1. Introduction to NMR

1.1. Nuclear magnetization

Atomic nuclei are inherently quantum mechanical

Conventional NMR $\leftrightarrow$ 10^10 spins

ensemble = vector quantity, "magnetization"

1.1. QM description of spins

Quantum state

example: angular momentum, measured along z axis $\rightarrow$ discrete states "eigenstates" $-I, -I+1, \ldots, I-1, I$

I = momentum quantum number.

Arbitrary state $|\psi\rangle$ can be written as a linear combo of basis states $|m\rangle$

$|\psi\rangle = \sum_m a_m |m\rangle$

Eigenvalue equation

$I^z |m\rangle = m \langle m | m\rangle$

Eigenvalue $m$ is a result of observation

$I^z =$ operator for angular momentum along z axis

discrete set of $|m\rangle$, can be represented as vectors

for $I = \frac{1}{2}$

$|I = \frac{1}{2}\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

$|I = -\frac{1}{2}\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$
operator $I_2$ is a matrix

$$I_2 = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Result of measurement \(=\) calculating

$$\langle w | I_2 | w \rangle$$

where \(w \to \text{row vector}\) conjugate to \(\psi\).

**Observable of** \(I_2\)

spin -1/2

$$\langle \frac{1}{2} | I_2 | \frac{1}{2} \rangle = \begin{bmatrix} 1, 0 \end{bmatrix} \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{1}{2}.$$

Suppose that nucleus is not in expected

$$| \psi \rangle = \sum_m a_m | m \rangle$$

result of measurement \(\rightarrow\) expectation value

$$\langle \psi | I_2 | \psi \rangle = \sum_{m, m'} a_m \alpha^*_m a^*_m, \langle m | I_2 | m' \rangle = \sum_{m, m'} a_m \alpha_m^* a^*_m, \langle m | m' \rangle$$

Since basis vectors are orthogonal

$$\langle \psi | I_2 | \psi \rangle = \sum_m | a_m |^2 m$$

ensemble of nuclei \(\rightarrow\) a mean of eigenvalues

single nuclear spin \(\rightarrow\) probability

$$| a_m |^2$$

of rotating

result \(m\)

3 directions \(\rightarrow\) 3 observable

$$I_x, I_y, I_z$$

$$I_x = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$I_y = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$$

$$I_z = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$
\[ [I_x I_y] = I_x I_y - I_y I_x = i I_z \]

Operator of rotation (about $z$ axis)
\[ R_z (\phi) = \exp (i \phi I_z) \]
with \( e^F = 1 + F + \frac{F^2}{2!} + \ldots \)

Raising and lowering operators
\[ I_+ = I_x + i I_y, \quad I_- = I_x - i I_y \]

Converse if \( I^2 = 1 + \frac{1}{2} \Rightarrow I^+ I^- \Rightarrow I^+ I_- \)

\[ I^+ | -\frac{1}{2} \rangle = | +\frac{1}{2} \rangle \quad \text{and} \quad I^- | +\frac{1}{2} \rangle = | -\frac{1}{2} \rangle \]

Spin evolution is described by Schrödinger equation
\[
\frac{i}{\hbar} \frac{\partial}{\partial t} \Psi (t) = \mathcal{H} \Psi (t) \]

If \( \mathcal{H} \) is constant
\[ \Psi (t) = U (t) \Psi (0) \]

Where \( U (t) = \exp (-i \mathcal{H} t / \hbar) \) - evolution operator

Atomic multipoles dipole moment proportional to angular momentum

Interaction energy \( \vec{r} \cdot \vec{B} \).
Usually we drop and show Hamiltonian with units of angular frequency

\[ \omega_0 = g B_0 \]

Example: Protons 40 MHz/\tau
\[ \psi^* \]

Large ensembles of different nuclei, different states
Average by a sum over subensembles each with probability \( p_i \)

\[ \langle \psi | I_2 | \psi \rangle = \sum \frac{p_i}{\psi} \langle \psi | I_2 | \psi \rangle \]

Example: Spin 1/2 system
\[ \psi = a_{1/2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + a_{-1/2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \]
\[ \langle \psi | I_2 | \psi \rangle = \frac{1}{2} \left( |a_{1/2}|^2 + |a_{-1/2}|^2 \right) \]

