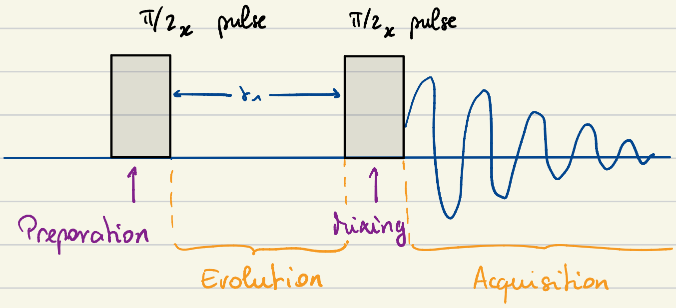
Great work!

BA5 JigSaw E 11/11/24

[redacted]

Ethylene groupe

Exercice 1:



Preparation: it's a $\frac{\pi}{2}$ pulse that brings the magnetization along the negative y-axis

Evolution: it is a period of time t_1
magnetization is transferred between J-coupled spins. They starts to process around the the z-axis
↳ precession motion depends on the chemical shift and the scalar coupling

Mixing: Second $\frac{\pi}{2}$ pulse ⇒ brings the magnetization to negative z-axis
↳ The magnitude depends on the precession frequency

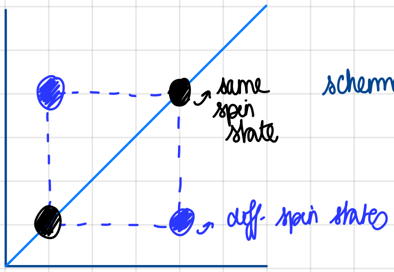
Acquisition: Decrease in transverse magnetization leads to an FID signal that is recorded

Results: A 2D fourier transformation is performed on the signal, giving us a 2D frequency spectrum.

Analysis: The method allows us to identify the coupled nuclear spins:
- diagonal points corresponds to spins coupled with themselves
- off-diagonal points corresponds to spins coupled with neighboring spins.

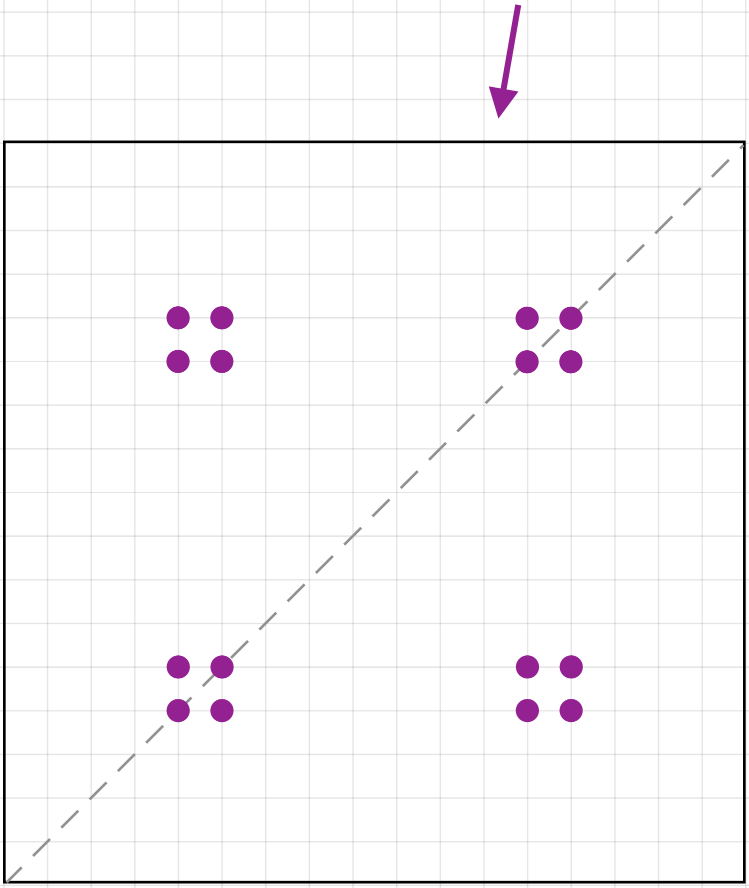
Great explanation! Also note that the evolution time (t1) is incremented for each step in the indirect dimension (the pulse sequence is repeated several times with different t1 values) continue

2. [Keeler Section 8.3] Consider a hypothetical molecule containing two protons, A and X, which are coupled together. Draw the schematic COSY spectrum.

