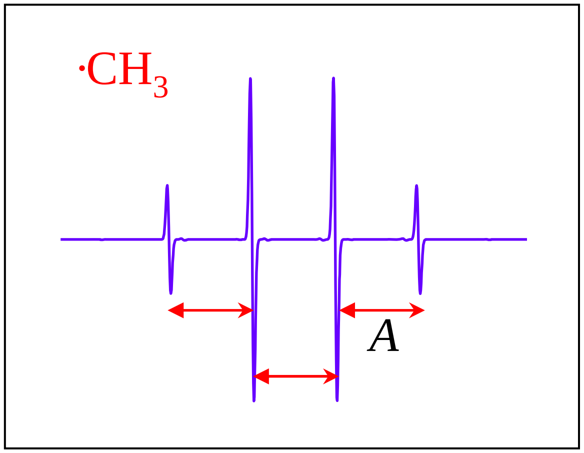
Interaction of the unpaired electron of a radical with magnetic nuclei (H, N, …) results in hyperfine splitting of ESR resonances.

Each nuclear spin contributes a local magnetic field depending on its m_I value. Thus, the protons in H atoms can have $m_I = \pm\frac{1}{2}$ resulting in two different local fields in addition to B_0.



Hyperfine Splitting by Many Nuclei

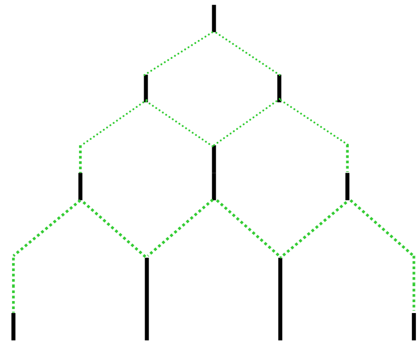
Most radicals contain more than one magnetic nucleus. Each couples to the unpaired electron to produce its own splitting.



Equivalent nuclei with total spin *I* give $2I+1$ lines. Thus, *n* equivalent spin-½ nuclei (e.g. protons) couple to give a spectrum of $n+1$ lines. Their relative intensities are given by the binomial coefficients of $(1+x)^n$.

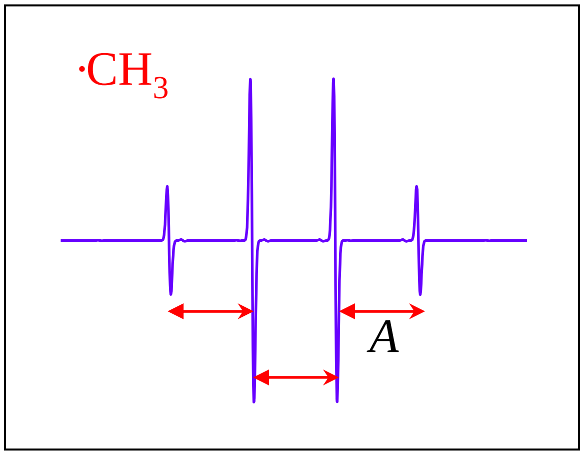
Pascal's triangle:

			1			
		1		1		
	1		2		1	
1		3		3		1

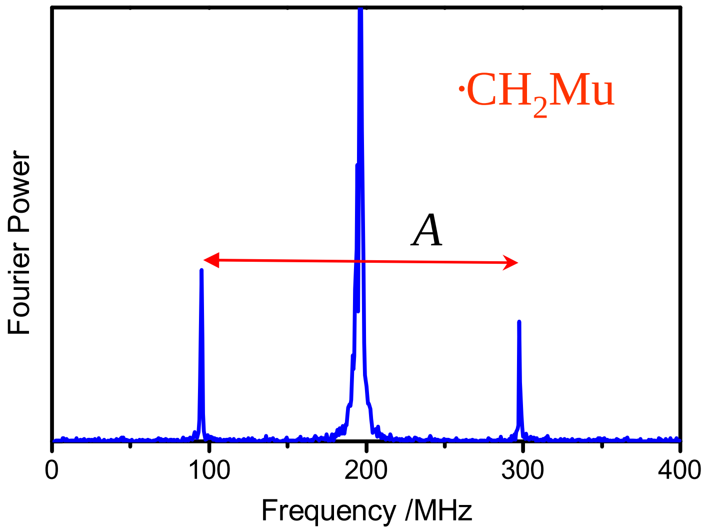


Hyperfine Constants can be measured by …

ESR



μSR



electron spin flip for states with different proton spin orientations

muon spin flip for states with different electron spin orientations

ESR Hyperfine Splitting – Electron Spin Terms

Spin Hamiltonian $\hat{H}_{spin} = g_e \beta B_z \hat{S} + a \hat{I} \cdot \hat{S} \simeq g_e \beta B_z \hat{S}_z + a \hat{I}_z \cdot \hat{S}_z$ at high field