Interpretation: difference in population between levels.
Thermal equilibrium
\[ T = 1/2 \exp \left( \pm \frac{\hbar}{k_B T} \sqrt{gB_0} / 2 k_B T \right) \exp \left( -\frac{\hbar gB_0}{2 k_B T} \right) + \exp \left( \frac{\hbar gB_0}{2 k_B T} \right) \]

\[ g \mu_B \ll k_B T (300 K) \]

\[ |a \pm n/2|^2 = \frac{1}{2} \left[ 1 \pm \frac{g \mu_B B_0}{2 k_B T} \right] \]

In general, for any \( I \)
\[ 1_{2m+1}^2 = \frac{1}{(2I+1)} \left[ 1 + m \hbar / 2 k_B T \right] \]

NMR experiment is measurement of \( x \) component

\[ J_x = \frac{1}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \]

\[ \langle \psi | J_x | \psi \rangle = \frac{1}{2} \left[ a^* \frac{1}{2} - a^* \frac{1}{2} + a \frac{1}{2} - a \frac{1}{2} \right] \]

different from \( J_z \)

Transverse magnetization vs longitudinal magnetization

\( a^* \) \( -a \) terms are connected with density function

Definition of operator \( \mathcal{O} = \sum_{\psi} P_\psi |\psi\rangle \langle \psi| \)

\[ \mathcal{O} \] - matrix, elements are
\[ P_{nn} = (\mu \mid \gamma_{1} \psi) \frac{\sum \gamma_{m} \langle \mu \mid \psi \rangle \langle \gamma_{m} \mid \psi \rangle}{\gamma_{m} \gamma_{n}} = \frac{\gamma_{m} \gamma_{n}}{\gamma_{m} \gamma_{n}} = \delta_{mn} \]

Expectation value of any operator \( O \) can be written as,
\[ \langle \psi \mid O \mid \psi \rangle = Tr(O\rho) \]

Schrödinger eq. for density matrix - Liouville eq.
\[ i \frac{\partial \rho}{\partial t} = [H, \rho] \]

Solution \( \rho(t) = \exp(-iHt)\rho(0)\exp(iHt) \)

For \( I = \frac{1}{2} \) system,
\[ \rho = \begin{bmatrix} \frac{1}{2} + \langle I_{z} \rangle & \langle I_{x} - iI_{y} \rangle \\ \langle I_{x} + iI_{y} \rangle & \frac{1}{2} - \langle I_{z} \rangle \end{bmatrix} \]

In macroscopic terms \( \rho \)

Magnetization vector
\[ \vec{M} = N\gamma B [\langle I_{x} \rangle \hat{x} + \langle I_{y} \rangle \hat{y} + \langle I_{z} \rangle \hat{z}] \]
\( S \) can be expressed as product of \( I_x, I_y, I_z \)
higher dimensions (coupled spins).
**Example:** 2 spin system:
\[
\begin{align*}
| \frac{1}{2}; \frac{1}{2} \rangle & \\
| -\frac{1}{2}; \frac{1}{2} \rangle & \\
| -\frac{1}{2}; -\frac{1}{2} \rangle & = | -\frac{1}{2}; \frac{1}{2} \rangle \quad 0 = \left( \begin{array}{c}
\vdots \\
\vdots \\
\vdots \\
\end{array} \right) \\
& \text{16 terms.}
\end{align*}
\]

**Basis operators**
\[
\begin{align*}
I_{1x}, I_{1y}, I_{1z} & \quad \text{polarisation, spin 1, 2} \\
I_{2x}, I_{2y}, I_{2z} & \quad \text{in phase x coherence} \\
I_{1y} I_{2x}, I_{1y} I_{2y} & \quad \text{in phase y coherence.}
\end{align*}
\]

**Other operators**
\[
\begin{align*}
I_{1x} I_{2x}, I_{1z} I_{2x} \\
I_{1y} I_{2z}, I_{1z} I_{2y} \\
I_{1x} I_{2x}, I_{1y} I_{2y} \\
I_{1x} I_{2y}, I_{1y} I_{2y} \\
I_{1z} I_{2z}
\end{align*}
\]

+ unity operator (16 in total).

