The Evans method

Measuring magnetic susceptibility by NMR—application
Magnetic Susceptibility

- Magnetic susceptibility is the ratio between magnetization $M$ of the material in a magnetic field and the field intensity $H$:
  \[ M = \chi \cdot H. \]
- Diamagnetic materials have $\chi < 0$
- Paramagnetic and ferromagnetic materials have $\chi > 0$ or $\gg 0$
Magnetic Field in an NMR

- $H''$ is the component of applied field due to given concentration of paramagnetic ions in solution
- $H'' = H_1 + H_2$
- $H_1$ = Lorentz or cavity field of induced magnetization in a sphere around the paramagnet = $(4\pi/3)M$
- $H_2$ is demagnetizing field, opposing applied field; $H_2 = -\alpha M$ ($\alpha$ depends on sample geometry and relative orientation of sample tube and external field)
- $H'' = [(4\pi/3)-\alpha]M$
- But $M = \chi H$
- So $H''/H = [(4\pi/3)-\alpha] \chi$
• Given: \( \frac{H''}{H} = [(4\pi/3) - \alpha] \chi \)

• But \( \Delta \frac{H''}{H} = \Delta \frac{f}{f} \)

• \( \Delta \frac{f}{f} = [(4\pi/3) - \alpha] \chi \)

• Finally, add a correction term for the magnetic susceptibility of the solvent and for the change in density of solution vs. solvent. This was all derived using mass susceptibilities \( (\chi_m) \)

\[
\chi_m = \frac{\Delta f}{\left(\frac{4\pi}{3} - \alpha\right)fm} + \chi_o + \frac{\chi_o(d_o - d_s)}{m}
\]
History

- Originally developed for permanent magnet application
- Applied field perpendicular to sample

\[ \alpha = 2\pi \]

\[ \chi_m = \frac{-3\Delta f}{2\pi fm} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m} \]

\[ \chi_m = \frac{3|\Delta f|}{2\pi fm} + \chi_o + \frac{\chi_0 (d_o - d_s)}{m} \]

- \( \Delta f \) = peak separation (Hz)
- \( f \) = NMR frequency (Hz)
- \( m \) = mass per cm\(^3\)
- \( \chi_m \) = mass susceptibility
History

- Modern instrumentation: coaxial superconducting magnet
- Applied field parallel to sample

\[ \alpha = 0 \]

\[ \chi_m = \frac{3\Delta f}{4\pi fm} + \chi_o + \frac{\chi_0(d_o - d_s)}{m} \]

\( \Delta f = \) peak separation (Hz)
\( f = \) NMR frequency (Hz)
\( m = \) mass per cm\(^3\)
\( \chi_m = \) mass susceptibility
Relationship to number of unpaired electrons

\[ \chi_P T = \text{constant for simple paramagnets (Curie Law)} \]

\[ \chi_P T = \frac{N_A g^2 \beta^2}{3k_B} [S(S+1)] = 0.50157[S(S+1)] \approx \frac{1}{2} [S(S+1)] \]

\[ \chi_P T \approx \frac{1}{8} n(n+2) \]

\[ 8 \chi_P T \approx n(n+2) \]

\( \chi_P \) = paramagnetic susceptibility

\( T \) = absolute temperature (K)

\( N_A \) = Avogadro’s number

\( g \) = magnetogyric constant for electron

\( \beta \) = Bohr magneton

\( k_B \) = Boltzmann constant

\( S \) = Total spin Quantum number

\( n \) = number of unpaired electrons

Must include Russell-Saunders coupling for 2\textsuperscript{nd} or 3\textsuperscript{rd} row

And also spin-orbit coupling for f block (CGS units)
Effective magnetic moment†

\[
\mu_{\text{eff}} = \sqrt{\frac{3k_B}{N_A \beta^2}} (\chi_P T) \approx \sqrt{7.9933 (\chi_P T)} \approx 2.827 \sqrt{\chi_P T}
\]

\[
\mu_{\text{eff}} = \sqrt{\frac{3k_B}{N_A \beta^2}} (\chi_P T) = \sqrt{\frac{3k_B}{N_A \beta^2}} \left( \frac{N_A g^2 \beta^2}{3k_B} [S(S+1)] \right) \approx \sqrt{4S(S+1)}
\]

\[
\mu_{\text{eff}} \approx 2 \sqrt{S(S+1)} = \sqrt{n(n+2)}
\]

\(\mu_{\text{eff}}\) is independent of temperature and unitless but is usually reported in units of Bohr magneton: \(\mu_B\)

\(\chi_P\) can be measured at any \(T\) and related to \(n\) or \(S\)

†The Chemist’s magnetic unit (CGS units)
Evans’ method

• Using $^1$H NMR to determine magnetic susceptibility
  – NMR tube
    • Sample solution
    • Capillary with pure solvent
  – NMR spectrum collected
    • NMR solvent in capillary (shifted peak)
    • NMR solvent in tube (reference peak)
  – Use peak shift to calculate unpaired electrons
Commonly published equation

- Use c for concentration (mol·L\(^{-1}\) = M)
- Ignore solvent diamagnetism
- Ignore density correction
- Combine constants
- Ignore sign of \(\Delta f\); take positive value

\[
\chi_m = \left| \frac{-3\Delta f \cdot 1000\,cm^3 \cdot m'}{4\pi f m} \right| \cdot \frac{n}{L} = \left| \frac{-3000\Delta f}{4\pi f c} \right| = \frac{477\Delta f}{2 fc}
\]

\(\Delta f\) = peak separation (Hz) \hspace{2cm} n = moles
\(f\) = NMR frequency (Hz) \hspace{2cm} c = \text{molar concentration}
\(m\) = mass concentration (g/mL) \hspace{2cm} \chi_m = \text{molar susceptibility}
\(m'\) = mass
Diamagnetic correction

- One unpaired electron can be detected even in a large molecule because the magnitude is \( \sim 1000 \) times greater.
- For careful work with large molecules, correct observed susceptibility for presence of paired e\(^-\).
- \( \chi_D \) tabulated.
- \( \chi_D \) opposite sign to \( \chi_P \)!

\[
\chi_{\text{meas}} = \chi_P + \chi_D \\
\chi_P = \chi_{\text{meas}} - \chi_D
\]