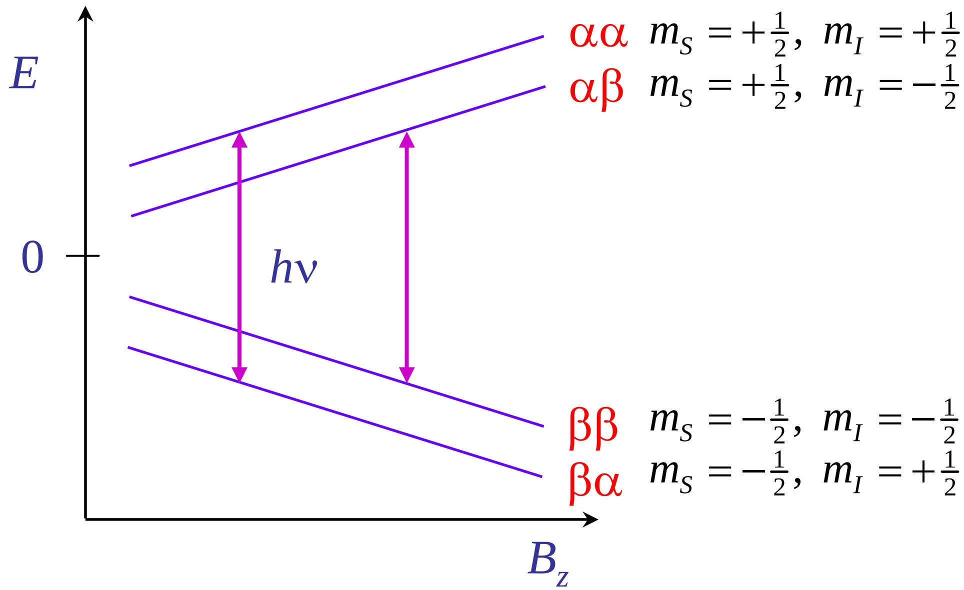
Zeeman Hyperfine

$$E = g_e \beta B_z m_S + a\, m_S m_I$$

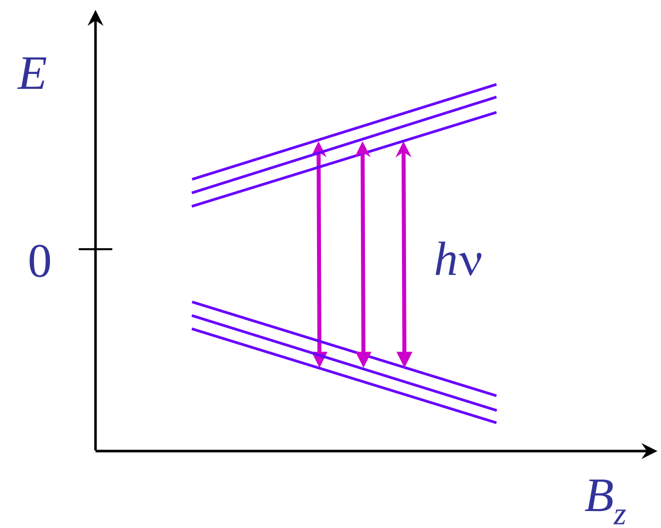
$A = a/h$

Selection rules: $\Delta m_S = \pm 1,\ \Delta m_I = 0$ $\quad h\nu = \Delta E = g_e \beta B_z + a\, m_I$

H atom



D atom



Hyperfine Splitting – Electron and Nuclear Spin Terms

Spin Hamiltonian $\hat{H}_{spin} = g_e \beta B_z \hat{S} - h\gamma_N B_z \hat{I} + a \hat{I}\cdot\hat{S} \simeq g_e \beta B_z \hat{S}_z - h\gamma_N B_z \hat{I}_z + a \hat{I}_z \cdot \hat{S}_z$

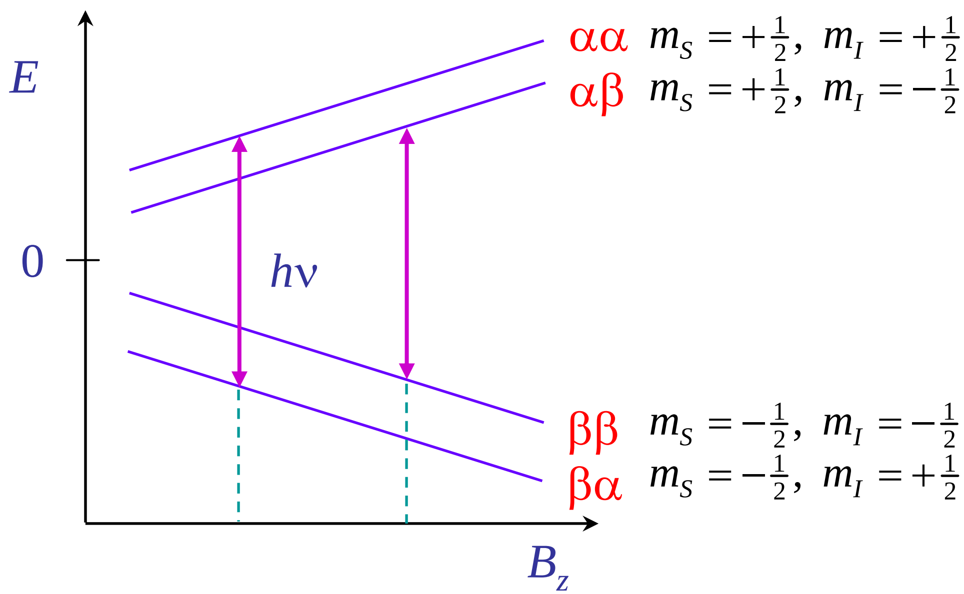
Zeeman   Hyperfine

$$E = \left(g_e \beta m_S - h\gamma_N m_I\right) B_z + a\, m_S m_I$$

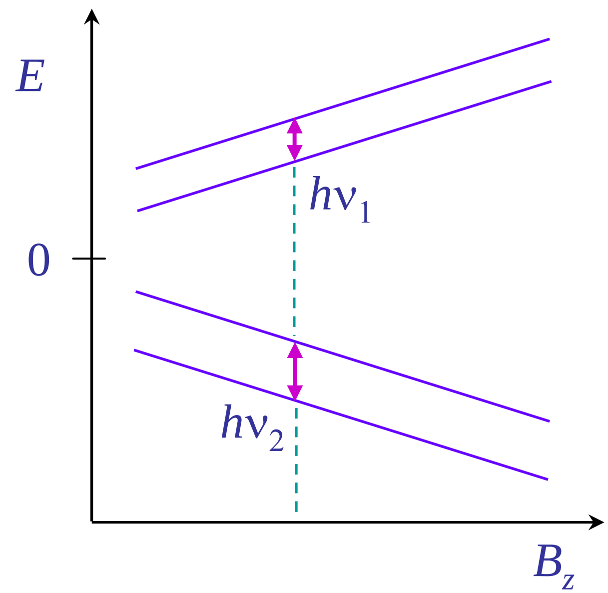
$$h\nu = \Delta E = g_e \beta B_z + a\, m_I$$

