Spin-Echo

The spin-echo pulse sequence:  $90^\circ x' - \tau - 180^\circ x' - \tau(\text{echo})$

- Spins echoes are widely used as part of larger pulse sequence to refocus the effects of:
  - 1) unwanted chemical shift precession
  - 2) magnet inhomogeneity
  - 3) heteronuclear J coupling

- The spin-echo does not refocus homonuclear J coupling

- The spin-echo pulse sequence can be used to measure the relaxation parameter $T_2$; it does not refocus the effect of $T_2$ relaxation

Typical delays and pulse lengths:

- $RD = \text{Recycling delay} \sim 1 \text{ sec.}$
- $\tau_a = \text{Spin-echo delay} \sim 50 \text{ ms}$  
- $AT = \text{Acquisition time} \sim 0.2 \text{ sec.}$
- $90^\circ \sim 10 \mu s$
- $180^\circ \sim 20 \mu s$
The spin-echo in vector diagram

A) Let's consider the non-coupled single spin case. Example: $^1$H in CHCl$_3$ (carbon not $^{13}$C-labeled) with $\nu_H = \nu_{rf} + 100$ Hz

$^1$H: $90^\circ x - \tau_a - 180^\circ y - \tau_a$ (echo)

Detected Signal after FT:

![Chemical shift graph]
$^1$H: 90°x - $\tau_a$ - 180°x - $\tau_a$ (echo)

Detected Signal after FT:

Note that the intensity is plotted relatively to the positive signal on the previous page. In practice, this signal would be drawn as a positive signal by adjusting the zero order phase correction by 180°.
Conclusions:

1) Chemical shift evolution (precession) is refocused by the spin-echo

2) Similarly the spin-echo refocuses magnet inhomogeneity ($\Delta B_o$):
   - The magnetic field $B_o$ is not perfectly homogeneous throughout the volume of the sample, therefore not all nuclei experience the same magnetic field.
   - The small differences in magnetic field ($\Delta B_o$) across the sample volume causes nuclei that are chemically equivalent to precess at different rate.
B) Let's consider a simple case of heteronuclear coupling, i.e. a two-spin AX system with $A = ^1H$ and $X = ^{13}C$

Example: $^{13}C$ in CHCl$_3$ (carbon is $^{13}C$-labeled) with $\nu_{rf} = \nu_H$

$^1J_{AX} = 209$ Hz

$^{13}C$: $90^\circ x - \tau_a - 180^\circ x - \tau_a$ (echo) - Acquisition time

Detected Signal after FT:

209 Hz

Chemical shift (Hz)
More on the two-spin AX system with \( A=^1H \) and \( X=^{13}C \) (e.g. \(^{13}CHCl_3\)):

1) Energy level diagram

2) Essentially equal population differences for the \(^{13}C\) transitions for \(^{13}CH_\alpha Cl_3\) and \(^{13}CH_\beta Cl_3\)

Population differences:
- \( \alpha\alpha \) to \( \alpha\beta \) transition: \((N + \Delta H + \Delta C) - (N + \Delta H) = \Delta C\)
- \( \beta\alpha \) to \( \beta\beta \) transition: \((N + \Delta C) - (N) = \Delta C\)
- \( \alpha\alpha \) to \( \beta\alpha \) transition: \((N + \Delta H + \Delta C) - (N + \Delta C) = \Delta H\)
- \( \alpha\beta \) to \( \beta\beta \) transition: \((N + \Delta H) - (N) = \Delta H\)

3) Two different Larmor frequencies as a result of C-H coupling

\[
\nu (^{13}CH_\alpha Cl_3) = \nu_c - 1/2^*JCH \\
\nu (^{13}CH_\beta Cl_3) = \nu_c + 1/2^*JCH
\]

with \( JCH = 209 \text{ Hz} \) and \( \delta = 77.7 \text{ ppm} \) (center of the doublet)

4) In the first delay \( \tau \) of the spin-echo experiment, a phase angle \( \Theta \) is created between these two vectors

\[
\Theta = 2\pi JCH^* \tau
\]

Examples: If \( \tau = 0 \) than \( \Theta = 0 \), if \( \tau = 1/(4J) \) than \( \Theta = \pi/2 = 90^\circ \), etc.
Pulse sequence of the J-modulated spin-echo experiment:

Vector diagrams for the J-modulated spin-echo experiment:
Chemical-shift refocusing in the J-modulated spin-echo experiment:

Example: J-modulated spin-echo experiment for three different CH groups (I, II, and III) whose Larmor frequencies $\nu$ and C-H coupling constants $J$ increase in the order: $\nu_1 < \nu_2 < \nu_3$ and $J_1 < J_3 < J_2$