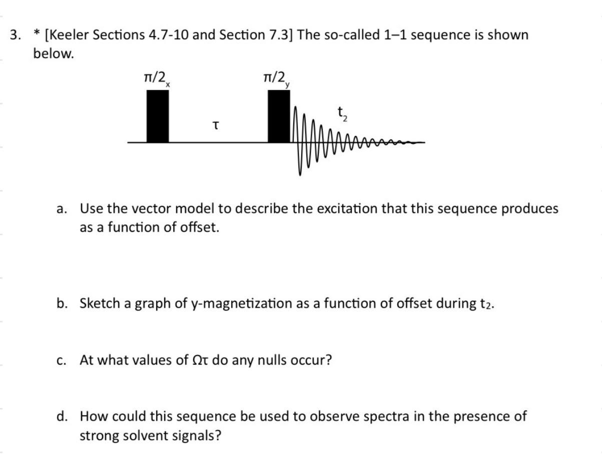


schematic COSY spectrum for 2 spin systems

Good start! Because of the J-coupling, we would see each of these 4 peaks further split in half in both dimensions, giving 16 peaks total.



question 3 :



3. * [Keeler Sections 4.7-10 and Section 7.3] The so-called 1–1 sequence is shown below.

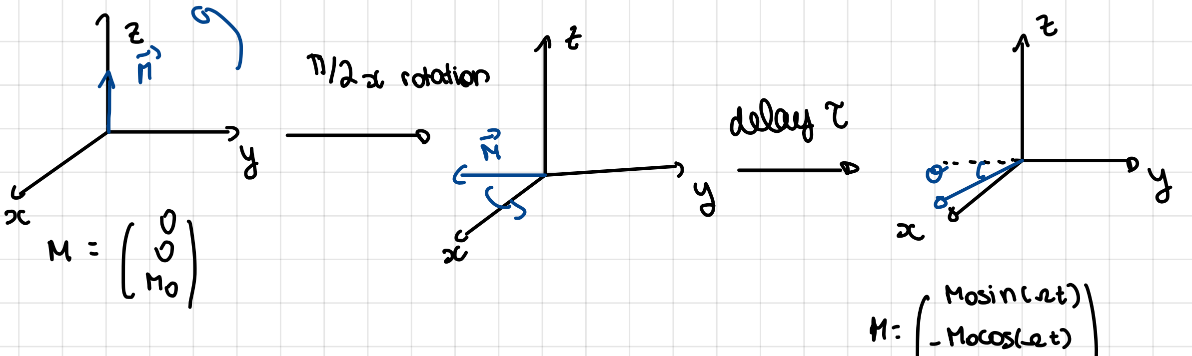
a. Use the vector model to describe the excitation that this sequence produces as a function of offset.

b. Sketch a graph of y-magnetization as a function of offset during t₂.

c. At what values of Ωτ do any nulls occur?

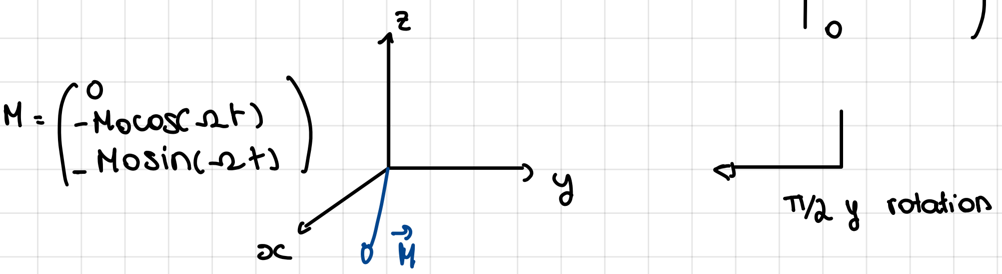
d. How could this sequence be used to observe spectra in the presence of strong solvent signals?

