Muonium

Paul Percival
Hydrogen-like Atoms

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

Assuming the orbital angular momentum is quantized,

\[ L = mvr = n\hbar \quad n = 1, 2, 3 \]

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

Rydberg constant
Muonium — a light isotope of hydrogen

Quantum mechanics gives the same result as the Bohr model

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

The properties of a single electron atom are determined by $m_r$

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, $\text{Mu}—\text{X}$,

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

$$\therefore \nu_{\text{Mu}X} = \sqrt{\frac{m_{\text{HX}}}{m_{\text{Mu}X}}} \nu_{\text{HX}} \approx 3 \nu_{\text{HX}}$$

if $m_X >> m_\mu$

$\Rightarrow$ 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)

\[ E_{\text{dipolar}} = \frac{1 - 3 \cos^2 \theta}{r^3} \mu_1 \mu_s \]

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

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

\[ E_{\text{dipolar}} = 0 \]

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

\[ a = \frac{8\pi}{3} g^2 g_{NN} |\psi(0)|^2 \]

Only \( s \) electrons have density at the nucleus.

For the H atom

\[ \psi_1 = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \]

\[ |\psi(0)|^2 = \frac{1}{\pi a_0^3} \]

\[ A_H = 1420 \text{ MHz} \]

\[ A_{Mu} = 4463 \text{ MHz} \]
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 $\hat{S}_z$:

$$\hat{S}_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \quad \hat{S}_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

The matrix elements are

$$\langle \alpha | \hat{S}_z | \alpha \rangle = \frac{1}{2} \quad \langle \beta | \hat{S}_z | \beta \rangle = -\frac{1}{2} \quad \Rightarrow \quad \hat{S}_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Similarly,

$$\hat{S}^2 |\alpha\rangle = s (s + 1) |\alpha\rangle = \frac{3}{4} |\alpha\rangle \quad \Rightarrow \quad \hat{S}^2 = \frac{3}{4} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\hat{S}^2 \hat{S}_z = \frac{3}{8} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \hat{S}_z \hat{S}^2$$

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

$$\hat{S}_x |\alpha\rangle = \frac{1}{2} |\beta\rangle \quad \hat{S}_x |\beta\rangle = \frac{1}{2} |\alpha\rangle$$

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

$$\hat{S}_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{S}_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} \quad \alpha \text{ and } \beta \text{ are not eigenfunctions of } \hat{S}_x \text{ and } \hat{S}_y$$

$$\hat{S}_x \hat{S}_y = \frac{1}{4} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} = \frac{1}{4} i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \Rightarrow \quad [\hat{S}_x, \hat{S}_y] = \frac{1}{2} i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i \hat{S}_z$$
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:

\[ \lambda = \pm \frac{1}{2} \]

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

Solve for coefficients and normalize

For \( \lambda = -\frac{1}{2} \)

\[ \left(0 + \frac{1}{2}\right)c_{11} + \frac{1}{2}c_{12} = 0 \]
\[ \frac{1}{2}c_{11} + \left(0 + \frac{1}{2}\right)c_{12} = 0 \]

\[ c_{11} = -c_{12} \quad c^2_{11} + c^2_{12} = 1 \quad c_{11} = \frac{1}{\sqrt{2}} = -c_{12} \]

For \( \lambda = \frac{1}{2} \)

\[ \left(0 - \frac{1}{2}\right)c_{21} + \frac{1}{2}c_{22} = 0 \]
\[ \frac{1}{2}c_{21} + \left(0 - \frac{1}{2}\right)c_{22} = 0 \]

\[ c_{21} = c_{22} \quad c^2_{21} + c^2_{22} = 1 \quad c_{21} = \frac{1}{\sqrt{2}} = c_{22} \]

\[ \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \]

\[ \begin{pmatrix} 1 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \]

\[ \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

arbitrary labelling of wave functions

\[ \hat{S}_x \]

is diagonal in the new basis
Spin Hamiltonian

\[ \hat{H} = \omega_e \hat{S}_e - \omega_p \hat{I}_z + \omega_0 \hat{S} \cdot \hat{I} \]

in units of \( \hbar \)

