

Solution Problem Set 1: PCIV Recapitulation

Problem 1: General Repetition Questions

1. Going into an interaction (rotating) frame with $\omega_{\text{rf}} = \omega_0$ removes the Zeeman interaction, which is big but rather uninteresting since it is the same for all nuclei with the same gyromagnetic ratio. The high-field approximation states that when the magnetic field is high enough¹, we can neglect all terms which become time-dependent when switching to the interaction frame, because they rotate fast enough such that they get averaged out. This leads to the second advantage: performing the interaction frame transformation, one loses the time dependence of the radio-frequency field, which significantly simplifies the theoretical treatment.

The Hamiltonian of a homonuclear J-coupled 2 spin system in the lab frame is given by the Zeeman term \hat{H}_Z , the chemical shift Hamiltonian \hat{H}_{CS} and the J-coupling:

$$\begin{aligned}\hat{H} &= \hat{H}_Z + \hat{H}_{\text{CS}} + \hat{H}_J \\ &= \omega_0(\hat{I}_{1z} + \hat{I}_{2z}) - \omega_0(\sigma_{\text{iso}}^{(1)} \cdot \hat{I}_{1z} + \sigma_{\text{iso}}^{(2)} \cdot \hat{I}_{2z}) + 2\pi J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2)\end{aligned}\quad (1)$$

To obtain the rotating frame operator, we perform the rotation: $\hat{H}' = \hat{R}(t)\hat{H}\hat{R}(t)^{-1}$ with the rotation operator $\hat{R}(t) = e^{i\hat{H}_0 t} = e^{i\sum_l \omega_{\text{rf}} \hat{I}_{lz} t}$. During this transformation, the \hat{I}_{lz} operators do not get rotated, since they point along the z axis, which corresponds to the rotation axis. The scalar product $(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2)$ remains invariant under this transformation, since scalars are independent of the coordinate system (see AMR lecture notes chapter 3). We are therefore left with:

$$\hat{H}' = \Omega_1 \hat{I}_{1z} + \Omega_2 \hat{I}_{2z} + 2\pi J(\vec{\hat{I}}_1 \cdot \vec{\hat{I}}_2), \quad (2)$$

where Ω_1, Ω_2 are the rotating frame frequencies ($\Omega_i = (1 - \sigma_{\text{iso}}^{(i)})\omega_0 - \omega_{\text{rf}}$), which can be interpreted as the chemical shifts of the nuclei (in angular frequencies).

In the heteronuclear case, under the high-field approximation, we lose the $\hat{I}_x \hat{S}_x, \hat{I}_y \hat{S}_y$ terms, since the x and y components of both spins start rotating with different frequencies and can be neglected under the secular approximation. We are therefore left with:

$$\hat{H}' = 2\pi J \hat{I}_z \hat{S}_z. \quad (3)$$

2. The dipolar interaction can be rewritten in the laboratory frame using the dipolar alphabet as:

$$\hat{H}_D = \frac{\mu_0}{4\pi} \frac{\gamma_1 \gamma_2 \hbar}{r_{12}^3} [\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F}]. \quad (4)$$

¹Later in the lecture we will understand what “high enough” means.

Transforming into the rotating frame \hat{I}_{iz} terms, remain time-independent (secular). \hat{I}^+, \hat{I}^- become time dependent because they are constructed from \hat{I}_x, \hat{I}_y operators. Under the high-field approximation we can neglect such terms in the rotating frame. Inspecting the definitions of $\hat{A}, \hat{B}, \hat{C}, \dots$ one finds that \hat{A} contains only \hat{I}_{iz} operators, hence it is secular and can't be neglected. $\hat{C}, \hat{D}, \hat{E}, \hat{F}$ all contain either raising or lowering operators. Under the transformation they rotate either with ω_{rf} or $2\omega_{rf}$ and can be ignored. The term \hat{B} is special since it consists of so-called flip-flop operators ($\hat{I}_i^+ \hat{I}_j^-$). In the homonuclear case the raising and the lowering operator rotate with opposite frequency, the time dependence therefore cancels out and \hat{B} stays secular in the rotating frame. In the heteronuclear case, the rotation frequencies of the two nuclei are different, hence \hat{B} keeps a time-dependence in the rotating frame and will be omitted under the high-field approximation.