Resonant excitation and rotating frame.

\[
\begin{align*}
& B_0 \quad \text{Example oscillating B-field} \\
\text{longitudinal static field} & B_0
\end{align*}
\]
Hamiltonian (lab frame)

\[ H_{\text{lab}} = -J B_0 l_z - 2 J B_1 \cos\omega t \cdot I_x \]

\[ B_1 = \frac{2}{3} B_1 \cos \omega t \]

\[ \frac{1 - \gamma}{2} = 2 \text{ two circularly polarized components} \]

Case \( B_1 < B_0 \), counter-rotating term can be ignored.

Coordinate transformation. Rotation field is stationary.

\[ H_{\text{rot}} = -J (B_0 - \omega I_f) - J B_1 I_x \]

1.2 Semi-classical description of NMR. Ensemble of spins (magnetization vector)

\[ \vec{M} \]

\[ \frac{d\vec{M}}{dt} = J \vec{M} \times \vec{B} \] (1)

Precession at rate \( \omega = \pm \vec{B} \)

Static field \( B_0 \), rotating field \( B_1 \).

\[ B_1(t) = B_1 \cos \omega t \cdot I_x - B_1 \sin \omega t \cdot I_z \]

\( \hat{i}, \hat{j}, \hat{k} \) - unit vectors along \( x, y, z \).

Equation (1x) transforms into
\[ \begin{align*}
\frac{dM_x}{dt} &= \tau [MyB_0 + M_2 B_1 \sin \omega t] \\
\frac{dM_y}{dt} &= \tau [M_2 B_1 \cos \omega t - M_x B_0] \\
\frac{dM_z}{dt} &= \tau [-M_x B_1 \sin \omega t - My B_1 \cos \omega t]
\end{align*} \]

Initial condition: \( \tilde{M} = M_0 \hat{e}_z, \quad \omega = \frac{\tau}{1 + B_1} \)

\begin{align*}
M_x &= M_0 \sin \omega t \sin \omega t \\
M_y &= M_0 \sin \omega t \cos \omega t \\
M_z &= M_0 \cos \omega t
\end{align*}

Simultaneous precession about \( B_0, B_1 \)

Laboratory frame

Rotating frame

Relaxation
Spin system interacts with both "spin lattice relaxation"

Phenomenological description
\[ \frac{dM_2}{dt} = -\frac{(M_2 - M_0)}{T_1} \]

with solution:

\[ M_2(t) = M_2(0) \exp\left(-\frac{t}{T_1}\right) + M_0 \left(1 - \exp\left(-\frac{t}{T_1}\right)\right) \]

\( T_1 \) - spin-lattice, "longitudinal" relaxation time

Protons in dielectric materials

0, \( t = 10 \) seconds.

Decoherence, dephasing, \( T_2 \) time

\[ \frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2} \]

\[ M_{x,y}(t) = M_{x,y}(0) \exp\left(-\frac{t}{T_2}\right) \]

Bloch equations:

\[ \frac{dM_x}{dt} = \gamma \left(M_y B_0 + M_z B_1 \sin\omega t\right) - \frac{M_x}{T_2} \]

\[ \frac{dM_y}{dt} = \gamma \left(M_z B_1 \cos\omega t - M_x B_0\right) - \frac{M_y}{T_2} \]

\[ \frac{dM_z}{dt} = \gamma \left(-M_x B_1 \sin\omega t - M_y B_0 \cos\omega t\right) - \frac{M_z - M_0}{T_1} \]
Solutions, case of weak RF field steady state:

\[ (\delta B_2)^2 < < 1 \]

\[
M_x = (\omega I M_0) \frac{T_2^2 \delta \omega}{1 + (T_2 \delta \omega)^2} = \omega I M_0 G(\delta \omega)
\]

\[
M_y = (\omega I M_0) \frac{T_2}{1 + (T_2 \delta \omega)^2} = \omega I M_0 F(\delta \omega)
\]

where \( F \) and \( G \) are absorption and dispersion lineshapes.

\[
G(\delta \omega) = \frac{T_2^2 \delta \omega}{1 + (T_2 \delta \omega)^2}
\]

\[
F(\delta \omega) = \frac{T_2}{1 + (T_2 \delta \omega)^2}
\]
Spin Echos

Erwin Hahn, key for development of pulsed methods. \( w = H_0 \), pulses (\( H_1 \))

\[ t = 0 \]

\[ t = 0^+ \]

\[ t = \tau \]

\[ t = 2\tau \]