3) a)



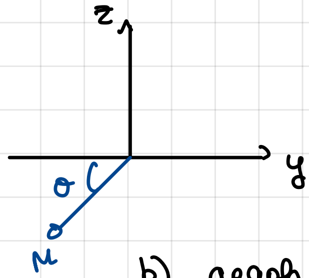
$M = \begin{pmatrix} 0 \\ 0 \\ M_0 \end{pmatrix}$

$M = \begin{pmatrix} M_0 \sin(\Omega t) \\ -M_0 \cos(\Omega t) \\ 0 \end{pmatrix}$

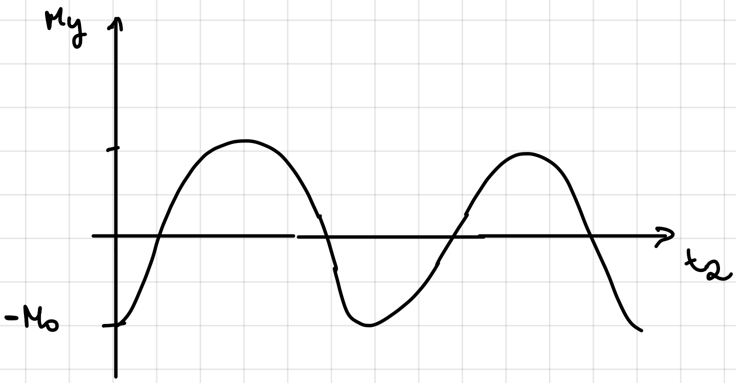


$M = \begin{pmatrix} 0 \\ -M_0 \cos(\Omega t) \\ -M_0 \sin(\Omega t) \end{pmatrix}$

in y-z plane:



b) graph of y- magnetization during t_2



$M_y = -M_0 \cos(\Omega t)$

x-axis should be a function of offset (Ωτ), see next set of solutions

c) $M_y = -M_0 \cos(\Omega t)$

Nulls occur at $\cos(\Omega t) = 0 \Rightarrow \Omega t = \frac{\pi}{2} + k\pi$ with $k \in \mathbb{N}$

d) In presence of strong solvent signals, to observe spectra, the magnetization vector for the solvent needs to be align with the z-axis at the end of the pulse sequence.

This means that the y-component of the magnetization must be equal to zero.

$\Rightarrow \theta = \Omega_{\text{solvent}}\, \tau = \frac{\pi}{2} + k\pi$ with $k \in \mathbb{N}$

$$\boxed{\tau = \frac{\pi/2 + k\pi}{\Omega_{\text{solvent}}}}$$

NMR Jigsaw 3E

October 2024

1 Exercise 1

The COSY sequence follows the following structure

- two $\frac{\pi}{2}$ pulses separated by a delay
- a second period, during which the measurement is recorded

An example of the pulse sequence can found in exercise 3, where the first pulse is around the x axis and the second around the y axis:

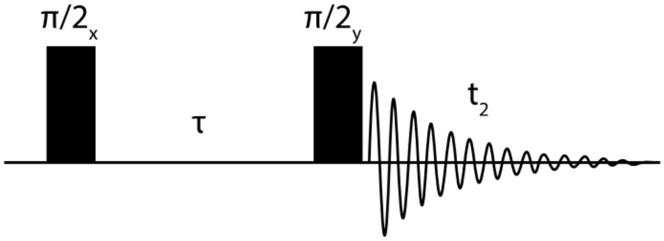


Figure 1: COSY Pulse Sequence

The preparation period starts at the first $\frac{\pi}{2}$ pulse, which starts up the magnetization. The mixing period starts after the second $\frac{\pi}{2}$ pulse. In the 2D spectrum, we can find 2 observables

The mixing period *is* the second pulse. The detection period (t2) starts after the second pulse.

- around the diagonal axis, we see the resonances of each of the nuclei found in the compound
- cross-peaks reveal couplings between nuclei pairs. We can also see which protons are J-coupled this way.