3. A realistic sample of magnetically equivalent spins-1/2 like protons in a tube of water contains about $\sim 10^{22}$ spins. The protons can be in a $|\alpha\rangle$ or a $|\beta\rangle$ state but the majority is in a superposition state. When describing macroscopic quantities like the magnetization it is possible to treat the wavefunction of each spin individually and then add the results, but due to the high number of spins in the ensemble this is rather impractical. The density operator describes the quantum state of the entire ensemble, without the need of referring to the individual spin states.
4. The Liouville-von-Neumann equation describes the time evolution of the density operator $\hat{\rho}(t)$ of the system:

$$\frac{d\hat{\rho}(t)}{dt} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)]. \quad (5)$$

An example for a time-dependent Hamiltonian is the rf Hamiltonian in the lab frame ($\hat{H}_{rf} = \sum_i \gamma_i \hat{I}_{ix} \vec{B}_1(t)$, with $B_1(t) = B_1(\cos[(\omega_{rf}t + \varphi(t))])$, linear polarization in x direction).

Problem 2: Dipolar Interaction in Water Molecules

1. The spin part of the dipolar Hamiltonian in matrix representation is given by

$$\begin{aligned} & \left(2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2} \left(\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+ \right) \right) = \\ & 2 \cdot \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \otimes \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} - \frac{1}{2} \left(\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \right) \\ & = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & -1 & 0 \\ 0 & -1 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (6) \end{aligned}$$

2. This last matrix is already block-diagonal and we can directly extract the eigenvalues $\lambda_1 = 1/2$, $\lambda_4 = 1/2$. Now we only have to diagonalize the central block:

$$\begin{vmatrix} -\frac{1}{2} - \lambda & -\frac{1}{2} \\ -\frac{1}{2} & -\frac{1}{2} - \lambda \end{vmatrix} \stackrel{!}{=} 0 \quad (7)$$

$$\left(-\frac{1}{2} - \lambda\right)^2 - \frac{1}{4} = 0 \quad (8)$$

$$\lambda^2 + \lambda + \frac{1}{4} - \frac{1}{4} = 0 \quad (9)$$

$$\lambda(\lambda + 1) = 0 \quad (10)$$

$$\lambda = 0, -1 \quad (11)$$

The four eigenvalues are therefore $\lambda_1 = 1/2$, $\lambda_2 = -1$, $\lambda_3 = 0$, $\lambda_4 = 1/2$.

As stated in hint 2 of the exercise sheet the eigenvectors corresponding to these eigenvalues are: $|\alpha\alpha\rangle$, $\frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle)$, $\frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle)$, $|\beta\beta\rangle$. The 0-quantum state $\frac{1}{2}(|\alpha\beta\rangle - |\beta\alpha\rangle)$ cannot take part in any transitions as mentioned by hint 1. Therefore, only transitions between the eigenvalues $1/2$ and -1 are allowed. We will observe two lines with frequency:

$$\omega_{12} = 1/2 + 1 = +3/2, \quad \omega_{24} = -1 - 1/2 = -3/2$$

The absolute splitting of the two lines is then given by: $|\Delta\omega| = |\omega_{24} - \omega_{12}| = 3$. At this point we have to remember that up to now, we have only treated and diagonalized the spin part of the Hamiltonian. The spatial part of the Hamiltonian comes in as an additional multiplicative factor (as can be seen from the formula for the dipolar Hamiltonian given in the exercise sheet). We can see that the actual splitting is proportional to the dipolar coupling constant, or even more precisely $|\Delta\omega| = 3d\frac{1-3\cos^2\theta}{2}$ (note that the orientation dependence also influences the size of the line splitting, this will be discussed in the next part).

