Solution Problem Set 2

Problem 1: Sample Spinning and AHT

1. The time-dependent coefficients $\omega_{\mathrm{IS}}(t)$, $\omega_{\mathrm{I}}(t)$ and $\omega_{\mathrm{S}}(t)$ are a consequence of the sample rotation. Therefore, they have frequency components at integer multiples n of the spinning frequency where the integer n can go from -2 to 2. For one of the three coefficients we can write

$$\omega_\Lambda(t) = \sum_{n=-2}^{2} \omega_\Lambda^{(n)} e^{\omega_{\mathrm{r}} t}.$$

For the total Hamiltonian this leads to

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

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

2. To calculate the dipolar-coupling Hamiltonian in spherical-tensor notation, we assume the high-field approximation to be valid. This means that we do not need all tensor elements but only the time-independent part in the rotating frame. Therefore, the heteronuclear dipolar-coupling Hamiltonian is given by

$$\hat{\mathcal{H}} = A_{2,0}^{(\mathrm{lab})}\hat{T}_{2,0} = A_{2,0}^{(\mathrm{lab})}\frac{2}{\sqrt{6}}\hat{I}_z\hat{S}_z.$$

Note that the high-field truncated form of the heteronuclear dipolar coupling contains only the $\hat{I}_z\hat{S}_z$ term and not the zero-quantum terms that are time dependent with the difference of the Larmor frequencies (secular approximation). Now we have to calculate the $A_{2,0}^{(\mathrm{lab})}$ term in the laboratory frame by first rotating the spatial part of the tensor from the PAS to the rotor-fixed frame to the laboratory frame. This can be implemented by two successive Euler rotations with the angles (α, β, γ) and $(-\omega_{\mathrm{r}} t, -\theta_{\mathrm{r}}, 0)$, respectively. The first rotation describes the orientation of the crystallite in the rotor-fixed frame (powder average) while the second one describes the orientation of the rotor axis and the rotation and introduces the time dependence. The dipolar-coupling tensor is always axially symmetric, so we have only a single element ($\rho_{2,0}$) in the PAS. Therefore, the rotations can be written as

$$A_{2,0}^{(\mathrm{lab})} = \sum_{n=-2}^{2} \mathfrak{D}_{n,0}^{2}(-\omega_{\mathrm{r}} t, -\theta_{\mathrm{r}}, 0)\mathfrak{D}_{0,n}^{2}(\alpha, \beta, \gamma)\rho_{2,0}.$$

The first rotation is basically the powder averaging and we do not gain any insight by expanding the $\mathfrak{D}_{m',m}^{2}(\alpha, \beta, \gamma)$ term except for the fact that we are dealing with an axially symmetric tensor. This means that we only need to consider one term of the reduced Wigner elements with $m' = 0$.

$$\mathfrak{D}^2_{m',m}(\alpha,\beta,\gamma) = \sum_{m'=-2}^{2} e^{-im'\alpha} d^2_{m',m}(\beta) e^{-i\gamma m} = e^{-i0\alpha} d^2_{m',m}(\beta) e^{-i\gamma m} = \mathfrak{D}^2_{0,m}(0,\beta,\gamma)$$

However, the second rotation is the one that leads to the time dependence and it needs to be expanded

$$A^{(\text{lab})}_{2,0} = \sum_{n=-2}^{2} e^{\omega_\text{r} t} d^2_{n,0}(-\theta_\text{r}) \mathfrak{D}^2_{0,n}(0,\beta,\gamma)\rho_{2,0}.$$

This gives us now exactly the Fourier series that we had in Eq. (2) and combining this with the spin part leads to

$$\hat{\mathcal{H}}(t) = \frac{1}{\sqrt{6}}\left(\sum_{n=-2}^{2} e^{\omega_\text{r} t} d^2_{n,0}(-\theta_\text{r}) \mathfrak{D}^2_{0,n}(0,\beta,\gamma)\rho_{2,0}\right) 2\hat{I}_z\hat{S}_z = \sum_{n=-2}^{2} \omega_\text{IS}^{(n)} e^{\omega_\text{r} t} 2\hat{I}_z\hat{S}_z. \quad (3)$$

