Solution Problem Set 3

Problem 1: Recoupling and Decoupling

1. In Problem Set 4 we have seen that the values for n and k are limited in range to $n = \pm 1$ and ± 2 and $k = \pm 1$. Therefore, there are only two possible first-order resonance conditions at $\omega_\mathrm{r} = \omega_\mathrm{1I}$ and $2\omega_\mathrm{r} = \omega_\mathrm{1I}$.

2. The effective Hamiltonian in first order can now be constructed from the resonance conditions and we obtain for $\omega_\mathrm{r} = \omega_\mathrm{1I}$

$$\begin{aligned}\hat{\bar{\mathcal{H}}} &= \hat{\mathcal{H}}^{(0,0)} + \hat{\mathcal{H}}^{(1,-1)} + \hat{\mathcal{H}}^{(-1,1)} \\ &= \omega_\mathrm{S}^{(0)}\hat{S}_z - \omega_\mathrm{IS}^{(1)}\hat{I}^-\hat{S}_z - \frac{1}{2}\omega_\mathrm{I}^{(1)}\hat{I}^- - \omega_\mathrm{IS}^{(-1)}\hat{I}^+\hat{S}_z - \frac{1}{2}\omega_\mathrm{I}^{(-1)}\hat{I}^+\,, \end{aligned} \tag{1}$$

where we used the Fourier components of the Hamiltonian that we given on the exercise sheet (see Problem Set 4 for their derivation)

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

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

For $2\omega_\mathrm{r} = \omega_\mathrm{1I}$ we obtain

$$\begin{aligned}\hat{\bar{\mathcal{H}}} &= \hat{\mathcal{H}}^{(0,0)} + \hat{\mathcal{H}}^{(2,-1)} + \hat{\mathcal{H}}^{(-2,1)} \\ &= \omega_\mathrm{S}^{(0)}\hat{S}_z - \omega_\mathrm{IS}^{(2)}\hat{I}^-\hat{S}_z - \frac{1}{2}\omega_\mathrm{I}^{(2)}\hat{I}^- - \omega_\mathrm{IS}^{(-2)}\hat{I}^+\hat{S}_z - \frac{1}{2}\omega_\mathrm{I}^{(-2)}\hat{I}^+ \end{aligned} \tag{4}$$

These are the Hamiltonians for the rotary-resonance conditions where the CSA and the heteronuclear dipolar coupling are recoupled simultaneously.

3. The non-resonant first-order effective Hamiltonian is given by

$$\hat{\bar{\mathcal{H}}}^{(1)} = \hat{\mathcal{H}}^{(0,0)} = \omega_\mathrm{S}^{(0)}\hat{S}_z\,, \tag{5}$$

which corresponds to the isotropic chemical shift of the S spin. The non-resonant second order term of the effective Hamiltonian is given by

$$\begin{aligned}\hat{\bar{\mathcal{H}}}^{(2)} &= -\frac{1}{2}\sum_{\nu,\kappa}\frac{\left[\hat{\mathcal{H}}^{(-\nu,-\kappa)}, \hat{\mathcal{H}}^{(\nu,\kappa)}\right]}{\nu\omega_\mathrm{r} + \kappa\omega_\mathrm{1I}} \\ &= -\frac{1}{2}\sum_{\nu,\kappa}\frac{\left[\omega_\mathrm{IS}^{(-\nu)}\hat{I}^{-\kappa}\hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(-\nu)}\hat{I}^{-\kappa}, \omega_\mathrm{IS}^{(\nu)}\hat{I}^{\kappa}\hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(\nu)}\hat{I}^{\kappa}\right]}{\nu\omega_\mathrm{r} + \kappa\omega_\mathrm{1I}}\,. \end{aligned} \tag{6}$$

Since κ can only assume the values ± 1, we can rewrite this as

$$\begin{aligned}\hat{\bar{\mathcal{H}}}^{(2)} = &- \frac{1}{2} \sum_{\nu=-2}^{2} \frac{\left[\omega_{\mathrm{IS}}^{(-\nu)} \hat{I}^{-}\hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(-\nu)}\hat{I}^{-}, \omega_{\mathrm{IS}}^{(\nu)}\hat{I}^{+}\hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(\nu)}\hat{I}^{+}\right]}{\nu\omega_{\mathrm{r}} + \omega_{1\mathrm{I}}} \\ &- \frac{1}{2} \sum_{\nu=-2}^{2} \frac{\left[\omega_{\mathrm{IS}}^{(-\nu)} \hat{I}^{+}\hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(-\nu)}\hat{I}^{+}, \omega_{\mathrm{IS}}^{(\nu)}\hat{I}^{-}\hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(\nu)}\hat{I}^{-}\right]}{\nu\omega_{\mathrm{r}} - \omega_{1\mathrm{I}}} . \end{aligned} \tag{7}$$

Further simplifications are possible using the commutator rules

$$\left[\hat{I}^{-}\hat{S}_z, \hat{I}^{+}\hat{S}_z\right] = -\frac{1}{2}\hat{I}_z \tag{8}$$

$$\left[\hat{I}^{-}\hat{S}_z, \hat{I}^{+}\right] = -2\hat{I}_z\hat{S}_z \tag{9}$$

$$\left[\hat{I}^{-}, \hat{I}^{+}\right] = -2\hat{I}_z \tag{10}$$

leading to

$$\begin{aligned}\hat{\bar{\mathcal{H}}}^{(2)} = &\frac{1}{4} \sum_{\nu=-2}^{2} \left(\frac{\omega_{\mathrm{I}}^{(\nu)}\omega_{\mathrm{I}}^{(-\nu)} + \omega_{\mathrm{IS}}^{(\nu)}\omega_{\mathrm{IS}}^{(-\nu)}}{\nu\omega_{\mathrm{r}} + \omega_{1\mathrm{I}}}\hat{I}_z + \frac{\omega_{\mathrm{I}}^{(\nu)}\omega_{\mathrm{IS}}^{(-\nu)} + \omega_{\mathrm{IS}}^{(\nu)}\omega_{\mathrm{I}}^{(-\nu)}}{\nu\omega_{\mathrm{r}} + \omega_{1\mathrm{I}}} 2\hat{S}_z\hat{I}_z \right) \\ &- \frac{1}{4} \sum_{\nu=-2}^{2} \left(\frac{\omega_{\mathrm{I}}^{(\nu)}\omega_{\mathrm{I}}^{(-\nu)} + \omega_{\mathrm{IS}}^{(\nu)}\omega_{\mathrm{IS}}^{(-\nu)}}{\nu\omega_{\mathrm{r}} - \omega_{1\mathrm{I}}}\hat{I}_z + \frac{\omega_{\mathrm{I}}^{(\nu)}\omega_{\mathrm{IS}}^{(-\nu)} + \omega_{\mathrm{IS}}^{(\nu)}\omega_{\mathrm{I}}^{(-\nu)}}{\nu\omega_{\mathrm{r}} - \omega_{1\mathrm{I}}} 2\hat{S}_z\hat{I}_z \right) . \end{aligned} \tag{11}$$

We obtain two types of terms: (i) The one-spin $\hat{I}_z$ terms that are fictitious fields along the rf-field direction and (ii) residual coupling terms $2\hat{I}_z\hat{S}_z$ that are cross terms between the heteronuclear dipolar coupling and the I-spin chemical-shielding tensor.