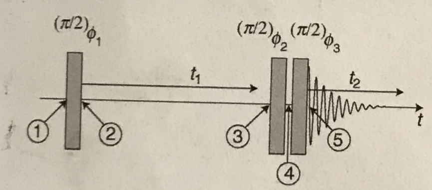
Solution to Exercise 16.2 from Spin Dynamics (2nd, Malcolm H. Levitt)

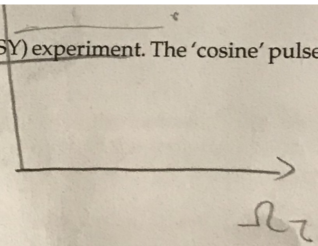
Zheng Zuo

April 2nd, 2020

The Problem 16.2 in book Spin Dynamics (p.451-452)

16.2 This exercise investigates the *double-quantum-filtered* COSY (2QF-COSY) experiment. The 'cosine' pulse sequence is as follows:





The phase table is as follows:

Cycle counter m	ϕ_1	ϕ_2	ϕ_3	ϕ_{rec}
0	$3\pi/2$	0	$\pi/2$	0
1	$3\pi/2$	0	π	$3\pi/2$
2	$3\pi/2$	0	$3\pi/2$	π
3	$3\pi/2$	0	0	$\pi/2$

Assume a homonuclear AX spin system. The short delay between the last two $\pi/2$ pulses may be ignored.

(i) Take the first step in the phase cycle procedure (m = 0). For simplicity, start with an initial spin density operator $\hat{\rho}_{①} \sim \hat{I}_{1z}$. What is the spin density operator at time point ④?

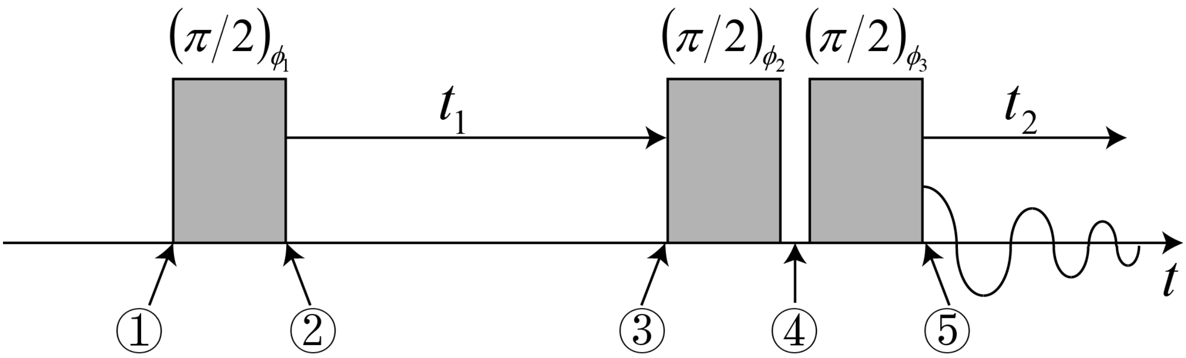
(ii) ~~Convert the x- and z-operators at time point ④~~ into shift operators. Which coherence orders are excited at this point?

(iii) The phase cycle has the effect of suppressing all signal components that do not pass through (±2)-quantum coherences at time point ④. Select the operators that have order ±2 and apply the final $\pi/2$ pulse. What is the spin density operator at time point ⑤? To bring out the meaning of the final expression, replace all products of trigonometric functions by single trigonometric functions.

(iv) Repeat the calculation for the 'sine' component of the States procedure, in which the first pulse has phase π instead of phase $3\pi/2$. Use the same initial density operator.

(v) Repeat the calculations using the full form of the initial spin density operator, $\hat{\rho}_{①} \sim \hat{I}_{1z} + \hat{I}_{2z}$. Sketch the form of the two-dimensional spectrum and remark on the shapes of the diagonal peaks and cross-peaks. What are the favourable properties of the double-quantum-filtered COSY spectrum? Are there any disadvantages of double-quantum-filtered COSY compared with ordinary COSY?