$$h\nu = \Delta E = h\gamma_N B_z \pm \tfrac{1}{2} a$$

ESR

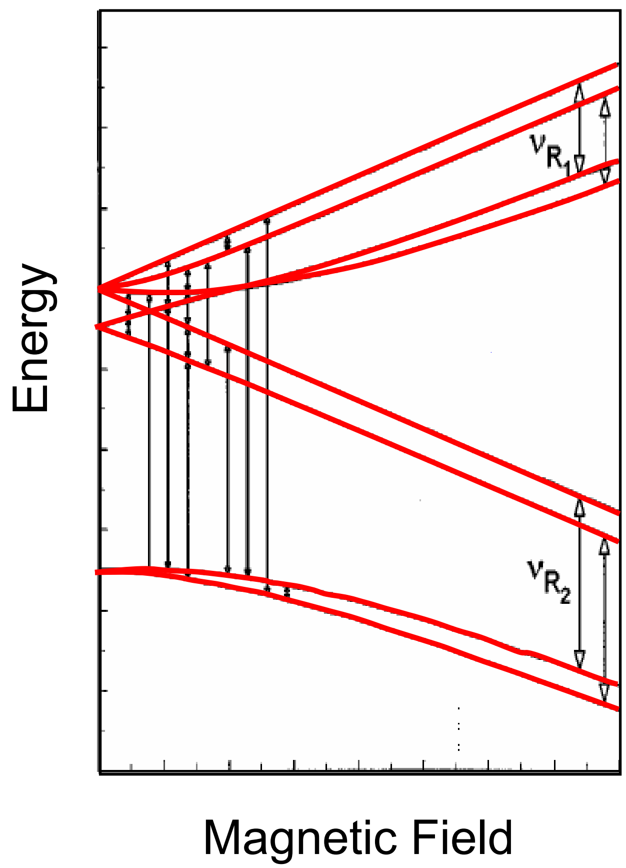


μSR

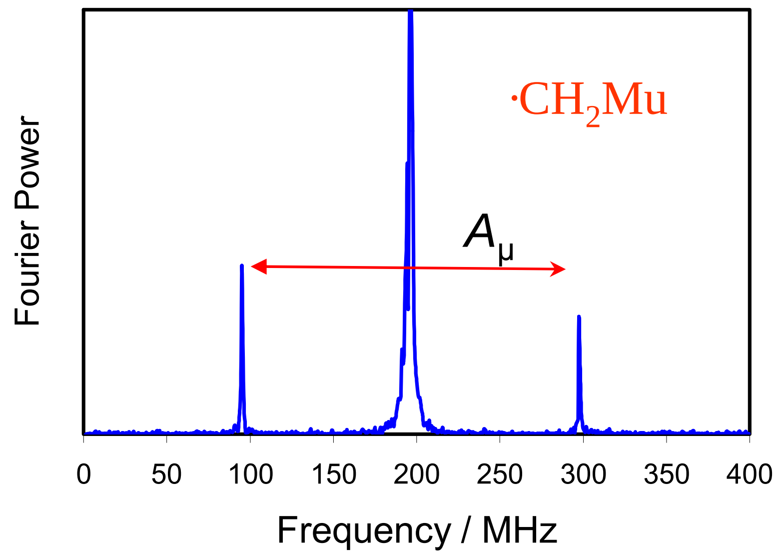


TF-μSR of Muoniated Free Radicals

The unpaired electron has the largest magnetic moment. At high enough field the muon spin flip transitions are degenerate for a given electron spin orientation.



example for 1 electron, 1 muon, 1 proton

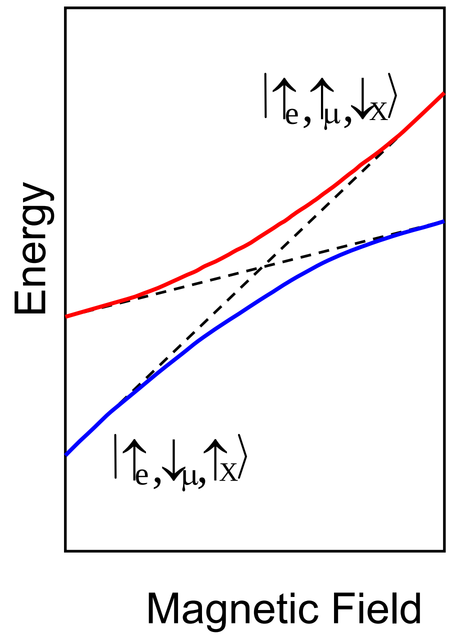


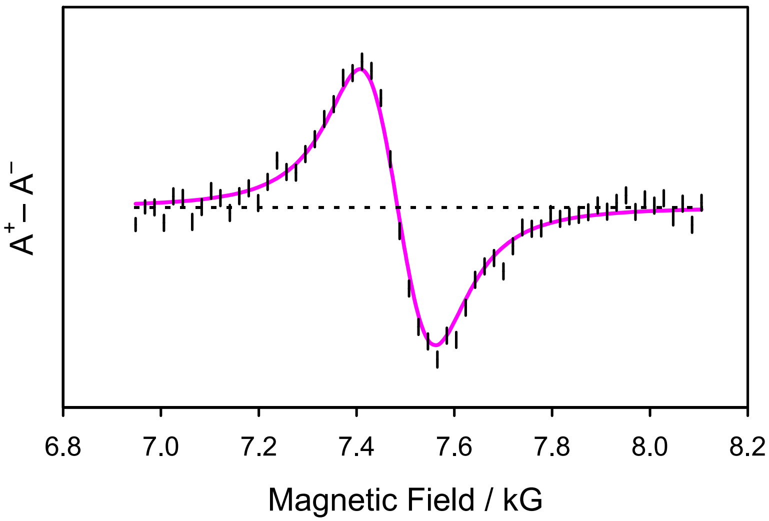
$$A_\mu = \upsilon_{R2} - \upsilon_{R1}$$

μSR ≡ ENDOR

Muon Avoided Level Crossing Resonance

MuLCR involves counting positrons in directions along and opposite to the magnetic field. The difference is proportional to the longitudinal muon spin polarization. Mixing of spin levels related by flip-flop transitions of the muon and another nucleus results in loss of spin polarization at a field determined by the muon and nuclear hfcs.