The dipolar coupling parameter d is given (in Hz) by

$$d = -\frac{1}{2\pi} \frac{\mu_0 \gamma_H^2 \hbar}{4\pi r^3} \quad (12)$$

with the given geometry and the proton-proton distance of 1.51 \AA this gives a coupling strength of 34.7 kHz .

Rmk: The eigenvectors can be calculated by solving the systems of equations:

$$\frac{1}{2} \begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = -1 \begin{pmatrix} u \\ v \end{pmatrix} \quad (13)$$

$$-\frac{1}{2}(u + v) = -u \quad (14)$$

$$\frac{1}{2}u - \frac{1}{2}v = 0 \Rightarrow u = v \quad (15)$$

$$\text{EV}_2 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{2}(|\alpha\beta\rangle + |\beta\alpha\rangle). \quad (16)$$

$$\frac{1}{2} \begin{pmatrix} -1 & -1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = 0 \begin{pmatrix} u \\ v \end{pmatrix} \quad (17)$$

$$-u - v = 0 \Rightarrow u = -v \quad (18)$$

$$\text{EV}_3 = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix} = \frac{1}{\sqrt{2}} |\alpha\beta\rangle - |\beta\alpha\rangle \quad (19)$$

3. Following the instructions on the exercise sheet, we gather the eigenvectors in a transformation matrix \hat{U} :

$$\hat{U} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (20)$$

The inverse of this matrix is in this case simple: $\hat{U}^{-1} = \hat{U}$. The transformation product $\hat{U}\hat{F}_x\hat{U}^{-1}$ can be written out as:

$$\hat{F}'_x = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \quad (21)$$

By stepwise matrix multiplication we obtain:

$$\hat{F}'_x = \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} \cdot \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & 0 & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 \end{pmatrix}. \quad (22)$$

Since the off-diagonal elements of the detection operator in the eigenbasis of the Hamiltonian can be related to the spectral intensities (for more details see chapter 5.6 of the PCIV script), we see what we wanted to prove. The column, encoding possible transitions from and to the zero quantum state $\frac{1}{2}(|\alpha\beta\rangle - |\beta\alpha\rangle)$ has all elements equal to 0, hence no transition is allowed. From this matrix representation we also see that we have 2 spectral lines with equal intensities. More precisely the intensities are given by 1/2 and are calculated by computing the product between the detection and the $\hat{\sigma}_0$ (starting operator) in the eigenbasis of the Hamiltonian.

The allowed transitions could also have been extracted from a symmetry argument in this case. Since we assume that both ^1H spins have the same chemical shift, the Hamiltonian has a permutation symmetry under permutation of the two spins. This implies that the eigenfunctions can only be symmetric or anti-symmetric under an exchange of the two spins². Allowed transitions can only occur between states with the same symmetry under permutation of the two spins ($|\alpha\rangle \rightarrow |\beta\rangle$), which corresponds indeed to the transitions between states $1 \rightarrow 2$, $2 \rightarrow 4$. Note that the transition $1 \rightarrow 4$ is not allowed because the total magnetic quantum number M of the state does not change by ± 1 .

²Being more formal: they can only transform according to the irreducible representation (symmetric and anti-symmetric) of the permutation group.

4. The dipolar Hamiltonian is given by

$$\hat{H} = \frac{\mu_0 \hbar \gamma_1 \gamma_2}{4\pi r_{1,2}^3} \frac{1 - 3 \cos^2 \Theta}{2} \left(2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2} \left(\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+ \right) \right) \quad (23)$$

The orientation dependence is described by the term $(1 - 3 \cos^2 \Theta)/2$, which reaches its extrema, -1 and 0.5, for $\Theta = 0 + m\pi$ and $\Theta = \pi/2 + m\pi$ ($m \in \mathbb{Z}$), respectively. The splittings are given by the differences between the Eigenvalues of \hat{H} and therefore only the absolute value of $(1 - 3 \cos^2 \Theta)/2$ is relevant. The maximum splitting is observed for $\Theta = 0 + m\pi$, i.e. for the ^1H - ^1H vector parallel to the external magnetic field \vec{B}_0 . The dipolar spectrum of H_2O with $\vec{r}_{\text{HH}} \parallel \vec{B}_0$, i.e. with the maximal dipolar splitting, contains two resonance lines separated by (in Hz)

$$\Delta\nu = 2 \cdot \frac{3}{2} \left| -\frac{\mu_0 \gamma_H^2 \hbar}{4\pi r^3} \right| = 104 \text{ kHz} \quad (24)$$