Pulse sequence for 2QF-COSY (double-quantum-filtered COSY)



Cycle counter m	ϕ_1	ϕ_2	ϕ_3	ϕ_{rec}
0	$3\pi/2$	0	$\pi/2$	0
1	$3\pi/2$	0	π	$3\pi/2$
2	$3\pi/2$	0	$3\pi/2$	π
3	$3\pi/2$	0	0	$\pi/2$

Calculation of density product operator(s)

(i, ii, iii) The product operators in cosine version pulse sequence (cycle m=0)

$$
\begin{aligned}
\hat{\rho}_1 &= \hat{I}_{1z} \\
&\downarrow_{(\pi/2)_{-y}} \\
\hat{\rho}_2 &= -\hat{I}_{1x} \\
&\downarrow_{U2} \\
&-\hat{I}_{1x} \\
&\downarrow_{U1} \\
&-\hat{I}_{1x}\cos(\Omega_1 t_1) - \hat{I}_{1y}\sin(\Omega_1 t_1) \\
&\downarrow_{J_{12}} \\
\hat{\rho}_3 &= -\cos(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{1x} + \sin(\pi J t_1) 2\hat{I}_{1y}\hat{I}_{2z}] \\
&+ \sin(\Omega_1 t_1)[-\cos(\pi J t_1)\hat{I}_{1y} + \sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2z}] \\
&\downarrow_{(\pi/2)_x} \\
\hat{\rho}_4 &= -\cos(\Omega t_1)[\cos(\pi J t_1)\hat{I}_{1x} - \sin(\pi J t_1) 2\hat{I}_{1z}\hat{I}_{2y}] \\
&+ \sin(\Omega_1 t_1)[-\cos(\pi J t_1)\hat{I}_{1z} - \underbrace{\sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2y}}_{\textit{Double coherence}}] \\
\hat{\rho}_{4,\pm 2} &= -\sin(\Omega_1 t_1)\sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2y} \\
&\downarrow_{(\pi/2)_y} \\
\hat{\rho}_{5,\cos} &= \sin(\Omega_1 t_1)\sin(\pi J t_1) 2\hat{I}_{1z}\hat{I}_{2y} \\
&= [\cos(\Omega_1 t_1 - \pi J t_1) - \cos(\Omega_1 t_1 + \pi J t_1)]\hat{I}_{1z}\hat{I}_{2y}
\end{aligned}
$$

(iv) The product operators for the sine version pulse sequences

$$
\begin{aligned}
\hat{\rho}_1 &= \hat{I}_{1z} \\
&\downarrow_{(\pi/2)_{-x}} \\
\hat{\rho}_2 &= -\hat{I}_{1y} \\
&\downarrow_{U2} \\
&-\hat{I}_{1y} \\
&\downarrow_{U1} \\
&-\hat{I}_{1y}\cos(\Omega_1 t_1) - \hat{I}_{1x}\sin(\Omega_1 t_1) \\
&\downarrow_{J_{12}} \\
\hat{\rho}_3 &= \cos(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{1y} - \sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2z}] \\
&- \sin(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{1x} + \sin(\pi J t_1) 2\hat{I}_{1y}\hat{I}_{2z}] \\
&\downarrow_{(\pi/2)_x} \\
\hat{\rho}_4 &= \cos(\Omega t_1)[\cos(\pi J t_1)\hat{I}_{1z} + \underbrace{\sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2y}}_{\textit{Double coherence}}] \\
&- \sin(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{1x} - \sin(\pi J t_1) 2\hat{I}_{1z}\hat{I}_{2y}] \\
\hat{\rho}_{4,\pm 2} &= \cos(\Omega_1 t_1)\sin(\pi J t_1) 2\hat{I}_{1x}\hat{I}_{2y} \\
&\downarrow_{(\pi/2)_y} \\
\hat{\rho}_{5,\sin} &= -\cos(\Omega_1 t_1)\sin(\pi J t_1) 2\hat{I}_{1z}\hat{I}_{2y} \\
&= [\sin(\Omega_1 t_1 - \pi J t_1) - \sin(\Omega_1 t_1 + \pi J t_1)]\hat{I}_{1z}\hat{I}_{2y}
\end{aligned}
$$

Construction of phase-sensitive 2D peaks according to States Method

$$
\begin{aligned}
\hat{\rho}_{States} &= \hat{\rho}_{\cos} + i\,\hat{\rho}_{\sin} \\
&= [\exp^{i(\Omega_1-\pi J)t_1} - \exp^{i(\Omega_1+\pi J)t_1}]\hat{I}_{1z}\hat{I}_{2y} \\
&= [\exp^{i(\Omega_1-\pi J)t_1} - \exp^{i(\Omega_1+\pi J)t_1}][\underbrace{\frac{i}{4}\hat{I}_1^{\alpha}\hat{I}_2^{-}}_{\hat{\rho}_{\alpha-}} - \underbrace{\frac{i}{4}\hat{I}_1^{\beta}\hat{I}_2^{-}}_{\hat{\rho}_{\beta-}} + \dots]
\end{aligned}
$$

Density operator $\hat{I}_{1z}\hat{I}_{2y}$ indicates an antiphase absorption peak, centered around frequency Ω_2^0 in the Ω_2 dimension. Therefore, equation signifies the doubly antiphase cross-peak, jus like in the normal COSY scenario.