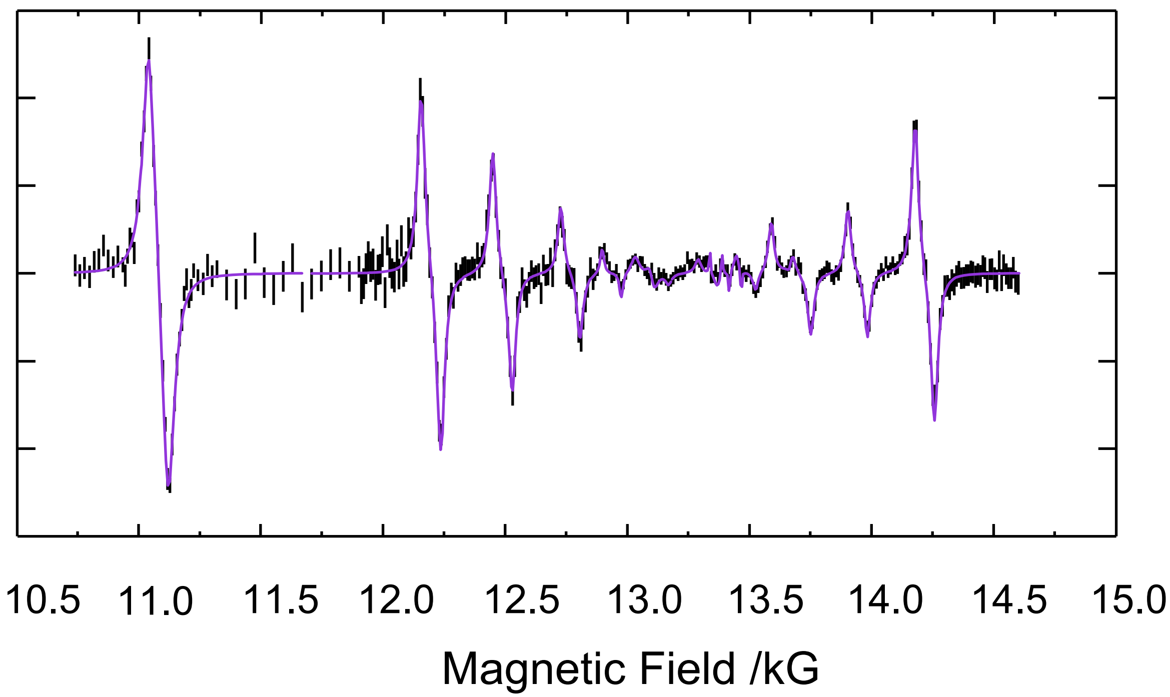


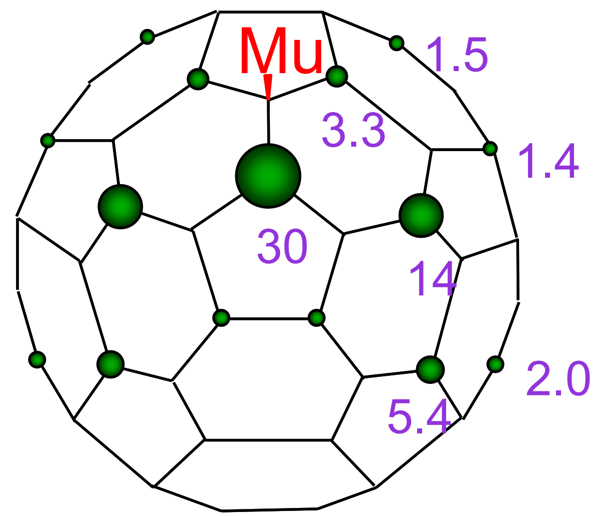
$$B_{\mathrm{LCR}} = \frac{1}{2}\left[\frac{\left(A_\mu - A_p\right)}{\left(\gamma_\mu - \gamma_p\right)} - \frac{\left(A_\mu + A_p\right)}{\gamma_e}\right]$$

The differential line shape is from field modulation.

Hyperfine constants are used to map unpaired spin in radicals

$Mu^{13}C_{60}$ Avoided Level Crossing Resonance



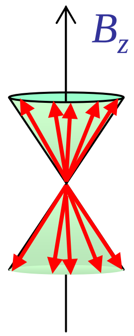


% Unpaired Spin Density

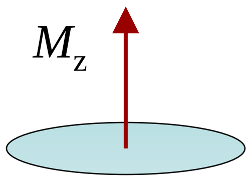
Percival, Addison-Jones, Brodovitch, Ji, et al., Chem. Phys. Lett., 245 (1995) 90

The Vector Model of Magnetic Resonance

It is important to distinguish between…

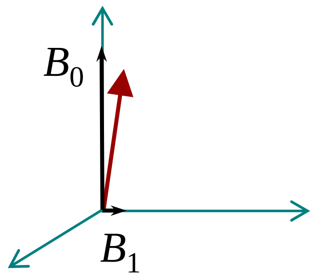


precession of individual spins



motion of the total magnetization

An oscillating magnetic field transverse to the applied field B_0 can be represented by a static vector B_1 in the rotating reference frame.



Alignment of the magnetization along the combined magnetic field results in a small component of M in the xy plane, where it can induce a signal in the pick-up coil.

The Bloch Equations

The motion of magnetization in a magnetic field is described by the Bloch Equations.

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M}\times\mathbf{B}) - \frac{\mathbf{i}M_x + \mathbf{j}M_y}{T_2} - \frac{\mathbf{k}(M_z - M_\infty)}{T_1}$$

$$\mathbf{M} = \mathbf{i}M_x + \mathbf{j}M_y + \mathbf{k}M_z$$

longitudinal relaxation to Boltzmann equilibrium

transverse relaxation to zero; no change in energy

$\mathbf{B} = \mathbf{B}_0 + \mathbf{B}_1$ where $\mathbf{B}_0 = (0,0,B_0)$ and $\mathbf{B}_1(t) = (2B_1\cos wt, 0, 0)$ a linear oscillating field

or two counter-rotating fields: $\mathbf{B}_1(t) = (B_1\cos wt, -B_1\sin wt, 0) + (B_1\cos wt, +B_1\sin wt, 0)$

Transform to a coordinate system rotating about *z* at frequency ω.

$$\left(\frac{d\mathbf{M}}{dt}\right)_{\text{rot}} = \left(\frac{d\mathbf{M}}{dt}\right)_{\text{lab}} - \boldsymbol{\omega}\times\mathbf{M}$$

$$\frac{dM_{x'}}{dt} = (\gamma B_0 - \omega)M_y - \frac{M_{x'}}{T_2}$$

$$\frac{dM_{y'}}{dt} = \gamma B_1 M_{z'} - (\gamma B_0 - \omega)M_{x'} - \frac{M_{y'}}{T_2}$$

$$\frac{dM_{z'}}{dt} = -\gamma B_1 M_{y'} - \frac{(M_z - M_\infty)}{T_1}$$

at ⇒ resonance

$$\frac{dM_{x'}}{dt} = -\frac{M_{x'}}{T_2}$$

$$\frac{dM_{y'}}{dt} = \gamma B_1 M_{z'} - \frac{M_{y'}}{T_2}$$

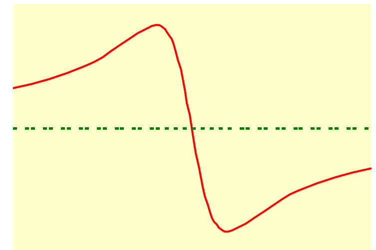
$$\frac{dM_{z'}}{dt} = -\gamma B_1 M_{y'} - \frac{(M_z - M_\infty)}{T_1}$$

The Resonance Line Shape

Solution of the Bloch Equations gives the resonance line shape.

