Exercise 1 – Some insight into CW decoupling

1- NMR Interactions in solids

Consider a two-spin system (S-I) under CW decoupling applied on the I channel. Write the corresponding Hamiltonian in the rotating frame (using Cartesian operators) including

- Isotropic chemical shift $\omega^{iso}_{S/I}$
- Chemical shift anisotropy $\omega^{ani}_{S/I}$
- Dipolar interaction $\omega^{dip}_{SI}$
- Indirect (J) interaction
- CW RF field strength $\omega_2$ along the x axis

Until specified otherwise, we assume that there is no sample spinning (i.e., $\omega_2 = 0$).

In the following the part of the Hamiltonian describing the interactions will be denoted $\mathcal{H}_0$ and the CW irradiation on the I-channel will be denoted $\mathcal{H}_1$.

2- Spins rotation under RF field

We want to calculate the effect of the CW RF irradiation on the internal Hamiltonian $\mathcal{H}_0$. For that we first need to rewrite the Hamiltonian into the “interaction frame” defined by the CW irradiation.

Give a reason for doing so?

Write down the transformation of the operators $I_x$, $I_y$ and $I_z$ in the frame rotating around the x axis at $\omega_2$. Calculate the full Hamiltonian in the (RF) interaction frame (noted $\mathcal{H}_0'$).

3- AHT for a 2-spin system

3.1 In the interaction frame defined above the Hamiltonian of the system $\mathcal{H}_0'$ is periodic of period $\tau_c = \frac{2\pi}{\omega_2}$. 

Show that we only need to know the short time evolution of the system over one cycle $\tau_c$, i.e. $U_0(\tau_c) = \tilde{T} \exp \left( -i \int_0^{\tau_c} dt' \mathcal{H}_0'(t') \right)$, to describe the state of the system at any integer multiple of the cycle time.

3.2 By definition, the effective Hamiltonian of the system over a cycle time $\tau_c$ can be written:

$$U_0(\tau_c) = \exp(-i\tilde{H} \tau_c)$$

And the average Hamiltonian over a cycle $\tau_c$ can be calculated using the Magnus expansion. Using the formulae below, derive an average Hamiltonian (to the second order) in the interaction frame over the cycle time $\tau_c$.

**Magnus Expansion:**

$$\tilde{H}^{(1)} = \frac{1}{\tau_c} \int_0^{\tau_c} \mathcal{H}_0'(t) dt$$

$$\tilde{H}^{(2)} = \frac{-i}{2\tau_c} \int_0^{\tau_c} dt_2 \int_0^{t_2} dt_1 [\mathcal{H}_0'(t_2), \mathcal{H}_0'(t_1)]$$

Discuss the effect of the CW irradiation.

4- **CW decoupling under MAS**

4.1 In the following, we now consider that the sample is spinning at the magic angle with a MAS frequency $\omega_R/2\pi$. The CSA and heteronuclear dipolar tensors will be written as periodic function of the MAS frequency $\omega_R$: $\omega_{\text{CSA}}^{\text{dip}} = \sum_{k=-2}^{2} \omega_{\text{CSA}}^{(k)} e^{-i k \omega_R t}$ and $\omega_{\text{HET}}^{\text{dip}} = \sum_{k=-2}^{2} \omega_{\text{HET}}^{(k)} e^{-i k \omega_R t}$.

What is the effective Hamiltonian obtained assuming perfect MAS averaging and no RF irradiation applied? What is the ideal Hamiltonian for a perfect heteronuclear decoupling?

4.2 The Hamiltonian in the interaction frame derived earlier ($\mathcal{H}_0'$) contains a second time-dependency through the rotation of the sample. The application of AHT requires that one can find a unique period (or frequency modulation). In order to simplify this 2-frequency dependent problem, we assume that $\omega_1$ and $\omega_R$ are commensurate, i.e. $\omega_1 = \frac{p}{q} \omega_R = \alpha \omega_R$ with $(p,q)$ integer numbers.

Calculate the effective Hamiltonian to the second order as a function of $\alpha$. 
Discuss the special cases where $\alpha = 1, 2$.

4.3 Rewrite the previous result in the limit of very strong CW irradiation ($\alpha \to \infty$). Comment the relative importance of the various terms and compare this result to the one obtained in the static case.

5- Why TPM works better? Ref. Bennett et al., JCP, 1995

5.1 Let us consider now a RF decoupling scheme called Two Pulse Phase Modulation (TPPM). In this case the RF field amplitude is constant equal to $\omega_1$ and the phase alternates between $\phi = \phi_0$ and $\phi = -\phi_0$ with a cycle time equal to $\tau_c$ (corresponding to a modulation frequency $\omega_c / 2\pi$):

Write the RF irradiation on the I-channel.

5.2 Such irradiation scheme can be decomposed into two components along the $x$- and $y$-axis. The $x$-component is typically much larger than the $y$-component and equivalent to a (constant) CW irradiation along the $x$-axis. The $y$-component is smaller in amplitude ($\varphi_0 \ll 1$) and oscillates between two values with a period $\tau_c$. In order to simplify the problem we will “truncate” the full TPPM irradiation with respect to its main component (i.e. $x$-axis). Show that the $y$-component of the TPPM sequence can produce a second averaging step if $\omega_c = \omega_1 \cos \varphi_0$. Write the corresponding effective field (to the lowest order in the Magnus expansion) in the interaction frame defined by the $x$-component.

5.3 Using the results from questions 1 and 3, discuss the effect of this second component on the residual heteronuclear terms.