Problem Set 2

Problem 1: Sample Spinning and AHT

The time-dependent Hamiltonian for an I-S heteronuclear two-spin system under sample rotation can be written as

$$\hat{\mathcal{H}}(t) = \omega_{\mathrm{IS}}(t) 2\hat{I}_z\hat{S}_z + \omega_{\mathrm{I}}(t)\hat{I}_z + \omega_{\mathrm{S}}(t)\hat{S}_z \tag{1}$$

with the time-dependent coefficients $\omega_{\mathrm{IS}}(t)$, $\omega_{\mathrm{I}}(t)$ and $\omega_{\mathrm{S}}(t)$ given by the transformation of the dipolar-coupling and the chemical-shift tensors from the principal axes system (PAS) to the laboratory-frame coordinate system.

1. Write the time-dependent Hamiltonian of Eq. (1) as a Fourier series of the MAS frequency using the Fourier coefficients $\omega_{\mathrm{IS}}^{(n)}$, $\omega_{\mathrm{I}}^{(n)}$ and $\omega_{\mathrm{S}}^{(n)}$.

2. Calculate the Fourier coefficients $\omega_{\mathrm{IS}}^{(n)}$ for a heteronuclear dipolar coupling with an anisotropy δ_{IS} under sample rotation about an angle θ_{r} with the static magnetic field.

3. Explicitly calculate the analytical expressions for $\omega_{\mathrm{IS}}^{(0)}$, $\omega_{\mathrm{IS}}^{(\pm 1)}$ and the $\omega_{\mathrm{IS}}^{(\pm 2)}$ terms assuming that the rotation angle is the magic angle, i.e. $\theta_{\mathrm{r}} = \theta_{\mathrm{m}} = \arccos(1/\sqrt{3})$.

Hints:
A second-rank tensor characterized by the anisotropy δ and the asymmetry η has the following spherical-tensor elements in the PAS: $\rho_{2,0} = \sqrt{3/2}\delta$, $\rho_{2,\pm 1} = 0$, and $\rho_{2,\pm 2} = -0.5\delta\eta$.
Rotate the tensor in two steps from the PAS to the rotor-fixed frame using the angles (α, β, γ) for the first rotation step (powder averaging) and in a second step into the laboratory frame using the angles $(-\omega_{\mathrm{r}}t, -\theta_{\mathrm{r}}, 0)$ (MAS rotation).
The Wigner rotation matrix elements are given by $\mathfrak{D}^l_{m'm}(\alpha, \beta, \gamma) = e^{-i\alpha m'} d^l_{m'm}(\beta) e^{-i\gamma m}$ and the reduced Wigner matrix elements $d^l_{m'm}(\beta)$ can be found at the end of this exercise for rank 2.
The transformation of spherical-tensor elements between two coordinate systems is given by

$$A_{lm}^{(new)} = \sum_{m'=-l}^{l} \mathfrak{D}^l_{m'm}(\alpha, \beta, \gamma) A_{lm'}^{(old)}.$$

4. Calculate the first-order average Hamiltonian of the time-dependent dipolar-coupling Hamiltonian as a function of the angle θ_{r}. At which angle is the dipolar-coupling Hamiltonian scaled to zero?

Hints:
The first-order average Hamiltonian is the time average over one rotor period

$$\hat{\bar{\mathcal{H}}}^{(1)} = \frac{1}{\tau_{\mathrm{r}}} \int_0^{\tau_{\mathrm{r}}} dt \hat{\mathcal{H}}(t)$$

with $\tau_{\mathrm{r}} = 2\pi/\omega_{\mathrm{r}}$.

