1 Exercise: Time-Dependent Hamiltonians

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

$$\hat{\mathcal{H}}(t) = \omega_{\mathrm{IS}}(t)2\hat{I}_z\hat{S}_z + \omega_{\mathrm{I}}(t)\hat{I}_z + \omega_{\mathrm{S}}(t)\hat{S}_z \qquad [1.1]$$

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 chemical-shift tensors from the principal-axes system (PAS) to the laboratory-frame coordinate system.

1.1 Sample Spinning and AHT

- Write the time-dependent Hamiltonian of Eq. [1.1] as a Fourier series of the MAS frequency using the Fourier coefficients $\omega_{\mathrm{IS}}^{(n)}$, $\omega_{\mathrm{I}}^{(n)}$, and $\omega_{\mathrm{S}}^{(n)}$.
- 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.
- 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 $(-\omega_{\mathrm{r}}t, -\theta, 0)$ (MAS rotation).

The Wigner rotation matrix elements are given by $\mathfrak{D}_{m'm}^{\ell}(\alpha, \beta, \gamma) = e^{-i\alpha m'} d_{m'm}^{\ell}(\beta) e^{-i\gamma m}$ and the reduced Wigner rotation matrix elements $d_{m'm}^{\ell}(\beta)$ can be found in the Appendix for ranks zero to two.

The transformation of spherical-tensor elements between two coordinate systems is given by

$$A_{\ell m}^{(\text{new})} = \sum_{m' = -\ell}^{\ell} \mathfrak{D}_{m'm}^{\ell}(\alpha, \beta, \gamma) A_{\ell m'}^{(\text{old})} \quad . \qquad [1.2]$$

- Calculate the first-order average Hamiltonian of the time-dependent dipolar-coupling Hamiltonian as a function of the angle θ. 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

$$\bar{\hat{\mathcal{H}}}^{(1)} = \frac{1}{\tau_{\text{r}}}\int_0^{\tau_{\text{r}}} dt \hat{\mathcal{H}}(t) \qquad [1.3]$$

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

1.2 Interaction-Frame Transformation

We now look at the effect of irradiating the protons by a constant cw radio-frequency field. The Hamiltonian of Eq. [1.1] is then changed to

$$\hat{\mathcal{H}}(t) = \sum_{n=-2}^{2} \omega_{\text{IS}}^{(n)} e^{-in\omega_{\text{r}}t} 2\hat{I}_z\hat{S}_z + \sum_{n=-2}^{2} \omega_{\text{I}}^{(n)} e^{-in\omega_{\text{r}}t} \hat{I}_z + \sum_{n=-2}^{2} \omega_{\text{S}}^{(n)} e^{-in\omega_{\text{r}}t} \hat{S}_z + \omega_{1\text{I}}\hat{I}_x \quad . \qquad [1.4]$$

- 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 $U_1 = e^{(\pi/2)\hat{I}_y}$.

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 $U_2(t) = e^{-\omega_{1\text{I}}t\hat{I}_z}$.

The total interaction-frame Hamiltonian is defined as $\hat{\hat{\mathcal{H}}}(t) = U_2(t)U_1\hat{\mathcal{H}}(t)U_1^{\dagger}U_2^{\dagger}(t)$.

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

1.3 Floquet Calculations

Using the Fourier series of the time-dependent Hamiltonian calculated in the previous section

$$\hat{\tilde{\mathcal{H}}}(t) = \sum_{n=-2}^{2} \sum_{k=-1}^{1} \hat{\mathcal{H}}^{(n,k)} \cdot e^{in\omega_r t} \cdot e^{ik\omega_{1I} t} , \qquad [1.5]$$

we can now analyze the possible resonance conditions.

- Write down all possible resonance conditions $n\omega_r + k\omega_{1I} = 0$ that can be realized in the Hamiltonian of Eq. [1.5].

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 $n_0\omega_r + k_0\omega_{1I} = 0$.

- 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 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., $\omega_1 \gg 2\omega_r$.

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

Hints:

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

$$\hat{\bar{\mathcal{H}}} = \hat{\bar{\mathcal{H}}}^{(1)} + \hat{\bar{\mathcal{H}}}^{(2)} = \hat{\mathcal{H}}^{(0,0)} - \frac{1}{2}\sum_{\nu,\kappa} \frac{[\hat{\mathcal{H}}^{(-\nu,-\kappa)}, \hat{\mathcal{H}}^{(\nu,\kappa)}]}{\nu\omega_r + \kappa\omega_1} \qquad [1.6]$$

2 Appendices

2.1 Matrix Properties

A real matrix A with elements A_{ij} is called *symmetric* if

$$A^T = A \qquad [2.1]$$

where A^T is the transpose of the matrix, i.e., for all elements the condition $A_{ij} = A_{ji}$ is fulfilled. The real matrix A is called *antisymmetric* if

$$A^T = -A \ , \qquad [2.2]$$

i.e., for all elements the condition $A_{ij} = A_{ji}$ is fulfilled. The real matrix A is called *orthogonal* if

$$A^T = A^{-1} \ . \qquad [2.3]$$

A complex matrix A with elements A_{ij} is called *hermitian* if

$$A^\dagger = A \qquad [2.4]$$

where $A^\dagger$ is the adjoint (transposed and complex conjugate) of the matrix, i.e., for all elements the condition $A_{ij} = A_{ji}{}^*$ is fulfilled. The complex matrix A is called *unitary* if

$$A^\dagger = A^{-1} \ . \qquad [2.5]$$

The matrix representation of a Hamiltonian is always a Hermitian matrix. Form this it follows that the matrix representation of a propagator is always a unitary matrix and, therefore, the propagation of a density operator is always a unitary transformation.

2.2 Wigner Rotation Matrix Elements

2.2.1 Rank 0 Elements

Rank 0 tensors are quantities that transform like a scalar. They have only a single component, which is independent of the coordinate system. Therefore, the Wigner rotation matrix element is given by

$$\mathfrak{D}^{0}_{00} = d^{0}_{00}(\beta) = 1 \ . \qquad [2.6]$$

2.2.2 Rank 1 Elements

Rank 1 tensor are vectors and their respective reduced Wigner rotation elements $d^{1}_{m',m}(\beta)$ are given by

Table 2.1: Reduced Wigner Rotation Matrix Elements of Rank 1

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

2.2.3 Rank 2 Elements

Rank 2 tensors are second-rank tensors and the reduced Wigner rotation matrix elements are given by $d^2_{m',m}(\beta)$

Table 2.3: Reduced Wigner Rotation Matrix Elements of Rank 2

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