Comparing the various terms leads directly to the definition of the $\omega_\text{IS}^{(n)}$ terms

$$\omega_\text{IS}^{(n)} = \frac{1}{\sqrt{6}} d^2_{n,0}(-\theta_\text{r}) \mathfrak{D}^2_{0,n}(0,\beta,\gamma)\rho_{2,0}. \quad (4)$$

3. We can start from Eq. (4) which we can simplify further by setting $\theta_\text{r} = \theta_\text{m} = \arccos(1/\sqrt{3})$

$$\begin{aligned} d^2_{0,0}(-\theta_\text{m}) &= (3\cos^2(-\theta_\text{m}) - 1)/2 = 0 \\ d^2_{\pm1,0}(-\theta_\text{m}) &= \mp\sqrt{3/8}\sin(-2\theta_\text{m}) = \pm 1/\sqrt{3} \\ d^2_{\pm2,0}(-\theta_\text{m}) &= \sqrt{3/8}\sin^2(-\theta_\text{m}) = 1/\sqrt{6}. \end{aligned}$$

Taking into account $\rho_{2,0} = \sqrt{3/2}\delta$, this allows us now to calculate the Fourier coefficients

$$\begin{aligned} \omega_\text{IS}^{(0)} &= \frac{1}{\sqrt{6}} \cdot 0 \cdot d^2_{0,0}(\beta) e^{-i0\gamma}\sqrt{\frac{3}{2}}\delta = 0 \\ \omega_\text{IS}^{(\pm1)} &= \frac{1}{\sqrt{6}} \cdot \left(\pm\frac{1}{\sqrt{3}}\right) \cdot \left(\mp\sqrt{\frac{3}{8}}\sin(2\beta)\right) e^{\mp i\gamma}\sqrt{\frac{3}{2}}\delta = \frac{-1}{4\sqrt{2}}\sin(2\beta)e^{\mp i\gamma}\delta \\ \omega_\text{IS}^{(\pm2)} &= \frac{1}{\sqrt{6}} \cdot \left(\frac{1}{\sqrt{6}}\right) \cdot \left(\sqrt{\frac{3}{8}}\sin^2(\beta)\right) e^{\mp 2i\gamma}\sqrt{\frac{3}{2}}\delta = \frac{1}{8}\sin(\beta)^2 e^{\mp 2i\gamma}\delta. \end{aligned}$$

4. To calculate the average Hamiltonian in first order, we have to integrate the Hamiltonian of Eq. (3) over one rotor period

$$\hat{\bar{\mathcal{H}}}^{(1)} = \frac{1}{\tau_\text{r}}\int_0^{\tau_\text{r}} dt \hat{\mathcal{H}}(t) = \frac{1}{\tau_\text{r}}\int_0^{\tau_\text{r}} dt \sum_{n=-2}^{2} \omega_\text{IS}^{(n)} e^{\omega_\text{r} t} 2\hat{I}_z\hat{S}_z$$

For the integral we have

$$\frac{1}{\tau_r}\int_0^{\tau_r} e^{in\omega_r t}dt = \frac{1-e^{in2\pi}}{in2\pi} = \frac{1-\sum_{m=0}^{\infty}\frac{(in2\pi)^m}{m!}}{in2\pi} = \frac{\sum_{m=1}^{\infty}\frac{(in2\pi)^m}{m!}}{in2\pi} = \sum_{m=0}^{\infty}\frac{(in2\pi)^m}{(m+1)!}$$

Therefore it evaluates for $n \neq 0$ to zero, and for $n = 0$ to one.