All spins are in phase at \( t = 2\tau \)

After \( 2\tau \) out of phase again owing to field inhomogeneity

Signals: Free induction decay, echo
QM treatment of spin echo experiment

\[ B_1 \]

0 \quad t_1 \quad t_2 \quad t_3 \quad t

\[ \psi \text{ obeys Schrödinger equation} \]

\[- \frac{i}{\hbar} \frac{\partial \psi}{\partial t} = H \psi \]

\[ H = -\hbar \left( \left( \frac{\hbar c}{\omega} \right) I_z + B_1 I_x \right) \]

\[ B_1 \text{ - field in low.} \]

Inhomogeneous field \( B_0 \) \( \Rightarrow \) distribution function

\[ p(\omega) \Rightarrow \text{number of spins between } B_0 \text{ and } B_0 + \Delta B \]

\[ dn = np(\omega) d\omega \]

\[ N = \text{total number of spins} \]

MW pulses \( B_1 < B_0 \), but \( B_1 > B_0 \) in this case MW pulse Hamiltonian

\[ H = -\hbar \frac{1}{2} B_1 I_x \]

Between pulses, \( B_1 = 0 \)

\[ H = -\hbar \hbar \frac{1}{2} B_0 I_z \]

\[ H \text{ is time dependent but its time variation occurs only at} \]

\[ t = 0, t_1, t_2, t_3 \]
\[ \psi(t_2) = e^{i\frac{\hbar}{\mathcal{B}_0} t_2} x \psi(0), \quad \mathcal{B}_0 t_2 = \frac{\pi}{2} \]

\[ \psi(t_2) = e^{i\frac{\mathcal{B}_0}{2} (t_2 - t_1)} I_x \psi(t_1) \]

etc.

Convenient to define quantities:

\[ T(t, \mathcal{B}_0) \text{ and } X(\theta) \text{ by} \]

\[ T(t, \mathcal{B}_0) = e^{i\frac{\mathcal{B}_0}{2} t} I_x \]

\[ T \text{ generates development of wave function during time when } \mathcal{B}_0 = 0 \text{ for spins which are off resonance by } \mathcal{B}_0. \]

\[ X(\theta) = e^{i\theta I_x} \text{ - rotation about } \]

\[ \text{For } \theta = \frac{\pi}{2}, \quad X^{-1}(\frac{\pi}{2}) I_y X(\frac{\pi}{2}) = I_z \]

\[ \text{Spin components} \]

\[ I_y, I_z, I_x \]

\[ \text{transforms} \]

\[ (\frac{\pi}{2} \text{ - Pulse}) \]

\[ \text{For } \theta = \pi \text{ (Pi - Pulse)} \]

\[ X^{-1}(\pi) I_y X(\pi) = -I_y \]

\[ X^{-1}(\pi) I_z X(\pi) = -I_z \]

\[ X^{-1}(\pi) I_z X(\pi) = I_x \]

\[ \text{We consider } \mathcal{B}_0 \gg \mathcal{B}_0 \Rightarrow \text{neglect time evolution between } t_1 \text{ and } t_2. \]

\[ \Rightarrow \psi(t_2) = X(\frac{\pi}{2}) \psi(0) \]

\[ \psi(t_2) = T(t, \mathcal{B}_0) X(\frac{\pi}{2}) \psi(0) \]
we get $\psi(t)$ for time $t$ (after the second pulse)

$\psi(t) = T(t-t_0, b_0, \pi) T(t, b_0) \psi(0)$

for a single value of $b_0$.

Observable signal, $I_y$

for a single set of spins

$\langle I_y(t) \rangle = \int \psi^*(t) I_y \psi(t) \, d\tau$

$d\tau$ = volume element in spin space

we must sum over all spins with different determinants $b_0$

$\langle I_y, \text{total} (t) \rangle = N \int \rho(b_0) \psi(0) \psi^*(b_0, t) I_y \psi(b_0, t) \, d\tau$

it can be shown using properties of $\exp$ operators

$\int \psi^*(b_0, t) I_y \psi(b_0, t) \, d\tau =$

$= \int \psi^*(b_0) X^{-1} \chi^* \chi I_y t^{-1} (t, b_0) T^{-1} (t-t_0, b_0) X^{-1} \chi^* \chi I_y T(t, b_0) X \chi^* \chi X^{-1} \chi^* \chi \psi(0) \, d\tau$

we use $X^{-1} \chi = \chi X^{-1} = 1$

we do following transformation

$X^{-1} \chi^* \chi I_y T^{-1} (+ - t) X (\pi) =$

$= \underbrace{X^{-1} \chi^* \chi X^* \chi X^{-1} \chi^* \chi \chi^* \chi I_y X (\pi)}_{1}$

