Problem Set 3

Problem 1: Recoupling and Decoupling

In a previous problem set (Problem Set 4), you determined the Fourier series of the time-dependent Hamiltonian of a I-S heteronuclear two-spin system under sample rotation and continuous-wave irradiation of the protons (= I-spins). This Fourier series is given by

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^{2} \sum_{k=-1}^{1} \hat{\mathcal{H}}^{(n,k)} \cdot e^{in\omega_{\mathrm{r}}t} \cdot e^{ik\omega_{1\mathrm{I}}t}\,, \tag{1}$$

where ω_{r} corresponds to the sample rotation frequency and $\omega_{1\mathrm{I}}$ to the amplitude of the proton irradiation. The Fourier components $\hat{\mathcal{H}}^{(n,k)}$ are given by

$$\hat{\mathcal{H}}^{(n,0)} = \omega_{\mathrm{S}}^{(n)} \hat{S}_z \tag{2}$$

$$\hat{\mathcal{H}}^{(n,\pm 1)} = -\omega_{\mathrm{IS}}^{(n)} \hat{I}^{\pm} \hat{S}_z - \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^{\pm}\,. \tag{3}$$

In this exercise we will now analyze the possible resonance conditions.

1. Write down all possible resonance conditions $n_0\omega_{\mathrm{r}} + k_0\omega_{1\mathrm{I}} = 0$ that can be realized in the Hamiltonian of Eq. (1).

The first-order effective Hamiltonian is given by $\hat{\bar{\mathcal{H}}} = \sum_{n_0,k_0} \hat{\mathcal{H}}^{(n_0,k_0)}$, where the summation over n_0 and k_0 is restricted to the values that fulfill the resonance condition $n_0\omega_{\mathrm{r}} + k_0\omega_{1\mathrm{I}} = 0$.

2. Calculate the effective Hamiltonians for the resonance conditions identified in the previous question. Which interactions become time independent and, therefore, recoupled at the different conditions?

The non-resonant contributions ($n_0 = k_0 = 0$) are important under decoupling conditions where we try to avoid all resonance conditions. This can be achieved by making the rf field much bigger than the spinning frequency, i.e. $\omega_{1\mathrm{I}} \gg \omega_{\mathrm{r}}$.

3. Calculate the effective Hamiltonian outside the resonance conditions up to a second-order approximation.

Hint:
The non-resonant part of the effective Hamiltonian is given by

$$\hat{\bar{\mathcal{H}}} = \hat{\bar{\mathcal{H}}}^{(1)} + \hat{\bar{\mathcal{H}}}^{(2)} = \hat{\mathcal{H}}^{(0,0)} - \frac{1}{2}\sum_{\nu,\kappa} \frac{\left[\hat{\mathcal{H}}^{(-\nu,-\kappa)}, \hat{\mathcal{H}}^{(\nu,\kappa)}\right]}{\nu\omega_{\mathrm{r}} + \kappa\omega_{1\mathrm{I}}} \tag{4}$$