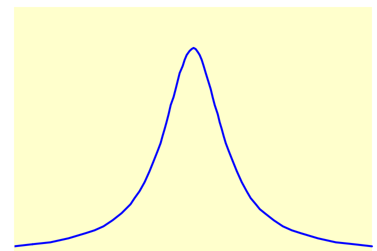
$$M_{x'} = M_\infty \frac{\gamma B_1 (\gamma B_0 - \omega) T_2^2}{1 + (\gamma B_0 - \omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}$$

dispersion



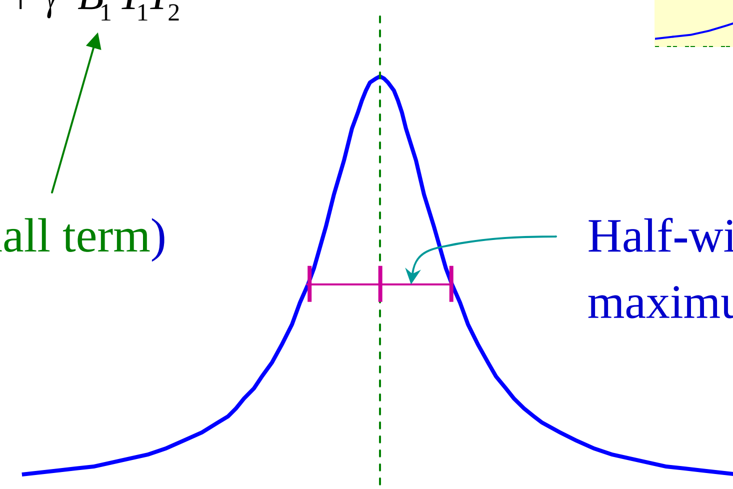
$$M_{y'} = M_\infty \frac{\gamma B_1 T_2}{1 + (\gamma B_0 - \omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}$$

absorption



$$M_{z'} = M_\infty \frac{1 + (\gamma B_0 - \omega)^2 T_2^2}{1 + (\gamma B_0 - \omega)^2 T_2^2 + \gamma^2 B_1^2 T_1 T_2}$$

If there is no saturation (small term)



Half-width at half maximum = $1/T_2$

Spin Relaxation

T_1 Spin-lattice relaxation — Longitudinal relaxation time

Spin polarization is lost by interaction with the surroundings.

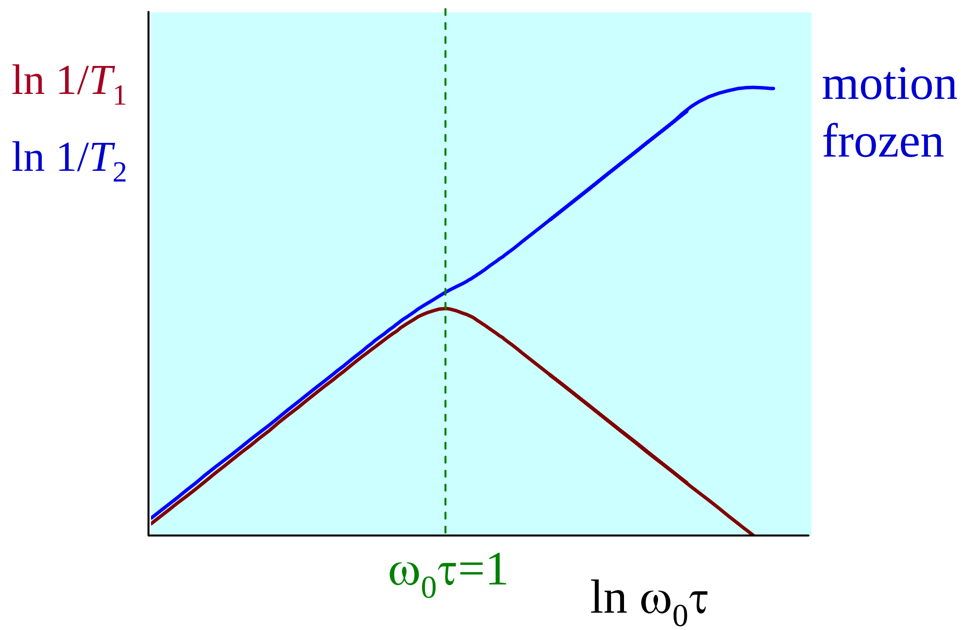
T_2 Spin-spin relaxation — Transverse relaxation time

Spins are dephased by interaction with each other, without loss of energy.

Spin relaxation depends both on the strength of an interaction and its fluctuation rate.
Details vary, but typical expressions are:

$$\frac{1}{T_1} = \omega_L^2 \left(\frac{2\tau}{1+\omega_0^2\tau^2} \right)$$

$$\frac{1}{T_2} = \omega_L^2 \left(\tau + \frac{\tau}{1+\omega_0^2\tau^2} \right)$$



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

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

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

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

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

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

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!