5. The powder spectrum is the sum of the spectra of all different orientations scaled with the respective probability to find that orientation. For a purely dipolar Hamiltonian between two spins, this results in a characteristic Pake pattern. The top of Figure 1 shows such a Pake pattern in the homonuclear case. Note that the splitting between the two extrema (feet) corresponds exactly to $3d$, as we have just calculated. Indeed the parallel orientation with respect to the magnetic field is the most unlikely, while the perpendicular orientation is the most likely. This is the reason why we can identify the two maxima in the Pake pattern with the perpendicular orientation. In a simple analogy, the likelihood of an orientation can be understood by considering the earth with the z -axis going through the two poles. There are only two poles ($\theta = 0$ orientation), while most points on the sphere can be found at an opening angle of $\theta = \pi/2$ (on the equator). In summary the probability of an orientation is proportional to $\sin \theta$ (where θ denotes the opening angle with respect to the external magnetic field).

6. In the heteronuclear case the $\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+$ term can be neglected in the high-field approximation (for more details see answer to Problem 1.2). The Hamiltonian of the heteronuclear dipolar coupling is already diagonal and the allowed transitions are between the Eigenvalues $1/2$ and $-1/2$. The maximum separation between the two resonance lines is (in Hz)

$$\Delta\nu = 2 \cdot \left| -\frac{\mu_0 \gamma_H \gamma_T \hbar}{4\pi r^3} \right| = 74 \text{ kHz} \quad (25)$$

A comparison of the homonuclear and the heteronuclear powder spectrum can be seen in Figure 1.

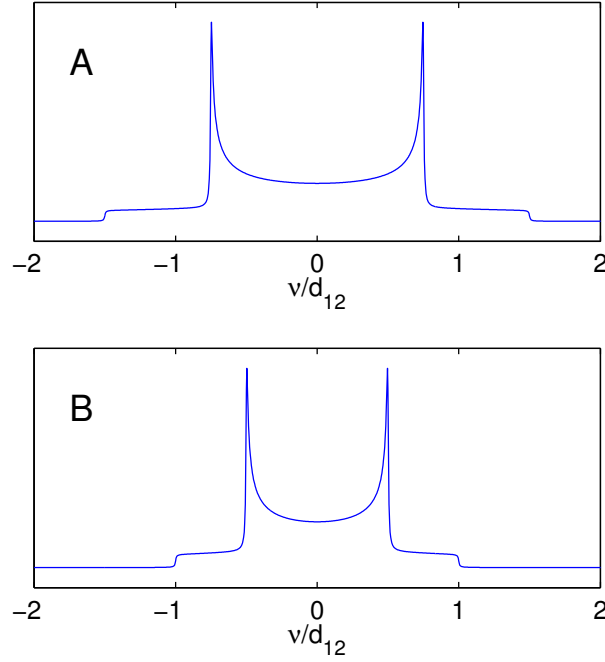


Figure 1: Powder spectrum of a homonuclear (A) and heteronuclear (B) dipolar-coupled spin pair (Pake doublet). The frequency scale is in units of the dipolar coupling constant $d_{I_1 I_2}$.

7. The molecular tumbling averages out the anisotropy (orientation dependence) of the NMR interactions in the liquid state. Since the dipolar coupling is a purely anisotropic interaction with no isotropic part, the pake pattern collapses to a single line positioned at the water chemical shift (ignoring J-coupling effects).