Electron

Nuclear

Zeeman interactions

hyperfine interaction

(isotropic case)

Consider a basis set of product spin functions

\[ |\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle \text{ and } |\beta\beta\rangle \equiv |m_s, m_i\rangle \]

Spin Hamiltonian

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

\[ = \frac{1}{2} \omega_e |\alpha\alpha\rangle - \frac{1}{2} \omega_p |\alpha\alpha\rangle + 0 + \frac{1}{4} \omega_0 |\alpha\alpha\rangle \]

|\alpha\alpha\rangle \text{ is an eigenfunction} \]

Spin Hamiltonian

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

\[ = \frac{1}{2} \omega_e |\alpha\beta\rangle + \frac{1}{2} \omega_p |\alpha\beta\rangle + \frac{1}{2} \omega_0 (0 + |\beta\alpha\rangle) - \frac{1}{4} \omega_0 |\alpha\beta\rangle \]

|\alpha\beta\rangle \text{ is not an eigenfunction}
H Atom Spin States – 2

Evaluating all matrix elements…

\[
\hat{H} = \begin{pmatrix}
\frac{1}{2} \omega_e - \frac{1}{2} \omega_p + \frac{1}{4} \omega_0 & 0 & 0 & 0 \\
0 & \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0 & \frac{1}{2} \omega_0 & 0 \\
0 & \frac{1}{2} \omega_0 & \frac{1}{2} \omega_e - \frac{1}{2} \omega_p - \frac{1}{4} \omega_0 & 0 \\
0 & 0 & 0 & -\frac{1}{2} \omega_e + \frac{1}{2} \omega_p + \frac{1}{4} \omega_0
\end{pmatrix}
\]

\[
E_1 = \frac{1}{2} \omega_e - \frac{1}{2} \omega_p + \frac{1}{4} \omega_0 \quad |1\rangle = |\alpha\alpha\rangle
\]

\[
E_4 = -\frac{1}{2} \omega_e + \frac{1}{2} \omega_p + \frac{1}{4} \omega_0 \quad |4\rangle = |\beta\beta\rangle
\]

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

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

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

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

\[c^2 + s^2 = 1\]
Summary of Muonium Energies and States

\[ E_1 = \frac{1}{2} \omega^e - \frac{1}{2} \omega^\mu + \frac{1}{4} \omega_0 \quad |1\rangle = |\alpha \alpha\rangle \]
\[ E_2 = \frac{1}{2} \left[ (\omega^e + \omega^\mu)^2 + \omega_0^2 \right]^{1/2} - \frac{1}{4} \omega_0 \quad |2\rangle = c |\alpha \beta\rangle + s |\beta \alpha\rangle \]
\[ E_3 = -\frac{1}{2} \left[ (\omega^e + \omega^\mu)^2 + \omega_0^2 \right]^{1/2} - \frac{1}{4} \omega_0 \quad |3\rangle = c |\beta \alpha\rangle - s |\alpha \beta\rangle \]
\[ E_4 = -\frac{1}{2} \omega^e + \frac{1}{2} \omega^\mu + \frac{1}{4} \omega_0 \quad |4\rangle = |\beta \beta\rangle \]

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

\[
c = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{\omega^e + \omega^\mu}{\left[ \omega_0^2 + \left( \omega^e + \omega^\mu \right)^2 \right]^{1/2}} \right\}^{1/2}
\]
\[
s = \frac{1}{\sqrt{2}} \left\{ 1 - \frac{\omega^e + \omega^\mu}{\left[ \omega_0^2 + \left( \omega^e + \omega^\mu \right)^2 \right]^{1/2}} \right\}^{1/2}
\]

\[ c^2 + s^2 = 1 \]