To be discussed in lecture L9: 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)

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

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

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

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

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

Consider a basis set of product spin functions $|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle$ and $|\beta\beta\rangle \equiv |m_S, m_I\rangle$

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

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

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

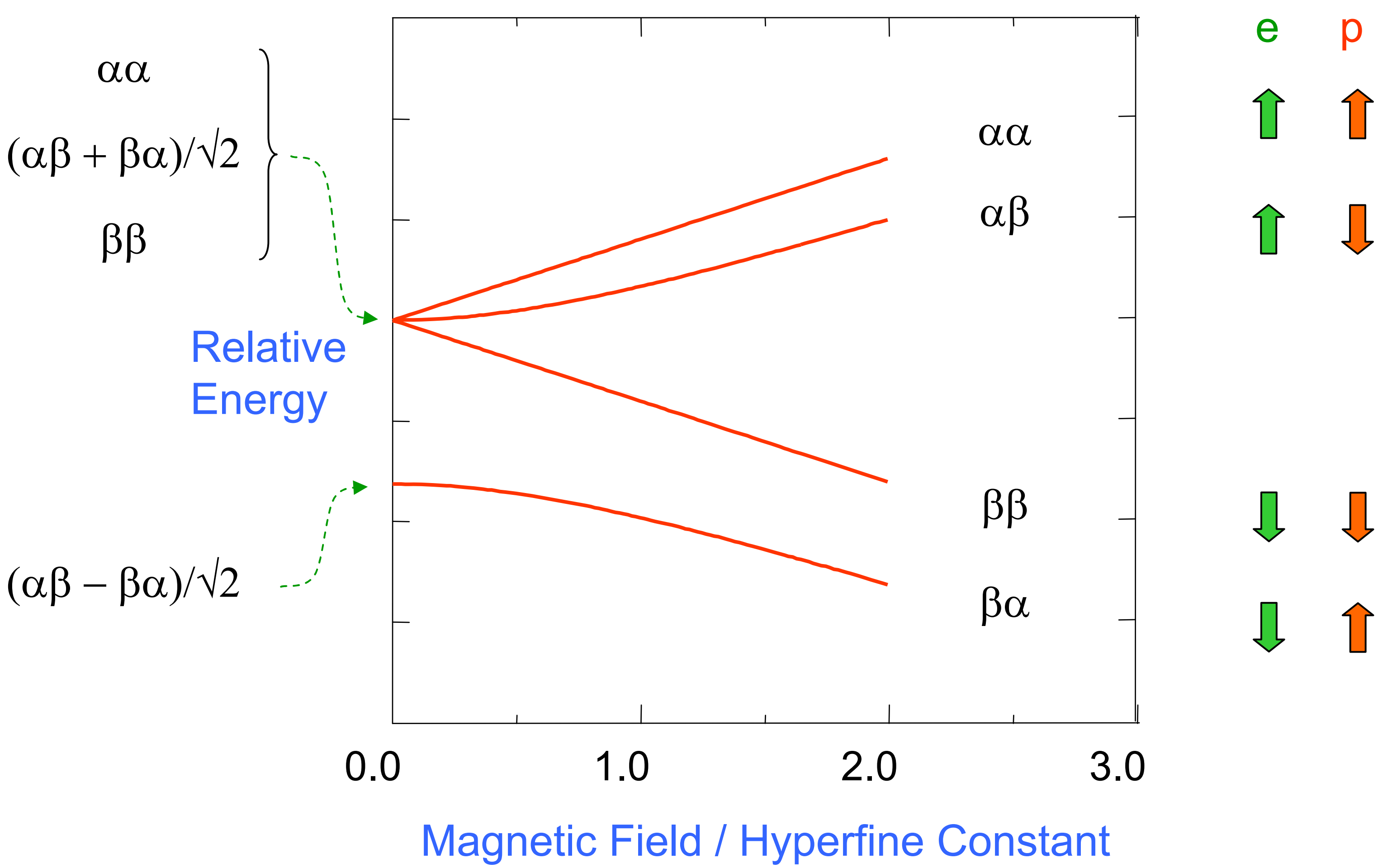
$$\hat{\mathbf{H}}|\alpha\beta\rangle = \omega_e \hat{\mathbf{S}}_z|\alpha\beta\rangle - \omega_p \hat{\mathbf{I}}_z|\alpha\beta\rangle + \tfrac{1}{2}\omega_0\left(\hat{\mathbf{S}}_+\hat{\mathbf{I}}_- + \hat{\mathbf{S}}_-\hat{\mathbf{I}}_+\right)|\alpha\beta\rangle + \omega_0\hat{\mathbf{S}}_z\hat{\mathbf{I}}_z|\alpha\beta\rangle$$

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

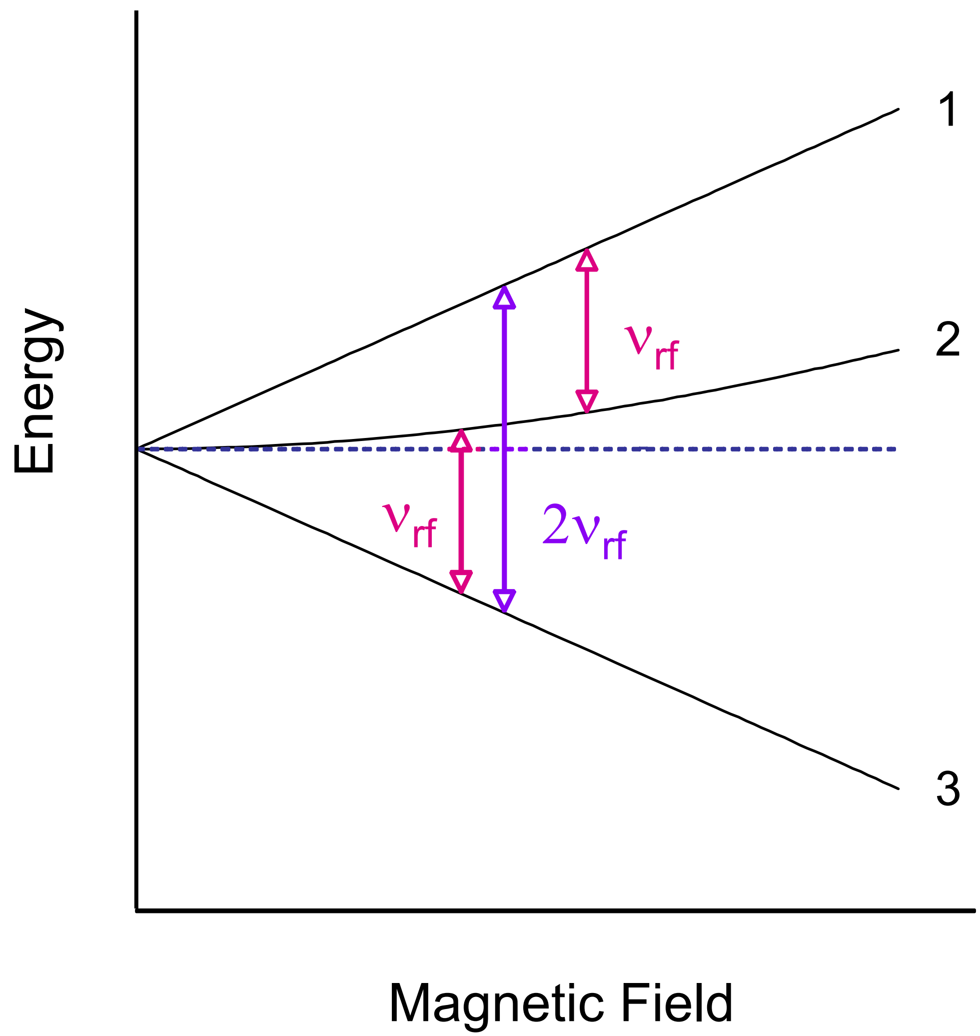
$|\alpha\beta\rangle$ is not an eigenfunction