Problem 3: In-Phase/Anti-Phase

Note: For this problem it is important to recall the calculations in product operator formalism. For example:

$$\hat{I}_z \xrightarrow{\hat{I}_y(\beta)} \begin{cases} \cos(\beta) \hat{I}_z = \cos(\beta) \hat{I}_z \\ i \sin(\beta) [\hat{I}_z, \hat{I}_y] = \sin(\beta) \hat{I}_x \end{cases} \quad (26)$$

1. The evolution of the state during detection is controlled by the Hamiltonian $\hat{\mathcal{H}} = \Omega_1 \hat{I}_{1z} + \Omega_2 \hat{I}_{2z} + 2\pi J_{12} \hat{I}_{1z} \hat{I}_{2z}$. To calculate the resulting spectrum we have to work out the effect of the three terms in turn. (Which we can do if all terms of the Hamiltonian commute!)

$$\hat{I}_{1x} \xrightarrow{\hat{I}_{2z}(\Omega_2 t)} \hat{I}_{1x} \xrightarrow{\hat{I}_{1z}(\Omega_1 t)} \begin{cases} \cos(\Omega_1 t) \hat{I}_{1x} \xrightarrow{2\hat{I}_{1z} \hat{I}_{2z}(\pi J_{12} t)} \begin{cases} \cos(\pi J_{12} t) \cos(\Omega_1 t) \hat{I}_{1x} \\ \sin(\pi J_{12} t) \cos(\Omega_1 t) 2\hat{I}_{1y} \hat{I}_{2z} \end{cases} \\ \sin(\Omega_1 t) \hat{I}_{1y} \xrightarrow{2\hat{I}_{1z} \hat{I}_{2z}(\pi J_{12} t)} \begin{cases} \cos(\pi J_{12} t) \sin(\Omega_1 t) \hat{I}_{1y} \\ -\sin(\pi J_{12} t) \sin(\Omega_1 t) 2\hat{I}_{1x} \hat{I}_{2z} \end{cases} \end{cases}$$

First we rotate around z due to the offset Ω_2 of spin 2, which does not affect our spin 1 term. Then we can rotate around z due to the offset Ω_1 of spin 1 and finally we consider the effect of the J-coupling $2\pi J_{12}\hat{I}_{1z}\hat{I}_{2z}$. As mentioned in the problem set, our detection operator is $\hat{I}^+ = \hat{I}_{1x} + i\hat{I}_{1y}$, hence only resulting terms containing \hat{I}_{1x} and \hat{I}_{1y} are of interest. Since the signal in NMR is represented as a complex number where real and imaginary parts correspond to magnetisation in x - and y -direction, we can construct the signal as follows:

$$\begin{aligned}
S(t) &= \cos(\pi J_{12}t) \cos(\Omega_1 t) + i \cos(\pi J_{12}t) \sin(\Omega_1 t) \\
&= \cos(\pi J_{12}t) e^{i\Omega_1 t} \\
&= \frac{1}{2} [e^{i\pi J_{12}t} + e^{-i\pi J_{12}t}] e^{i\Omega_1 t} \\
&= \frac{1}{2} [e^{i(\Omega_1 + \pi J_{12})t} + e^{i(\Omega_1 - \pi J_{12})t}]
\end{aligned} \tag{27}$$

where first the identity $\cos(x) + i \sin(x) = e^{ix}$ was employed, while in the next step the definition $\cos(x) = \frac{1}{2}[e^{ix} + e^{-ix}]$ was used.

Therefore, we obtain a signal containing two oscillations with frequencies $\Omega_1 + \pi J_{12}$ and $\Omega_1 - \pi J_{12}$ respectively. Fourier transform of this signal yields a spectrum consisting of two equally intense peaks at $\Omega_1 + \pi J_{12}$ and $\Omega_1 - \pi J_{12}$ is obtained.