(v) Using initial density operator $\hat{I}_{2z}$

For the full form of initial spin density operator $\hat{\rho}_1 \sim \hat{I}_{1z} + \hat{I}_{2z}$, if we starts with $\hat{I}_{2z}$,

$$
\begin{aligned}
\hat{\rho}_1 &= \hat{I}_{2z} \\
&\downarrow_{(\pi/2)_{-y}} \\
\hat{\rho}_2 &= -\hat{I}_{2x} \\
&\downarrow_{U2} \\
&- \hat{I}_{2x}\cos(\Omega_1 t_1) - \hat{I}_{2y}\sin(\Omega_1 t_1) \\
&\downarrow_{U1} \\
&- \hat{I}_{2x}\cos(\Omega_1 t_1) - \hat{I}_{2y}\sin(\Omega_1 t_1) \\
&\downarrow_{J_{12}} \\
\hat{\rho}_3 &= -\cos(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{2x} + \sin(\pi J t_1)2\hat{I}_{1z}\hat{I}_{2y}] \\
&+ \sin(\Omega_1 t_1)[-\cos(\pi J t_1)\hat{I}_{2y} + \sin(\pi J t_1)2\hat{I}_{1z}\hat{I}_{2x}] \\
&\downarrow_{(\pi/2)_x} \\
\hat{\rho}_4 &= -\cos(\Omega t_1)[\cos(\pi J t_1)\hat{I}_{2x} - \sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2z}] \\
&+ \sin(\Omega_1 t_1)[-\cos(\pi J t_1)\hat{I}_{2z} - \underbrace{\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2x}}_{Double\ coherence}] \\
\hat{\rho}_{4,\pm 2} &= -\sin(\Omega_1 t_1)\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2x} \\
&\downarrow_{(\pi/2)_y} \\
\hat{\rho}_{5,\cos} &= \sin(\Omega_1 t_1)\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2z} \\
&= [\cos(\Omega_1 t_1 - \pi J t_1) - \cos(\Omega_1 t_1 + \pi J t_1)]\hat{I}_{1y}\hat{I}_{2z}
\end{aligned}
$$