$= \underbrace{X^{-1} \chi^* \chi X^* \chi (\pi) I_y X (\pi)}_{3}$

$= \underbrace{(\pi) I_y X (\pi)}_{3}$
First deal with term 2

\[ x^{-1} \left( \frac{1}{\pi} \right) \, I_y \, x \left( \frac{1}{\pi} \right) = -I_y \]

**Term 2**

\[ x^{-1} \left( \frac{1}{\pi} \right) T \left( t - \tau \right) x \left( \frac{1}{\pi} \right) = x^{-1} \left( \frac{1}{\pi} \right) e^{i \beta_0 \left( t - \tau \right) I_2} X \left( \frac{1}{\pi} \right) \]

This term has \( I_2 \) exponent.

Use theorem: \( R^{-1} \left( e^{i \theta} \right) R = e^{i (R - \theta) G} \)

Therefore

\[ x^{-1} \left( \frac{1}{\pi} \right) \exp \left( i \beta_0 \left( t - \tau \right) I_2 \right) x \left( \frac{1}{\pi} \right) = \exp \left( -i \beta_0 \left( t - \tau \right) I_2 \right) = \quad \]

we therefore get

\[ \langle I_y \text{ total} \left( \frac{1}{\pi} \right) = N \int \rho \left( \beta_0 \right) \psi \left( \theta_0 \right) x \left( \frac{1}{\pi} \right) T^{-1} \left( t - \tau, \beta_0 \right) T \left( t - \tau, \beta_0 \right) \psi \left( \theta_0 \right) d^2 \ell \]

Special case, \( t - \tau = \tau \), i.e. \( t = 2 \tau \) (time of echoes)

At this time

\[ T^{-1} \left( t - \tau, \beta_0 \right) T \left( t, \beta_0 \right) = 1 \]

\[ \langle I_y \text{ total} \left( t = 2 \tau \right) = -N \int \rho \left( \beta_0 \right) \psi \left( \theta_0 \right) x \left( \frac{1}{\pi} \right) I_y \left( \frac{\tau}{\pi} \right) \psi \left( \theta_0 \right) d^2 \ell \]

\[ \beta_0 \text{ dislocated from integers over } d \ell \]

\[ \Rightarrow \text{ integrate over } d \beta_0 \]
\[
\psi_{\text{total}}(t - 2t) = -N\psi(t) \times \psi(t) = \psi(t) \psi(t)
\]

Identical to the state after \( \frac{t}{2} \) pulse.

\[
\langle I_y \text{ total}(t = 2t) \rangle = -N \langle I_x 10^- \rangle
\]

0 - time before \( t = 0 \)

N.B. noise \( \Rightarrow \) important advocate

Refocusing field inhomogeneity

Sample tube

NMR spectrometer

Transmitter coils

Amplifier

RF source + amplifier

Sweep coils
The theory of relaxation

Simple example - system of spins in fluctuating field.

\[ B_{L}(t) = B_{L}^{0} f(t) \]

\[ \langle f \rangle = 0 \quad \langle (f(t))^{2} \rangle = 1 \]

\[ B_{L}^{0} \] is RMS amplitude of field.

Hamiltonian \( H(t) = -\hbar \text{I} \times B_{L}^{0} f(t) \)

Perturbation theory shows that it induces transitions at rate

\[ W_{1} = \hbar^{2} \left( \delta^{2} + \text{I} \times B_{L}^{0} \right)^{2} Y(\omega_{0}) \]

\[ = \hbar^{2} \left[ B_{L}^{0} \right]^{2} \left( \text{I} \times B_{L}^{0} \right)^{2} Y(\omega_{0}) = \]

\[ = \frac{1}{4} \left[ B_{L}^{0} \right]^{2} Y(\omega_{0}) \]

\( Y(\omega_{0}) \) - power available from fluctuations at the relevant transition frequency.