2. To arrive at the signal for the anti-phase term $2\hat{I}_{1x}\hat{I}_{2z}$ we first notice that any spin 1 operator does not change the \hat{I}_{2z} part. Furthermore, the second rotation due to the chemical shift of spin 2 is around z and thus does not change \hat{I}_{2z} . Therefore, we can move on to evolution under J-coupling as second step. This gives:

$$2\hat{I}_{1x}\hat{I}_{2z} \xrightarrow{\hat{I}_{2z}(\Omega_2 t)} 2\hat{I}_{1x}\hat{I}_{2z} \xrightarrow{\hat{I}_{1z}(\Omega_1 t)} \begin{cases} \cos(\Omega_1 t) 2\hat{I}_{1x}\hat{I}_{2z} \xrightarrow{2\hat{I}_{1z}\hat{I}_{2z}(\pi J_{12}t)} \begin{cases} \cos(\pi J_{12}t) \cos(\Omega_1 t) 2\hat{I}_{1x}\hat{I}_{2z} \\ \sin(\pi J_{12}t) \cos(\Omega_1 t) \hat{I}_{1y} \end{cases} \\ \sin(\Omega_1 t) 2\hat{I}_{1y}\hat{I}_{2z} \xrightarrow{2\hat{I}_{1z}\hat{I}_{2z}(\pi J_{12}t)} \begin{cases} \cos(\pi J_{12}t) \sin(\Omega_1 t) 2\hat{I}_{1y}\hat{I}_{2z} \\ -\sin(\pi J_{12}t) \sin(\Omega_1 t) \hat{I}_{1x} \end{cases} \end{cases}$$

Applying the same detection operator as in the previous part and using similar mathematical manipulations we arrive at the signal

$$\begin{aligned}
S(t) &= -\sin(\pi J_{12}t) \sin(\Omega_1 t) + i \sin(\pi J_{12}t) \cos(\Omega_1 t) \\
&= i \sin(\pi J_{12}t) e^{i\Omega_1 t} \\
&= i \frac{1}{2i} [e^{i\pi J_{12}t} - e^{-i\pi J_{12}t}] e^{i\Omega_1 t} \\
&= \frac{1}{2} [e^{i(\Omega_1 + \pi J_{12})t} - e^{i(\Omega_1 - \pi J_{12})t}],
\end{aligned} \tag{28}$$

which is the same as in the previous part with the second term being negative.

3. The resulting spectra from both terms show a doublet at the same frequencies but in the \hat{I}_{1x} case both peaks will be positive, while for the $2\hat{I}_{1x}\hat{I}_{2z}$ case one will be positive while the other is negative. This is precisely the reason we call them 'In-' and 'Anti-Phase'.

4. The limitation of the product operator formalism can be seen by considering a spin system where not all terms of the Hamiltonian commute.

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2, \quad \left[\hat{\mathcal{H}}_1, \hat{\mathcal{H}}_2 \right] \neq 0$$

In this case we cannot split the propagator into a simple product

$$\hat{U} = e^{-i\hat{\mathcal{H}}t} = e^{-i(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)t} \neq e^{-i\hat{\mathcal{H}}_1t} e^{-i\hat{\mathcal{H}}_2t} = \hat{U}_1 \hat{U}_2 \implies \hat{U} \neq \hat{U}_1 \hat{U}_2$$

Hence, we cannot evolve the density operator with the different terms of the Hamiltonian separately

$$\begin{aligned} e^{-i\hat{\mathcal{H}}t} \hat{\rho} e^{i\hat{\mathcal{H}}t} &= e^{-i(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)t} \hat{\rho} e^{i(\hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2)t} \neq e^{-i\hat{\mathcal{H}}_1t} e^{-i\hat{\mathcal{H}}_2t} \hat{\rho} e^{i\hat{\mathcal{H}}_2t} e^{i\hat{\mathcal{H}}_1t} \\ \implies \hat{U} \hat{\rho} \hat{U}^\dagger &\neq \hat{U}_1 \hat{U}_2 \hat{\rho} \hat{U}_2^\dagger \hat{U}_1^\dagger \end{aligned}$$

As a result we can only use the product operator if all terms of the Hamiltonian commute with each other. A simple example where we cannot use the product operator formalism is the heteronuclear two-spin system with irradiation on the I -spin

$$\hat{\mathcal{H}} = \omega_1 \hat{I}_x + \omega_{IS} 2 \hat{I}_z \hat{S}_z$$

since $\left[\hat{I}_x, \hat{I}_z \right] = -i \hat{I}_y \neq 0$.