Similarly, for the sine version of pulse sequence,

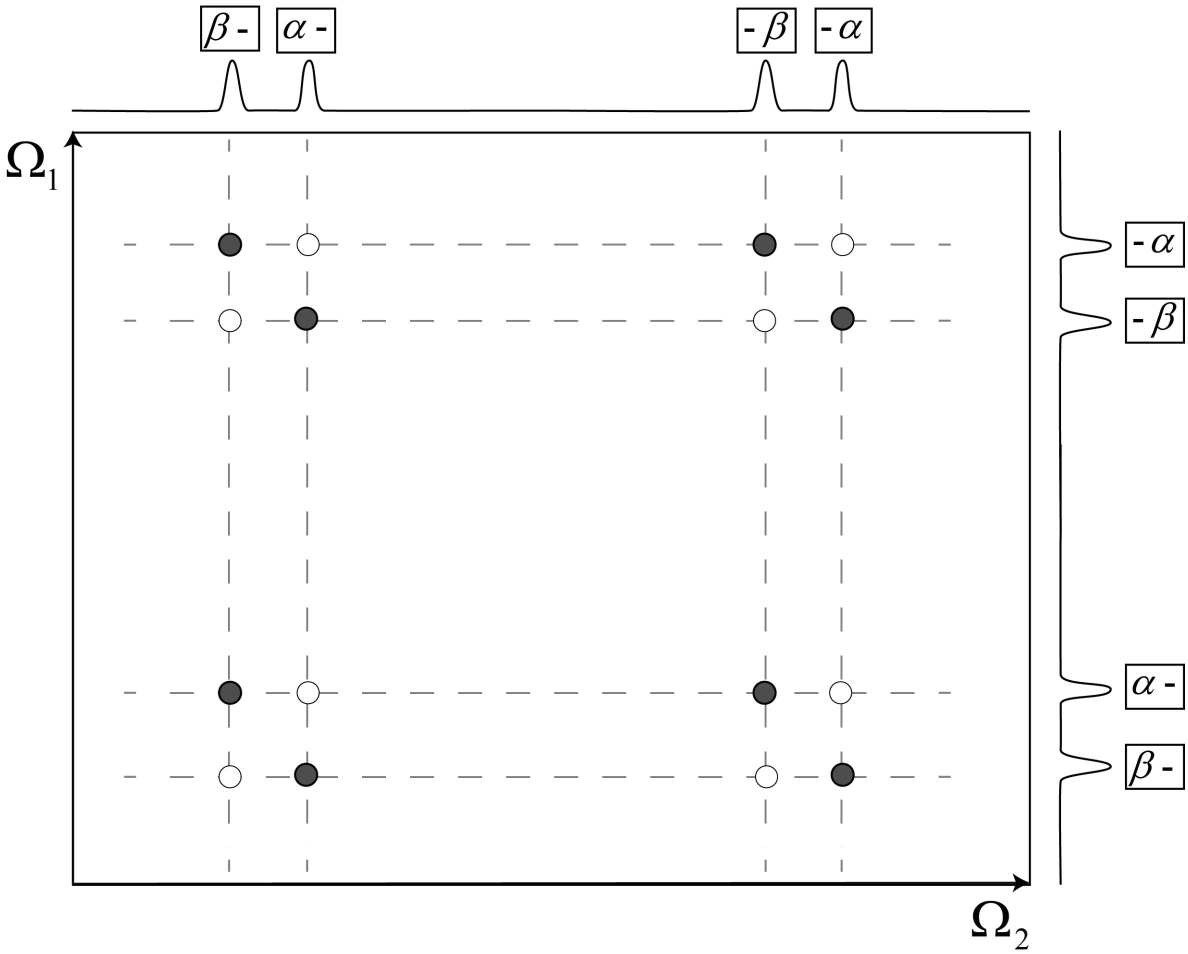
$$
\begin{aligned}
\hat{\rho}_1 &= \hat{I}_{2z} \\
&\downarrow_{(\pi/2)_{-x}} \\
\hat{\rho}_2 &= -\hat{I}_{2y} \\
&\downarrow_{U2} \\
&- \hat{I}_{2y}\cos(\Omega_1 t_1) - \hat{I}_{2x}\sin(\Omega_1 t_1) \\
&\downarrow_{U1} \\
&- \hat{I}_{2y}\cos(\Omega_1 t_1) - \hat{I}_{2x}\sin(\Omega_1 t_1) \\
&\downarrow_{J_{12}} \\
\hat{\rho}_3 &= \cos(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{2y} - \sin(\pi J t_1)2\hat{I}_{1z}\hat{I}_{2x}] \\
&- \sin(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{2x} + \sin(\pi J t_1)2\hat{I}_{1z}\hat{I}_{2y}] \\
&\downarrow_{(\pi/2)_x} \\
\hat{\rho}_4 &= \cos(\Omega t_1)[\cos(\pi J t_1)\hat{I}_{2z} + \underbrace{\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2x}]}_{\textit{Double coherence}} \\
&- \sin(\Omega_1 t_1)[\cos(\pi J t_1)\hat{I}_{2x} - \sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2z}] \\
\hat{\rho}_{4,\pm 2} &= \cos(\Omega_1 t_1)\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2x} \\
&\downarrow_{(\pi/2)_y} \\
\hat{\rho}_{5,\sin} &= -\cos(\Omega_1 t_1)\sin(\pi J t_1)2\hat{I}_{1y}\hat{I}_{2z} \\
&= [\sin(\Omega_1 t_1 - \pi J t_1) - \sin(\Omega_1 t_1 + \pi J t_1)]\hat{I}_{1y}\hat{I}_{2z}
\end{aligned}
$$

Overall,

$$
\begin{aligned}
\hat{\rho}_{States} &= \hat{\rho}_{\cos} + i\,\hat{\rho}_{\sin} \\
&= [\exp^{i(\Omega_1 - \pi J)t_1} - \exp^{i(\Omega_1 + \pi J)t_1}]\hat{I}_{1y}\hat{I}_{2z} \\
&= [\exp^{i(\Omega_1 - \pi J)t_1} - \exp^{i(\Omega_1 + \pi J)t_1}][\underbrace{\frac{i}{4}\hat{I}_1^-\hat{I}_2^\alpha}_{\hat{\rho}_{-\alpha}} - \underbrace{\frac{i}{4}\hat{I}_1^-\hat{I}_2^\beta}_{\hat{\rho}_{-\beta}} + \ldots]
\end{aligned}
$$

Density operator $\hat{I}_{1y}\hat{I}_{2z}$ indicates an antiphase absorption peak, centered around frequency Ω_1^0 in the Ω_2 dimension. Therefore, equation signifies the doubly antiphase diagonal peaks, which is different from the normal COSY scenario.

The form of DQF-COSY peaks



β -
α -
- β
- α
Ω1
- α
- β
α -
β -
Ω2