\( \rightarrow \) "spectral density" (related to \( f(t) \))

By will contribute equal term

\( B_{y} \) will not cause transitions.

\[ \Rightarrow W_{1} = \frac{1}{2} \hbar^{2} \left[ B_{L}^{0} \right]^{2} Y(\omega_{0}) \]
However, each transition alters the population difference by 2:

\[ T_1^{-1} = 2 \omega_2 = 2 \sqrt{N_0 x_2} T_e \, \gamma(\omega_0) \]

\( \gamma(\omega) \) can be expressed in terms of correlation function:

\[ \gamma(\omega) = \frac{1}{2} f(\omega) + f(-\omega) \]

usually \( \gamma(\omega) = \exp[-T_c \omega] \)

\( T_c \) - correlation time

\( \gamma(\omega) \) corresponds to \( \tilde{Y}(\omega) \)

(time domain vs. frequency domain - two functions are related by Fourier transformation)

\[ \tilde{Y}(\omega) = \int \gamma(\omega) \exp(-i\omega t) \, dt \]

\[ \gamma(\omega) = \frac{1}{2 \pi} \int \tilde{Y}(\omega) \exp(i\omega t) \, dt \]

\[ \rightarrow \text{substituting } (\omega) \quad \tilde{Y} = \frac{2T_c}{1 + \omega T_c^2} \]

For \( T_2 \) time we will obtain:

\[ T_2 = \delta^2 \left[ N_0 x_2 \right]^2 \frac{2T_c}{1 + \omega_0 T_c^2} \]

\( T_c \) is often related to random rotation:

\( \sim 10 \, \text{ps} \) for small molecules

\( \sim 10 \, \text{ns} \) for proteins
\( W_{tc} \sim 1 \)

\((W_{tc})^2 \ll 1 - "extreme\:\:narrowing\:\:conditions" \)

\[ T_1^{-1} \approx 2 \gamma^2 \left[ B_x^0 \right]^2 \tau_c \]

For small molecules (\( \omega_p = \tau_c \)) this holds \((\omega_0 \approx 100 \, \text{MHz})\).

The T1 time increases as \( \tau_c \) increases, i.e., mobility decreases (for example by lowering T).

When \( W_{tc} \) is reached, a new regime

\[ \left[ T_1 \right]^{-1} = \frac{k^2}{\omega_0} \left[ B_x^0 \right]^2 \quad (\text{macromolecules}) \]

\[ \log T_1 \]

\[ \log W_{tc} = 1 \]

\( T_1 = f(\omega_0) \Rightarrow \text{higher} \: B_0 \: \text{field leads to increase of} \: T_1 \)
Relaxation mechanisms for spin 1/2 nuclei
- dipole-dipole interaction with other nuclei
- interactions with electrons (radicals)

Studies of relaxation
Spin locking

\[
\left( \frac{\pi}{2} \right)_x \quad \text{-(long pulse)}
\]

\[
\text{if } B_z > B_L, T_1^* \text{ relaxation}
\]

\[
T_2^* \text{ relaxation measured by spin locking}
\]
Higher order echoes

\[ \frac{\tau}{2} - \frac{\tau}{2} = \frac{\tau}{2} - \frac{\tau}{2} = \frac{\tau}{2} - \frac{\tau}{2} = \frac{\tau}{2} - \frac{\tau}{2} \]

Filter out noise at all frequencies except \( \nu_0 = \frac{1}{2\tau} \)

\[ \Delta V (\text{width}) = \frac{2\nu_0}{N} \]

Robust for pulse errors.
variation of rotations \((x, y)\)-
phase cycling \( \rightarrow \text{relaxation} \)

The intensity of NMR signal:

\[ N_{+} - N_{-} = \Delta N_0 = N \frac{\Delta E}{2\hbar} \]

Magnetisation

\[ M_0 = \frac{1}{N} N \chi \frac{\Delta E}{k_B T} = \frac{1}{N} N (g \tau) B_0 / k_B T \]

\( (\text{Curie equation}) \)

Study state NMR experiment
Spin system absorbs energy from RF source at rate \( \kappa \), which depends on factor

1) Probability \( P(\text{per unit time and spin}) \)
   of a transition being induced

