Problem Set 1

Problem 1: Chemical-Shift Anisotropy and the Rotating-Frame Transformation

1. NMR Hamiltonians can be categorized as spin-spin or spin-field interactions. Write down the general expressions for Hamiltonians of such interactions. Which of them is the appropriate one to describe the chemical-shift interaction?

2. Calculate the laboratory-frame Hamiltonian for a single spin assuming that the B_0-field is aligned in the z-direction of the laboratory system. The chemical-shift tensor in the laboratory frame is defined as

$$\underset{\sim}{\sigma}^{\mathrm{LAB}} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}.$$

   How many different terms does the Hamiltonian in the laboratory frame have?

3. The theoretical description of NMR experiments is generally carried out in a coordinate system which is rotating with the Larmor frequency $\omega_0 = -\gamma B_0$ around the direction of the B_0 field ("rotating frame"). A transformation into the rotating frame can be carried out via a propagator

$$\hat{U} = \exp(-i\omega_0 \hat{I}_z t).$$

   Calculate the chemical-shift Hamiltonian in the rotating frame. Which terms become time dependent and with which frequency?

4. The secular approximation states that we can neglect terms that have a fast time dependence. Explain which terms can be neglected in the secular approximation. How many terms has the chemical-shift Hamiltonian in the rotating frame?
   Which terms of the chemical-shift tensor can we measure under high-field conditions?

Problem 2: Dipolar Coupling and the Spherical Tensor Notation

1. The laboratory-frame Hamiltonian can be expressed via the sum of scalar products between a spherical spatial- and a spin-tensor operator as

$$\hat{\mathcal{H}} = \sum_i \sum_l \sum_{m=-l}^{l} (-1)^m A_{l,m}^{(\mathrm{LAB})} T_{l,-m}$$

   Usually, the spatial part of the spherical-tensor is given in the principal-axes system (PAS). Starting from the expression for the spatial spherical-tensor components in the PAS ($\rho_{l,m}^{(\mathrm{PAS})}$), calculate the spatial components of the dipolar coupling Hamiltonian in the lab frame ($A_{l,m}^{(\mathrm{lab})}$).
   Hints: A second-rank tensor characterized by the anisotropy δ and the asymmetry η has the following spherical-tensor elements in the PAS: $A_{2,0}^{(\mathrm{PAS})} = \rho_{2,0}^{(\mathrm{PAS})} = \sqrt{3/2}\delta$, $A_{2,\pm1}^{(\mathrm{PAS})} = \rho_{2,\pm1}^{(\mathrm{PAS})} = 0$, and $A_{2,\pm2}^{(\mathrm{PAS})} = \rho_{2,\pm2}^{(\mathrm{PAS})} = -0.5\delta\eta$. The transformation of spherical-tensor elements between two coordinate systems is given by

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

   Use the rotation angles (α,β,γ) and the Wigner rotation matrix elements

$$\mathfrak{D}_{m',m}^{l}(\alpha,\beta,\gamma) = e^{-i\alpha m'} d_{m',m}^{l}(\beta) e^{-i\gamma m}.$$

   The parameters of the dipolar coupling Hamiltonian in spherical-tensor notations are $\delta = -2\frac{\mu_0\gamma_k\gamma_n\hbar}{4\pi r_{kn}^3}$ and $\eta = 0$.

2. If we transform the dipolar-coupling Hamiltonian into the rotating frame (see Excercise 1), which terms become time dependent and which terms are time independent?

3. Write down the dipolar-coupling Hamiltonian under the secular approximation.

4. If we do magic-angle spinning, the transformation from the PAS to the LAB coordinate system is carried out in two steps. In a first step, the transformation from the PAS to the rotor-fixed frame (ROT) is carried out using the rotations $\mathfrak{D}_{m,m'}^{l}(\alpha,\beta,\gamma)$ and in a second step, we rotate from the ROT frame to the LAB frame using the rotations $\mathfrak{D}_{m',m''}^{l}(-\omega_{\mathrm{r}}t, -\theta_{\mathrm{m}}, 0)$. Calculate the $A_{2,0}^{(\mathrm{LAB})}$ term under MAS and write down the complete rotating-frame Hamiltonian.

5. Which frequencies appear in the time-dependent secular rotating-frame Hamiltonian?