At zero field, \( c = s = \frac{1}{\sqrt{2}} \)

At low field, \( c \rightarrow \frac{1}{\sqrt{2}} \leftarrow s \)

At high field, \( c \rightarrow 1, \ s \rightarrow 0 \)
Energy levels of a two spin-$\frac{1}{2}$ system

Breit-Rabi diagram

\[ (\alpha\beta + \beta\alpha)/\sqrt{2} \]

\[ (\alpha\beta - \beta\alpha)/\sqrt{2} \]

Relative Energy

Magnetic Field / Hyperfine Constant

Long-field transitions

Trans. field transitions

\( \alpha\alpha \)

\( \alpha\beta \)

\( \beta\beta \)

\( \beta\alpha \)
Muonium Energies and States

conventional numbering

\[|1\rangle = |\alpha \alpha\rangle \]

\[E_1 = \frac{1}{4} \omega_0 + \omega_-\]

\[|2\rangle = c |\alpha \beta\rangle + s |\beta \alpha\rangle \]

\[E_2 = -\frac{1}{4} \omega_0 + \left[\omega_+^2 + \frac{1}{4} \omega_0^2\right]^{1/2} = -\frac{1}{4} \omega_0 + \frac{1}{2} \omega_0 \left[1 + x_B^2\right]^{1/2}\]

\[|3\rangle = |\beta \beta\rangle \]

\[E_3 = \frac{1}{4} \omega_0 - \omega_-\]

\[|4\rangle = c |\beta \alpha\rangle - s |\alpha \beta\rangle \]

\[E_4 = -\frac{1}{4} \omega_0 - \left[\omega_+^2 + \frac{1}{4} \omega_0^2\right]^{1/2} = -\frac{1}{4} \omega_0 - \frac{1}{2} \omega_0 \left[1 + x_B^2\right]^{1/2}\]

\[\omega_- = \frac{1}{2} \left(\omega_e - \omega_\mu\right)\]

\[\omega_+ = \frac{1}{2} \left(\omega_e + \omega_\mu\right)\]

\[x_B = \frac{\omega_e + \omega_\mu}{\omega_0}\]

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

\[s^2 = \frac{1}{2} \left(1 - \frac{x_B}{1 + x_B^2}^{1/2}\right)\]
Muonium in Zero and Longitudinal Field

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

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

\[
\omega_{24} = \omega_0 \left[ 1 + x_B^2 \right]^{1/2}
\]

The muon polarization along the field direction is

\[
P_z = \frac{1}{2} \left\{ 1 + \frac{x_B^2 + \cos \omega_{24} t}{1 + x_B^2} \right\}
\]
Repolarization 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

\[ P_\perp = \frac{1}{2} \left\{ c^2 \left( e^{i\omega_1 t} + e^{i\omega_4 t} \right) + s^2 \left( e^{i\omega_4 t} + e^{i\omega_2 t} \right) \right\} \]

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

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

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

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

at low field

usually (?) too high to detect

high field

low field

Magnetic Field

Paul Percival
Muonium in supercritical water

400°C, 245 bar

“triplet” precession

8 G

Muonium in supercritical water

400°C, 245 bar, 8 G

Diamagnetic signal subtracted

$A_{\text{Mu}} e^{-\lambda t}$
Muonium in Moderate Transverse Field

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

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

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

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

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

\[ \omega_{12} = \omega_- - \Omega \]

\[ \omega_{43} = \omega_- - \Omega - \omega_0 \]

\[ \omega_{14} = \omega_- + \Omega + \omega_0 \]

\[ \omega_{23} = \omega_- + \Omega \]

The splitting can be used to determine \( \omega_0 \)

\[ \omega_0 = \frac{1}{2} \left[ \left( \frac{\omega_{23} + \omega_{12} + 2\omega_{12}}{\omega_{23} - \omega_{12}} \right)^2 - \left( \frac{\omega_{23} - \omega_{12}}{\omega_{23} - \omega_{12}} \right)^2 \right] \]
Muonium in supercritical water at 196 G