2) Population difference between states

Detailed treatment shows that

\[ P \sim (g \tau B_0)^2 g(\nu) \]
\( g(v) \) - signal shape factor

rate of absorption of RF radiation

\[ R = P \cdot \Delta U \cdot \Delta n_0 = \frac{v^4 B_0^2 N B_1^2 g(v)}{T} \]

However NMR spectrometers do not detect \( R \) directly, but rather the rate of induced magnetisation change in the direction of receiver

\[ S = \frac{\Delta M}{\Delta t} \text{ This turns to be } R/B_1 \]

\[ \Rightarrow S = \frac{v^4 B_0^2 N B_1^2 g(v)}{T} \]

c) \( S \sim N \), large samples

d) \( S \sim j^4 \), high sensitivity for \( ^1H \), low for \( ^15 \text{N} \) (0.3 kHz/g)

e) \( S \sim B_0^2 \Rightarrow \) work at high fields is desirable

Electronic shielding

Diamagnetism: motion of electrons induced by \( B_0 \).

\[ \mathbf{B}_0 \]

\[ \omega_i = \left( \frac{e}{2me} \right) B_0 \]

associated magnetic moment

(Note that the circulation is right-handed and negative charge)
\[ \mu_i = -\left( \frac{e^2}{4m_e} \right) r^2 B_0 \sin^2 \theta \]

- \( F \) - vector connecting e and nucleus
- \( \theta \) - angle between \( F \) and \( B_0 \)

Effective field \( \vec{B} = B_0 \left( 1 - \frac{\delta}{\omega} \right) \)

Small fraction, \( \delta \) parts per million (ppm)

Nuclear frequency \( \nu_i = \frac{1}{2\pi} B_0 \left( 1 - \frac{\delta}{\omega} \right) \)

Reference sample \( TMS \) (tetramethylsilane, \( \text{CH}_3 \text{(CH}_3 \text{)}_4 \)

\[ \delta = 10^6 \left( \nu_{\text{sample}} - \nu_{\text{TMS}} \right) \]

\( \delta \) constant \( B_0 \)

Examples

- Benzene \( \delta_H = 7.37 \)
  \( \delta_C = 128.5 \)
- Water \( \delta_H = 4.76 \)

**Spin-spin coupling**

- More than 1 nucleus \( \Rightarrow \) complex, multiple structure
- \( I_1, I_2 \) resonance of spin \( I \) splits into \( 2I_1 + 1 \) lines, equal intensity
- \( I_2 \) splits into \( 2I_1 + 1 \) lines

3 nuclei \( (A, M, X) \)
Description of shapes

Wave functions

\[ \psi_{m_z = \pm \frac{1}{2}, J} \text{ for } m_z = \pm \frac{1}{2}, J \text{ to } m_z = -\frac{1}{2} \]

Basic product functions according to total component of angular momentum

\[ m_T = \sum m_f \]

\[ m_f = -\frac{3}{2}, \frac{1}{2} \quad \beta p \beta \\
-\frac{1}{2} \quad \beta d \beta, \beta p \beta, \alpha p \beta \\
+\frac{1}{2} \quad \beta d \beta, \alpha d \beta, \alpha p \beta \\
+\frac{3}{2} \quad \alpha d \beta \]

Selection rule for NMR transitions

\[ \Delta m_T = \pm 1, \Delta m_f (K \neq 0) = 0 \]

Energy spectrum

\[ h \omega = - \sum Y_l m_f + \sum Y_{l' k} m_{l'} m_{k} \]

where

\[ Y_l = (\frac{\delta_i}{2n}) B_0 \left( 1 - \delta_i \right) \]

Second term = coupling

Suggestion to avoid double counting
Example: two spin system

\[ \hbar \mathbf{H} = -V_A m_A - V_X m_X + J_{AX} m_A m_X \]

Labelling nuclei \( A \) and \( X \)

Allowed transitions

- \( A \) transitions: \( \Delta m_A = \pm 1 \) \( \Delta m_X = 0 \)
- \( X \) transitions: \( \Delta m_A = 0 \) \( \Delta m_X = \pm 1 \)

Spectra involving magnetic equivalence

AX2 spin system

Relative intensities

- AXp
- \( p \)
- 1: 1/1
- 2: 1/2/1
- 3: 1/3/3/1
- 4: 1/4/6/4/1