Problem 2: Interaction-Frame Transformation

We now look at the effect of irradiating the protons by a constant continuous-wave (cw) radio-frequency field. The Hamiltonian of Eq. (1) is then changed to

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^{2} \omega_{\mathrm{IS}}^{(n)} e^{in\omega_{\mathrm{r}}t} 2\hat{I}_z\hat{S}_z + \sum_{n=-2}^{2} \omega_{\mathrm{I}}^{(n)} e^{in\omega_{\mathrm{r}}t} \hat{I}_z + \sum_{n=-2}^{2} \omega_{\mathrm{S}}^{(n)} e^{in\omega_{\mathrm{r}}t} \hat{S}_z + \omega_{1\mathrm{I}}\hat{I}_x. \tag{2}$$

1. Calculate the time-dependent interaction-frame Hamiltonian using only the rf-field part for the interaction-frame transformation.

Hints:
In a first step rotate the I-spin part of the Hamiltonian by 90° about the -y axis such that the rf-field is along the new z axis. The propagator for such a rotation is given by $U_1 = e^{i(\pi/2)\hat{I}_y}$.
In a second step the Hamiltonian is rotated about the radio-frequency field leading to a time-dependent modulation. The propagator for this transformation is given by $U_2(t) = e^{-i\omega_{1\mathrm{I}}t\hat{I}_z}$.
The total interaction-frame Hamiltonian is defined as $\hat{\tilde{\mathcal{H}}}(t) = U_2(t)U_1\hat{\mathcal{H}}(t)U_1^\dagger U_2^\dagger(t)$.
We have already seen in Problem Set 1 that an interaction-frame transformation can be calculated using product-operator formalism. Use this to successively evaluate the interaction-frame transformation keeping in mind that the first propagator is just a $\pi/2$ pulse on the I-spins.

2. Write the calculated interaction-frame Hamiltonian as a Fourier series with the two frequencies $\omega_{1\mathrm{I}}$ and ω_{r}.

3. Assume that the rf-field amplitude is equal to the spinning frequency, i.e., $\omega_{1I} = \omega_{\mathrm{r}}$. Calculate the first-order average Hamiltonian under this condition.

4. Assume that the rf-field amplitude is equal to twice the spinning frequency, i.e., $\omega_{1I} = 2\omega_{\mathrm{r}}$. Calculate the first-order average Hamiltonian under this condition.

5. Assume that the rf-field amplitude is equal to half the spinning frequency, i.e., $2\omega_{1I} = \omega_{\mathrm{r}}$. Calculate the first-order average Hamiltonian under this condition.

$m' \backslash m$	-2	-1	0	+1	+2
-2	$\left(\frac{1+\cos\beta}{2}\right)^2$	$\frac{1+\cos\beta}{2}\sin\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$\frac{1-\cos\beta}{2}\sin\beta$	$\left(\frac{1-\cos\beta}{2}\right)^2$
-1	$-\frac{1+\cos\beta}{2}\sin\beta$	$\cos^2\beta-\frac{1-\cos\beta}{2}$	$\sqrt{\frac{3}{8}}\sin(2\beta)$	$\frac{1+\cos\beta}{2}-\cos^2\beta$	$\frac{1-\cos\beta}{2}\sin\beta$
0	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\sqrt{\frac{3}{8}}\sin(2\beta)$	$\frac{3\cos^2\beta-1}{2}$	$\sqrt{\frac{3}{8}}\sin(2\beta)$	$\sqrt{\frac{3}{8}}\sin^2\beta$
+1	$-\frac{1-\cos\beta}{2}\sin\beta$	$\frac{1+\cos\beta}{2}-\cos^2\beta$	$-\sqrt{\frac{3}{8}}\sin(2\beta)$	$\cos^2\beta-\frac{1-\cos\beta}{2}$	$\frac{1+\cos\beta}{2}\sin\beta$
+2	$\left(\frac{1-\cos\beta}{2}\right)^2$	$-\frac{1-\cos\beta}{2}\sin\beta$	$\sqrt{\frac{3}{8}}\sin^2\beta$	$-\frac{1+\cos\beta}{2}\sin\beta$	$\left(\frac{1+\cos\beta}{2}\right)^2$

Figure 1: The Wigner rotation-matrix elements of Rank 2.