400°C
245 bar
C$_{60}$Mu Radical Precession Frequencies in Low Magnetic Field

\[ \nu_{23} - \nu_{12} \text{ (MHz)} \]

\[ \nu_{34} \text{ (MHz)} \]

\[ \nu_{12} \text{ (MHz)} \]

\[ \nu_{12}, \nu_{23} \text{ (MHz)} \]

\[ \nu_{34} \text{ (MHz)} \]

\[ \nu_{12}, \nu_{23} \text{ (MHz)} \]

\[ \nu_{34} \text{ (MHz)} \]
Muon spin precession in D$_2$O 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
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$_2$O crystal at 230 K
Mu precession frequencies in low magnetic field

Isotropic hyperfine case:

- Magnetic Field
- Energy

Axial anisotropy:

- Magnetic Field
RF Transitions in Muonium at Low Magnetic Field

![Diagram showing transitions in muonium with labels for energy and magnetic field axes, indicating transitions at frequencies $\nu_{\text{rf}}$ and $2\nu_{\text{rf}}$.]

Paul Percival
TRIUMF Summer Institute, August 2011
RF$\mu$SR Spectrum of Mu@C$_{60}$ in C$_{60}$ Powder
Endohedral Muonium  $\text{Mu}@C_{60}$

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.

Muonium and Diamagnetic Fractions

<table>
<thead>
<tr>
<th>Substance</th>
<th>State</th>
<th>$P_M$</th>
<th>$P_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>gas</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>gas</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>gas</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Water</td>
<td>liquid</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Water ice</td>
<td>solid</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>liquid</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>CCl₄</td>
<td>liquid</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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**

- **MUON BEAM**
  - SLOWING DOWN OF FAST MUONS:
    - Energy loss through scattering with electrons
  - ELECTRON CAPTURE AND LOSS:
    - (many cycles)
  - EPITHERMAL SCATTERING OF MUONIUM:
    - Billiard-ball collisions with atoms and molecules
  - HOT ATOM REACTIONS
  - MUONIATED MOLECULES
  - THERMAL MUONIUM

Based on Brewer, Crowe, Gygax and Schenck (1975)

- **50 MeV**

- **2.3 keV**

- **200 eV**

- **20 eV**

- **1 eV**

Bethe-Bloch processes

Muon $E \sim$ electron orbital velocity

cf hot tritium reactions
The Spur Model for Mu Formation (in water) circa 1978

[ $e^{-}$ ... $\mu^{+}$ ... $\cdot$OH ]

终端辐射径迹的尖端

$e_{aq}^{-}$
$\mu_{aq}$

[ $\mu$ .. $e_{aq}^{-}$ ]

$P_{Mu}$
$P_{L}$
$P_{D}$

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**
  \[ \text{Mu}^* + RH \rightarrow \begin{cases} \text{MuH} + R \\ \text{MuR} + H \end{cases} \]
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)

\[
\begin{align*}
\text{e}^- & \rightarrow \text{Mu} \\
\mu^+ & \rightarrow H_2O \\
\text{PL} & \text{missing fraction} \\
\text{PMu} & \text{detectable muonium} \\
\text{PD} & \text{diamagnetic signal} \\
\end{align*}
\]
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 \( \hat{H} = \hat{H}_0 + \hat{h} \) where \( \hat{H}_0 \psi_n^0 = E_n^0 \psi_n^0 \)

Approximate energies

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

Approximate wave functions

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

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 \( E_j^0 - E_k^0 \)

Does not work for \( E_j^0 = E_k^0 \)!