A) Pulse sequence

B) Vector diagrams and spectra for $90^\circ x' - \tau$ (BB)-acquisition

C) Vector diagrams and spectra for the full experiment
Attached proton test (APT) with the J-modulated experiment:

Let's consider various types of carbons and their precession frequencies:

- quaternary carbon (Cq): \( \nu_c \)
- CH group: \( \nu_c \pm 1/2*J_{CH} \)
- CH2 group: \( \nu_c, \nu_c \pm J_{CH} \)
- CH3 group: \( \nu_c \pm 1/2*J_{CH}, \nu_c \pm 3/2*J_{CH} \)

Pulse sequence and vector diagram:

![Pulse sequence and vector diagram](image_url)

*Figure 8-11.*

J-modulated spin-echo experiment for \(^{13}\)C nuclei with 0, 1, 2 or 3 directly attached protons. The pulse sequence is the same as in Figures 8-9 and 8-10, but here only one special case, \( r = [J(C,H)]^{-1} \), is considered. The vector diagrams a to e show the starting situation and the evolution of the magnetization vectors for quaternary, CH, CH2 and CH3 carbon nuclei. Acquisition of the second half of the echo followed by Fourier transformation gives the signals shown (schematically) on the right.
The effect of pulse field gradients on transverse magnetization:

In high-resolution NMR, the magnetic field $B_0$ should be as homogenous as possible because small field variations $\Delta B_0$ causes undesirable peak broadening (e.g. bad shimming).

However, introducing field inhomogeneity by linear pulse field gradients can be very useful for removing remaining magnetization in the x-y plane:

- between FIDs
- within a pulse sequence for phase cycling
- within a pulse sequence for water suppression
- within a pulse sequence to measure diffusion constants

A) Nuclei within different volume slices experience different effective field strengths:

\[ v_i = \frac{\gamma}{2\pi} (B_0 + g_i) \]

![Diagram showing effect of pulse field gradients on nuclei in different volume slices.](image)

**Figure 8-5.** Effect of applying a linear field gradient along the direction of the field $B_0$ (the z-direction). The quantities $g_n$ are the contributions of the field gradient to the field $B_0$. $v_1$ to $v_5$ are the resonance frequencies for the five arbitrarily chosen slices 1 to 5. In the center of the observed sample (slice 3 in the example shown) $g_n$ is zero, while it is positive above the center and negative below it.

B) A single gradient dephases magnetization in the x-y plane:
C) Phase coherence is regained by a second gradient applied in opposite direction

**Figure 8-6.**
The behavior of the transverse magnetization under the influence of a field gradient. As in Figure 8-5, five slices are shown, the gradient field contribution $g_3$ in slice 3 at the center of the observed volume being zero. A 90° pulse establishes the transverse magnetization vectors $M_1$ to $M_5$. Owing to the field gradient contributions $g_1$ to $g_3$, these precess with different frequencies $\gamma$ to $\gamma_5$. $M_3$ remains along the $y'$-direction in the rotating frame, since both the magnetization and the frame have the same frequency $\gamma_0$, while the other transverse magnetization vectors rotate in the directions indicated by the small arrows (diagrams b and d). As a result of the fanning-out process the macroscopic transverse magnetization $M_{y'}$ for the sample as a whole (diagram d) eventually falls to zero.

**Figure 8-7.**
The gradient echo experiment. A: Pulse sequence. After the 90° pulse the field gradient $G$ is applied for a time $\tau$. A gradient of the same magnitude and duration is then applied in the opposite direction ($-G$).

B: The vector diagrams show the behavior of the transverse magnetization for slice $n$. During the first interval $\tau$, under the influence of the gradient $G$, it precesses through an angle $\Theta$ in the rotating frame (diagram b). During the second interval $\tau$ the process is reversed by the gradient $-G$, so that the transverse magnetization vector is again along the $y'$-direction, producing an echo.

The pulsed field gradient spin-echo experiment:
As for the standard spin-echo experiment, it refocuses
- chemical shift
- Heteronuclear J coupling
- magnetic field inhomogeneity

For simplification, let's consider a single $^1$H on resonance, in the absence of heteronuclear J coupling, and no magnetic field inhomogeneity:

Axial diffusion means that the value of $g_n$, and therefore the precession frequency $\nu_n$ changes between the first and the second pulse field gradients. In this case, refocusing is incomplete and the intensity of the signal is reduced.

This effect can be used to measure diffusion coefficients and for water suppression in macromolecular NMR.