Energy levels of a two spin-½ system

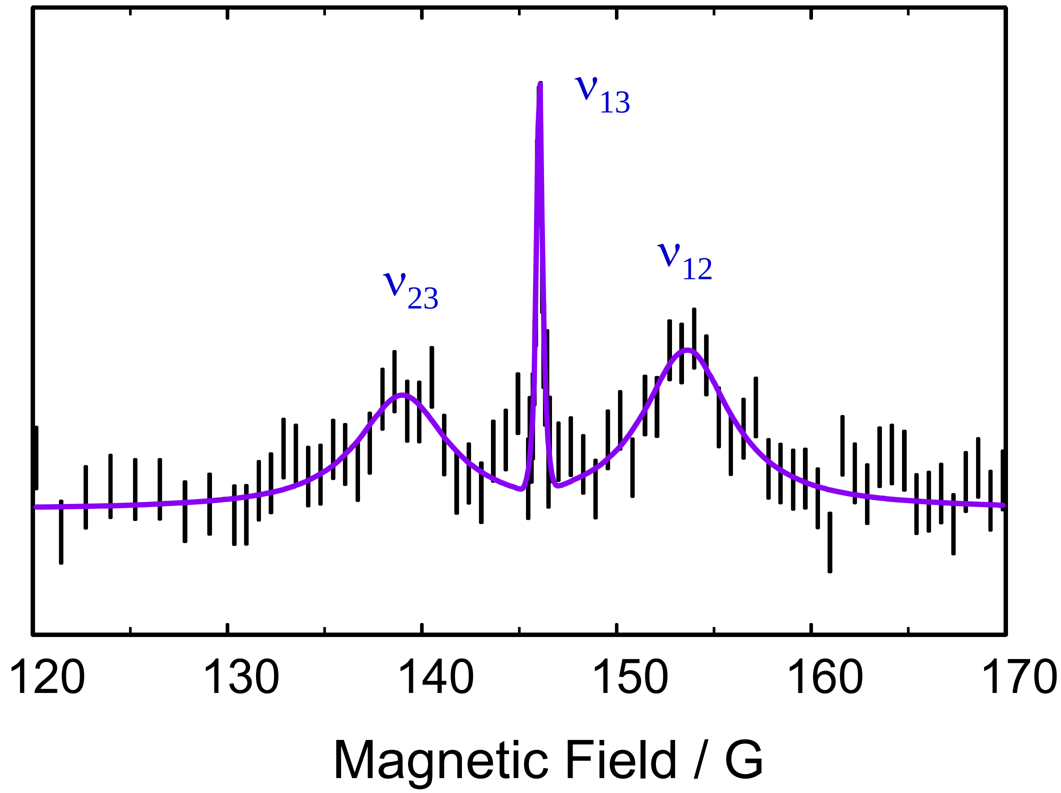
Breit-Rabi diagram

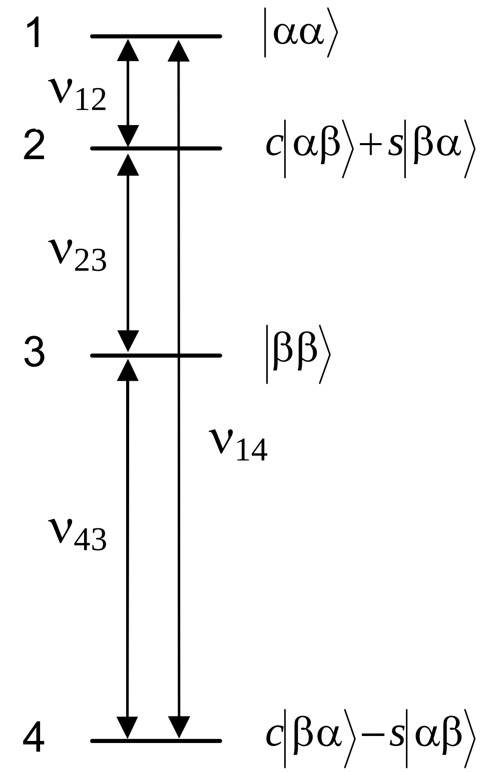


RF Transitions in Muonium at Low Magnetic Field



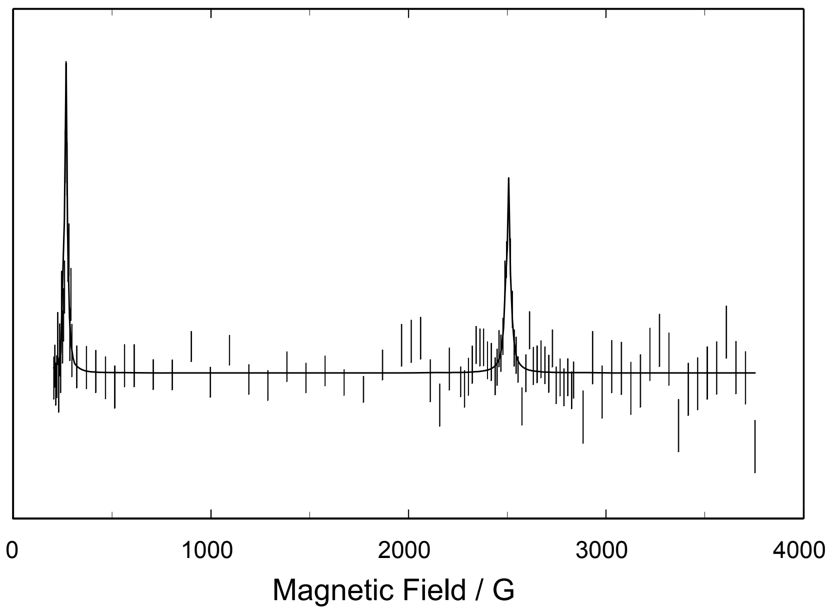
RFμSR Spectrum of Mu@C_{60} in C_{60} Powder