$$\begin{aligned}\hat{\bar{\mathcal{H}}}^{(1)} &= \frac{1}{\tau_\mathrm{r}}\int_0^{\tau_\mathrm{r}} dt\omega_\mathrm{IS}^{(0)}2\hat{I}_z\hat{S}_z = \omega_\mathrm{IS}^{(0)}2\hat{I}_z\hat{S}_z = \frac{1}{\sqrt{6}}d^2_{0,0}(-\theta_\mathrm{r})\mathfrak{D}^2_{0,0}(0,\beta,\gamma)\rho_{2,0}2\hat{I}_z\hat{S}_z \\ &= \frac{1}{\sqrt{6}}d^2_{0,0}(-\theta_\mathrm{r})d^2_{0,0}(\beta)\rho_{2,0}2\hat{I}_z\hat{S}_z = \frac{1}{\sqrt{6}}\left(\frac{3\cos^2\theta_\mathrm{r}-1}{2}\right)\left(\frac{3\cos^2\beta-1)}{2}\right)\rho_{2,0}2\hat{I}_z\hat{S}_z.\end{aligned}$$

The scaling of the magnitude of the Hamiltonian depends, therefore, on the angle θ_r of the rotation axis with the static magnetic field. Figure 1 shows the dependence of the reduced-Wigner matrix elements on the angle. We can see that the rotation about an angle θ_r scales the second-rank tensor by a factor $d^2_{0,0}(-\theta_\mathrm{r})$ between +1 and -1/2 and for the magic angle the scaling becomes zero and the dipolar coupling is, in first-order AHT, averaged out.

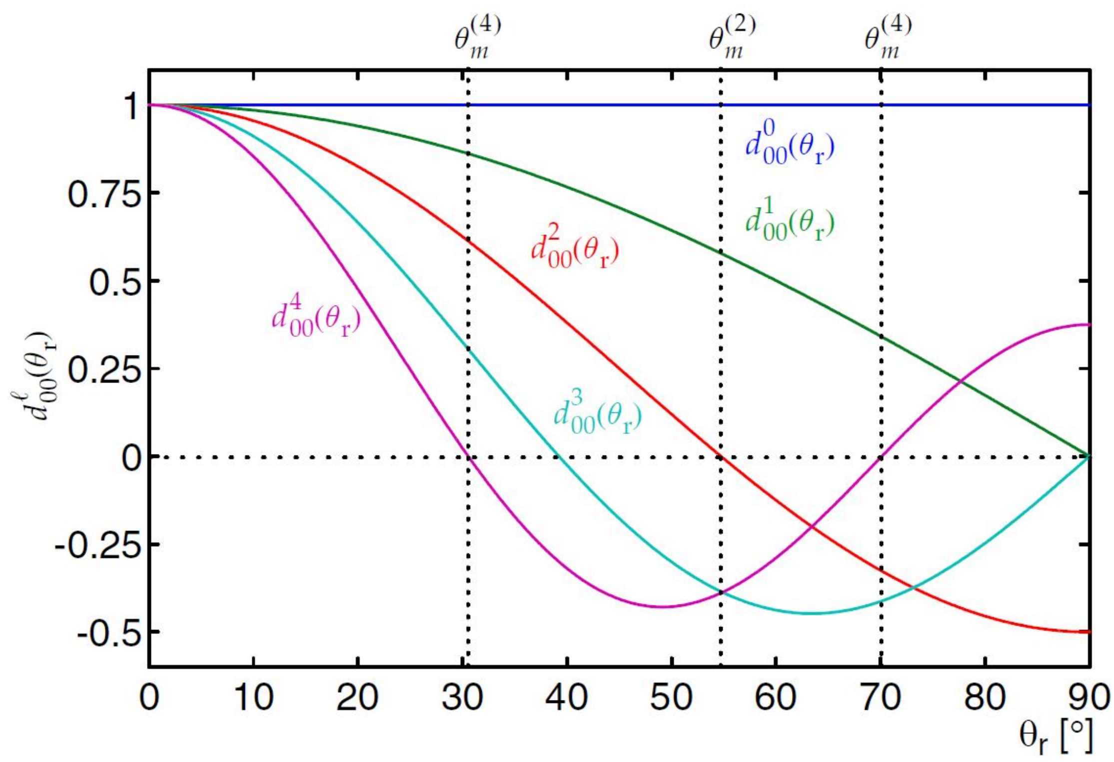

Figure 1: The angular dependence of the reduced Wigner rotation matrix elements $d^l_{0,0}(\theta_\mathrm{r})$ shows the differences in scaling by rotation about a single at an angle θ_r with the direction of the static magnetic field.

