Many nuclei possess a spin angular momentum (depending on the number of protons and neutrons) ⇒ they behave like magnets with spin quantum number $I$; their spins may have different orientations $m_I = -I, \ldots, +I$ with respect to an outside axis, e.g., $I = 1/2 \Rightarrow$ two orientations.
An outside magnetic field splits up the degenerate spin orientations.

\[ E_{m_I} = -\gamma_N \hbar B m_I = -g_I \mu_N B m_I \]

- \( \gamma_N \): magnetogyric ratio
- \( g_I \): nuclear g-factor
- \( \mu_N \): nuclear magneton

\[ \mu_N = \frac{e\hbar}{2m_p} \]

Resonance at \( h\nu = \gamma_N \hbar B \)

with \( B = 9.4 \text{T for } ^1\text{H} \)

\( \nu = 400 \text{ MHz} \)
Shielding and deshielding

A magnetic field will induce a circulating motion in the electrons, giving rise to a small additional magnetic field at the nucleus

\[ B_{\text{effective}} = B_{\text{applied}} - B_{\text{induced}} = B_{\text{applied}} (1 - \sigma) \]

\[ \nu = \frac{\gamma_N}{2\pi} B_{\text{applied}} (1 - \sigma) \]
Chemical shifts vary with environment: Assignment of resonances

Relative signal intensities reflect number of identical magnetic nuclei

\[ \delta = \frac{\nu - \nu^0}{\nu^0} \text{[ppm]} \]

TMS as reference
The fine structure: Spin-spin coupling

Energy difference $J$: Spin-spin coupling efficiency depends on distance (max. 4 bonds)

$X$ and $A$ exert effects on each other

$A$ resonance $\leftrightarrow$ other $\leftrightarrow X$ resonance
Fine structure: Multiple equivalent nuclei

2 X nuclei:

3 X nuclei:

1st X nucleus splits by J
2nd X nucleus splits by J
3rd X nucleus splits by J

1st A nucleus splits by J
2nd A nucleus splits by J

1 Pascal’s triangle
Fine structure: Values of J reveal geometry

Karplus equation

$$3 J_{HH} = A + B \cos \phi + C \cos 2\phi$$
Spin relaxation: Info on molecule dynamics

1. Spin-lattice relaxation by molecule tumbling at about resonance frequency (otherwise saturation and loss of signal)

2. Spin-spin relaxation by transient, yet long-lasting differences in local magnetic fields
Large molecules have many chemically identical nuclei: How can one identify those that are close together in 3D?

Let’s look at a simple AX spin system:

$$\begin{align*}
\alpha_A \beta_x \\
\beta_A \alpha_x \\
\alpha_A \alpha_x
\end{align*}$$
NOE: Changes in signal intensity

The direction and strength of signal intensity changes in an NOE experiment depend on the distance of A and X: Supramolecular structures can be studied!