2 Exercise 2

Each of these four peaks should be further split into four peaks — see example on above solutions

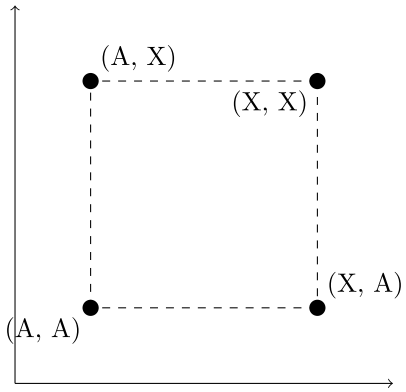


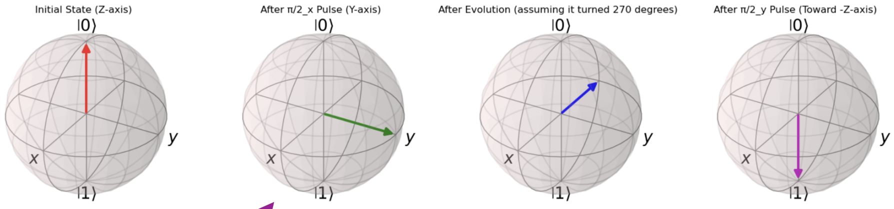
Figure 2: COSY spectrum for two coupled protons, A and X.

We find the above mentioned couplings of (A,A) and (X,X), resp. resonances of A and X, on the diagonal and cross peaks (A, X) and (X, A)

3 Exercise 3

3.1

We use the vector model seen in class to graph the following (QuTIP was used)

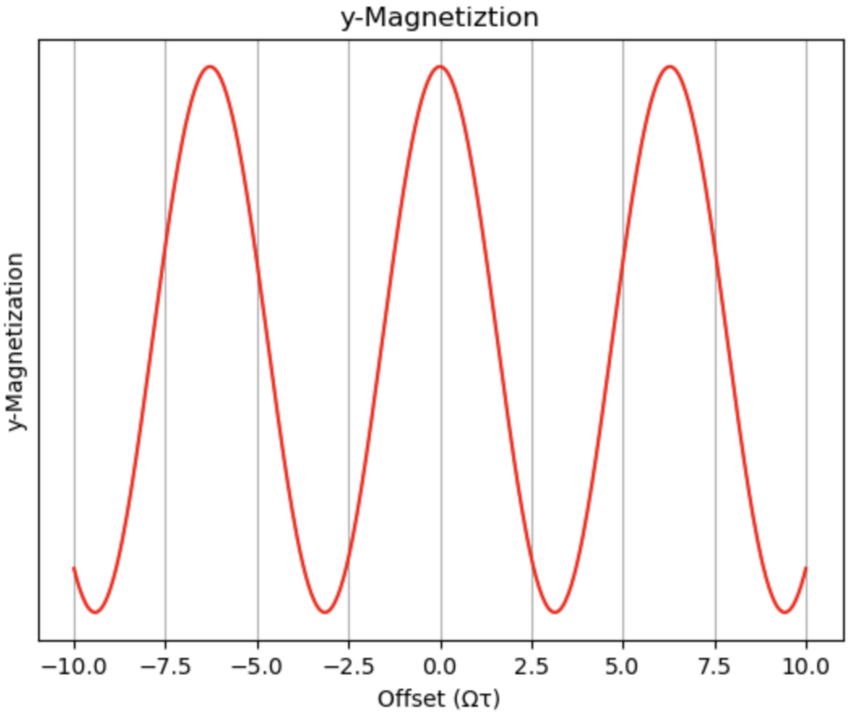


~~Figure 3: COSY Pulse Sequence~~

π/2_x pulse pushes +z-magnetization to the -y-axis

Note that, if the magnetization isn't nicely aligned along the x or y-axes, a π/2_y pulse would rotate transverse magnetization in to yz plane

3.2



It respects a cosine distribution.

3.3

Given the waveform observed in 3b, $\Omega\tau = (n + \frac{1}{2})\pi$ for $n > 1$ will result in nulls.

3.4

We often want to remove/suppress signals from solvents when doing spectroscopy in order to focus on the signals of interest. 3c tells us that we can adjust the offset to null out signals at certain frequencies. Therefore, if we know the resonance frequency of the solvent signal, we can selectively adjust τ so that the magnetization contributed by the solvent signals is nulled out, thus allowing us to focus on the frequencies we're actually interested in.