If necessary, use linear combinations to avoid this problem.
Perturbation Theory – Example of H spin states

\(\hat{H}^0 = \omega_e \hat{S}_z - \omega_p \hat{S}_z + \omega_0 \hat{S}_z \hat{S}_z\)  \(\hat{H}^1 = \frac{1}{2} \omega_0 \left( \hat{S}_+ \hat{S}_- + \hat{S}_- \hat{S}_+ \right)\)

0th order:  
\(E_1^0 = \hat{H}_{11}^0 = \frac{1}{2} \omega_e - \frac{1}{2} \omega_p + \frac{1}{4} \omega_0\)  \(|1^0\rangle = |\alpha \alpha\rangle\)

\(E_2^0 = \hat{H}_{22}^0 = \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0\)  \(|2^0\rangle = |\alpha \beta\rangle\)

\(E_3^0 = \hat{H}_{33}^0 = -\frac{1}{2} \omega_e - \frac{1}{2} \omega_p - \frac{1}{4} \omega_0\)  \(|3^0\rangle = |\beta \alpha\rangle\)

\(E_4^0 = \hat{H}_{44}^0 = -\frac{1}{2} \omega_e + \frac{1}{2} \omega_p + \frac{1}{4} \omega_0\)  \(|4^0\rangle = |\beta \beta\rangle\)

1st order:  
\(\hat{H}_{11}^1 = 0\)

\(\hat{H}_{22}^1 = 0\)

\(\hat{H}_{33}^1 = 0\)

\(\hat{H}_{44}^1 = 0\)

2nd order:  
\(\hat{H}_{12}^1 = 0, \ \hat{H}_{13}^1 = 0, \ \hat{H}_{14}^1 = 0, \ \hat{H}_{24}^1 = 0, \ \hat{H}_{34}^1 = 0, \ \hat{H}_{23}^1 = \frac{1}{2} \omega_0\)

\(\hat{H}_{21}^1 = 0, \ \hat{H}_{31}^1 = 0, \ \hat{H}_{41}^1 = 0, \ \hat{H}_{42}^1 = 0, \ \hat{H}_{43}^1 = 0, \ \hat{H}_{32}^1 = \frac{1}{2} \omega_0\)

\(E_2^0 - E_3^0 = \omega_e + \omega_p - \frac{1}{2} \omega_0\)

\(E_3^0 - E_2^0 = -\omega_e - \omega_p + \frac{1}{2} \omega_0\)

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

Exact:  
\(E_2 \to \frac{1}{2} \omega_e + \frac{1}{2} \omega_p - \frac{1}{4} \omega_0 + \frac{\frac{1}{4} \omega_0^2}{\omega_e + \omega_p}\)  \(\text{for } \omega_0 \ll \left(\omega_e + \omega_p\right)^2 \text{ high field}\)
Spin Symmetry and Selection Rules

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

\[ I \propto |\mu_{mn}|^2 = |\mu^x_{mn}|^2 + |\mu^y_{mn}|^2 + |\mu^z_{mn}|^2 \]

where \[ \mu^x_{mn} = \langle m | \hat{\mu}^x | n \rangle \] etc.

In magnetic resonance the relevant operator is the magnetic dipole.

For TF-\(\mu\)SR this involves muon-spin-flipping operators.

\[
\langle \psi_e \psi'_p | \hat{P}_i | \psi'_e \psi''_p \rangle = \langle \psi'_e | \psi''_e \rangle \langle \psi'_p | \psi''_p \rangle
\]

\[ = \langle \psi'_p | \hat{P}_i | \psi''_p \rangle \text{ if } \psi_e = \psi''_e \text{ and } \psi'_p = \psi''_p \]

i.e. \[ \langle m'_S | m''_S \rangle = 1 \text{ and } \langle m'_i | m''_i \rangle = 1 \]

\[ \Delta m_S = 0 \text{ and } \Delta m_i = 0 \]

The transition moment is zero ("forbidden" transition) if the electronic (or nuclear) spin states (\(\alpha, \beta\)) are orthogonal: \[ \langle \alpha | \beta \rangle = 0 \]

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