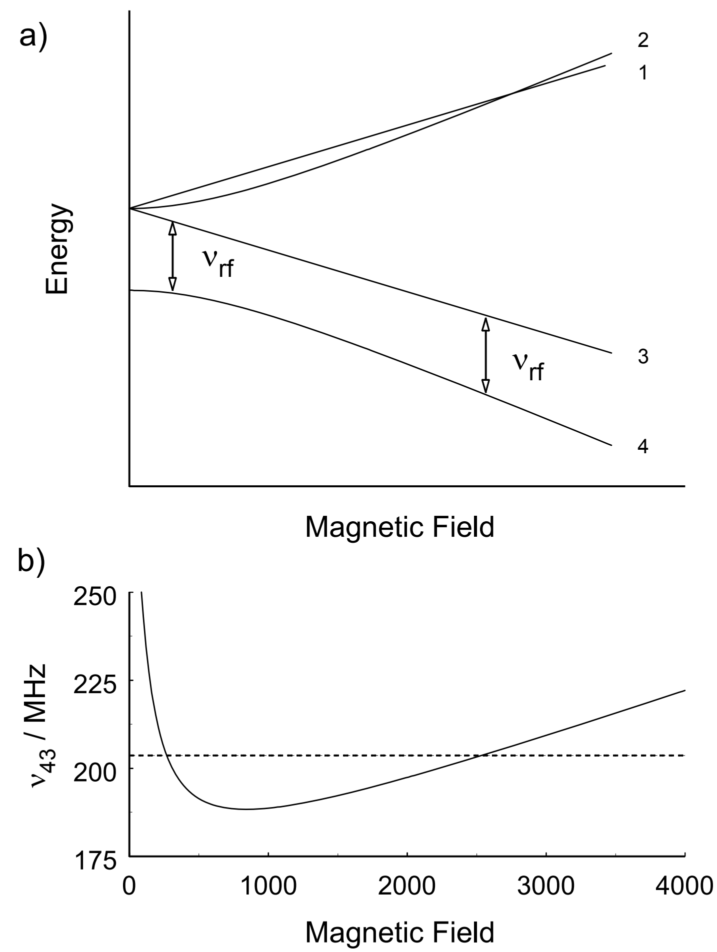




RF-μSR of $C_{60}Mu$ in solution

Because of the curvature of state 4, resonance is possible at two field positions.





Orbital Angular Momentum Operators

Classical: $\underset{\sim}{L} = \underset{\sim}{r} \times \underset{\sim}{p} = \begin{vmatrix} \underset{\sim}{i} & \underset{\sim}{j} & \underset{\sim}{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \left(yp_z - xp_y, zp_x - xp_z, xp_y - yp_z \right)$

QM: $\hat{L} = -i\hbar\left(\underset{\sim}{r} \times \nabla\right) = -i\hbar \begin{vmatrix} \underset{\sim}{i} & \underset{\sim}{j} & \underset{\sim}{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right)$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right)$$

$$\hat{L}^2 = \hat{L}\bullet\hat{L} = \hat{L}_x{}^2 + \hat{L}_y{}^2 + \hat{L}_z{}^2$$

In spherical polar coordinates

$$\hat{L}_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi} \right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi} \right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

Orbital Angular Momentum Operators – 2

$$\left[\hat{L}_x,\hat{L}_y\right]=i\hbar\hat{L}_z \quad =-\left[\hat{L}_y,\hat{L}_x\right]$$

$$\left[\hat{L}_y,\hat{L}_z\right]=i\hbar\hat{L}_x \quad =-\left[\hat{L}_z,\hat{L}_y\right]$$

$$\left[\hat{L}_z,\hat{L}_x\right]=i\hbar\hat{L}_y \quad =-\left[\hat{L}_x,\hat{L}_z\right]$$

$$\left[\hat{L}^2,\hat{L}_x\right]=\left[\hat{L}^2,\hat{L}_y\right]=\left[\hat{L}^2,\hat{L}_z\right]=0$$

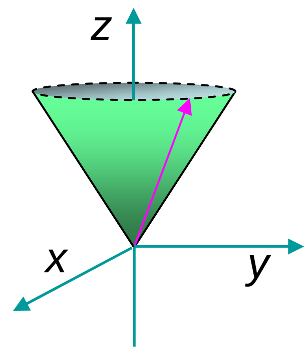
It is not possible to determine precise values of L_x and L_y simultaneously…

…but it is possible to determine precise values of L^2 and one component.

$$\hat{L}^2\,\mathrm{Y}_{l,m}(\theta,\phi)=\hbar^2 l(l+1)\,\mathrm{Y}_{l,m}(\theta,\phi)$$

$$\hat{L}_z\Phi_m(\phi)=m\hbar\,\Phi_m(\phi)$$

$$\hat{L}_z\,\mathrm{Y}_{l,m}(\theta,\phi)=m\hbar\,\mathrm{Y}_{l,m}(\theta,\phi)$$



Since $\left(\hat{L}^2-\hat{L}_z^{\,2}\right)\mathrm{Y}_{l,m}(\theta,\phi)=\left(\hat{L}_x^{\,2}+\hat{L}_y^{\,2}\right)\mathrm{Y}_{l,m}(\theta,\phi)=\left[l(l+1)-m^2\right]\mathrm{Y}_{l,m}(\theta,\phi)$

and the sum of the square components of angular momentum cannot be negative,

$\left[l(l+1)-m^2\right]\geqslant 0$ or $|m|\leqslant l$ i.e. $m=0,\pm 1,\pm 2,\ldots,\pm l$