Problem 2: Interaction-Frame Transformation

1. We have to do an interaction-frame transformation with the radio-frequency part of the Hamiltonian. It is often convenient to first tilt the coordinate system by 90° about the -y axis such that the rf-field is along the z axis of the tilted coordinate system. This is not really necessary but leads to average Hamiltonians that are quantized along the z axis in this tilted frame. The propagator for this transformation is $U_1 = e^{i(\pi/2)\hat{I}_y}$ leading to a Hamiltonian that is tilted for the I spins and has the form

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

The transformation into the interaction frame is now characterized by $U_2(t) = e^{-i\omega_{1\mathrm{I}}t\hat{I}_z}$ leading to an interaction-frame Hamiltonian of the form

$$\begin{aligned}\hat{\mathcal{H}}''(t) = &-\sum_{n=-2}^{2} \omega_{\mathrm{IS}}^{(n)} e^{in\omega_{\mathrm{r}}t} 2(\hat{I}_x\cos(\omega_{1\mathrm{I}}t) - \hat{I}_y\sin(\omega_{1\mathrm{I}}t))\hat{S}_z \\ &-\sum_{n=-2}^{2} \omega_{\mathrm{I}}^{(n)} e^{in\omega_{\mathrm{r}}t} (\hat{I}_x\cos(\omega_{1\mathrm{I}}t) - \hat{I}_y\sin(\omega_{1\mathrm{I}}t)) \\ &+\sum_{n=-2}^{2} \omega_{\mathrm{S}}^{(n)} e^{in\omega_{\mathrm{r}}t} \hat{S}_z.\end{aligned}$$

Note that this is already the Hamiltonian that is without the transformation Hamiltonian. ($\hat{\mathcal{H}}''(t) = \hat{\mathcal{H}}'(t) - \hat{\mathcal{H}}_1(t)$ which is the correction that comes from the Liuoville-von-Neumann equation in the interaction frame).
This is the interaction-frame Hamiltonian in the tilted rotating frame and we can try to clean it up a bit and write the trigonometric functions as exponential functions. This leads then to a Hamiltonian where we can extract the Fourier coefficients of the Hamiltonian

$$
\begin{aligned}
\hat{\mathcal{H}}''(t) = &-\sum_{n=-2}^{2} \omega_{\mathrm{IS}}^{(n)} e^{in\omega_{\mathrm{r}}t} 2\big(\hat{I}_x \frac{1}{2}(e^{i\omega_{1\mathrm{I}}t} + e^{-i\omega_{1\mathrm{I}}t}) - \hat{I}_y \frac{1}{2i}(e^{i\omega_{1\mathrm{I}}t} - e^{-i\omega_{1\mathrm{I}}t})\big)\hat{S}_z \\
&- \sum_{n=-2}^{2} \omega_{\mathrm{I}}^{(n)} e^{in\omega_{\mathrm{r}}t} \big(\hat{I}_x \frac{1}{2}(e^{i\omega_{1\mathrm{I}}t} + e^{-i\omega_{1\mathrm{I}}t}) - \hat{I}_y \frac{1}{2i}(e^{i\omega_{1\mathrm{I}}t} - e^{-i\omega_{1\mathrm{I}}t})\big) \\
&+ \sum_{n=-2}^{2} \omega_{\mathrm{S}}^{(n)} e^{in\omega_{\mathrm{r}}t} \hat{S}_z \\
= &-\sum_{n=-2}^{2} \omega_{\mathrm{IS}}^{(n)} e^{in\omega_{\mathrm{r}}t} \big(\hat{I}^+ e^{i\omega_{1\mathrm{I}}t} + \hat{I}^- e^{-i\omega_{1\mathrm{I}}t}\big)\hat{S}_z - \sum_{n=-2}^{2} \frac{1}{2}\omega_{\mathrm{I}}^{(n)} e^{in\omega_{\mathrm{r}}t} \big(\hat{I}^+ e^{i\omega_{1\mathrm{I}}t} + \hat{I}^- e^{-i\omega_{1\mathrm{I}}t}\big) \\
&+ \sum_{n=-2}^{2} \omega_{\mathrm{S}}^{(n)} e^{in\omega_{\mathrm{r}}t} \hat{S}_z \\
= &-\sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} e^{1\cdot i\omega_{1\mathrm{I}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^+ \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^+\big) - \sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} e^{-1\cdot i\omega_{1\mathrm{I}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^- \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^-\big) \\
&+ \sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} e^{0\cdot i\omega_{1\mathrm{I}}t} \omega_{\mathrm{S}}^{(n)} \hat{S}_z
\end{aligned}
$$

2. The time-dependent Hamiltonian can now be written as a Fourier series with two basic frequencies as

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

while the Fourier coefficients can be directly extracted out of the last equation in the previous task and we obtain

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

3. We can start with the Hamiltonian from Problem 1 and replace ω_{1I} by ω_{r} and obtain

$$
\begin{aligned}
\hat{\mathcal{H}}''(t) = &-\sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} e^{i\omega_{\mathrm{r}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^+ \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^+\big) - \sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} e^{-i\omega_{\mathrm{r}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^- \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^-\big) \\
&+ \sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} \omega_{\mathrm{S}}^{(n)} \hat{S}_z \\
= &-\sum_{n=-2}^{2} e^{i(n+1)\omega_{\mathrm{r}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^+ \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^+\big) - \sum_{n=-2}^{2} e^{i(n-1)\omega_{\mathrm{r}}t} \big(\omega_{\mathrm{IS}}^{(n)} \hat{I}^- \hat{S}_z + \frac{1}{2}\omega_{\mathrm{I}}^{(n)} \hat{I}^-\big) \\
&+ \sum_{n=-2}^{2} e^{in\omega_{\mathrm{r}}t} \omega_{\mathrm{S}}^{(n)} \hat{S}_z
\end{aligned}
$$

The first-order average Hamiltonian is given by

$$\hat{\bar{\mathcal{H}}}^{(1)} = \frac{1}{\tau_\mathrm{r}} \int_0^{\tau_\mathrm{r}} dt \hat{\mathcal{H}}''(t)$$

which will only be non zero for terms that are time independent. For the first term, this is given for $n = -1$, for the second term for $n = +1$ and for the third term for $n = 0$.

$$\hat{\bar{\mathcal{H}}} = -\left(\omega_\mathrm{IS}^{(-1)} \hat{I}^+ \hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(-1)} \hat{I}^+\right) - \left(\omega_\mathrm{IS}^{(+1)} \hat{I}^- \hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(+1)} \hat{I}^-\right) + \omega_\mathrm{S}^{(0)} \hat{S}_z$$

This is the Hamiltonian at the so-called $n = 1$ rotary-resonance condition where the CSA tensor and the heteronuclear dipolar coupling are recoupled.

4. For $\omega_{1I} = 2\omega_\mathrm{r}$ we can do exactly the same but replace ω_{1I} by $2\omega_\mathrm{r}$ which will give

$$\hat{\bar{\mathcal{H}}} = -\left(\omega_\mathrm{IS}^{(-2)} \hat{I}^+ \hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(-2)} \hat{I}^+\right) - \left(\omega_\mathrm{IS}^{(+2)} \hat{I}^- \hat{S}_z + \frac{1}{2}\omega_\mathrm{I}^{(+2)} \hat{I}^-\right) + \omega_\mathrm{S}^{(0)} \hat{S}_z$$

This is the Hamiltonian at the so-called $n = 2$ rotary-resonance condition where the CSA tensor and the heteronuclear dipolar coupling are recoupled.

5. For $2\omega_{1I} = \omega_\mathrm{r}$, we replace ω_r by $2\omega_{1I}$ which will give only a time-independent contribution from the third term, leading to:

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

This is the so-called HORROR condition where only the Homonuclear dipolar coupling would be recoupled which we did not include in this exercise for simplicity.