

Solution Problem Set 1

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

1. The Hamiltonians for interactions in NMR can be described in a general form by

$$\hat{\mathcal{H}}^{(k,n)} = \vec{\hat{I}}_k \cdot \hat{A}^{(k,n)} \cdot \vec{\hat{I}}_n$$

for spin-spin interactions and

$$\hat{\mathcal{H}}^{(k,B)} = \vec{\hat{I}}_k \cdot \hat{A}^{(k,B)} \cdot \vec{B}$$

for interactions between a spin and the magnetic field \vec{B} . A is a 3x3 matrix that describes the strength and angular dependence of the corresponding interaction. Since the chemical shift interaction is a spin-field interaction the latter expression can be used to characterize it.

2. The chemical shift Hamiltonian in a matrix representation is represented by

$$\hat{\mathcal{H}}_{CS}^{(k)} = \vec{\hat{I}}_k \cdot (-\gamma) \hat{\sigma}^{(k)} \vec{B}_0.$$

With

$$\vec{\hat{I}}_k = (\hat{I}_{kx}, \hat{I}_{ky}, \hat{I}_{kz})$$

and

$$\vec{B}_0 = (0, 0, B_0)$$

this gives

$$\hat{\mathcal{H}}_{CS}^{(k)} = (\hat{I}_{kx}, \hat{I}_{ky}, \hat{I}_{kz}) \cdot (-\gamma^{(k)}) \begin{pmatrix} \sigma_{xx}^{(k)} & \sigma_{xy}^{(k)} & \sigma_{xz}^{(k)} \\ \sigma_{yx}^{(k)} & \sigma_{yy}^{(k)} & \sigma_{yz}^{(k)} \\ \sigma_{zx}^{(k)} & \sigma_{zy}^{(k)} & \sigma_{zz}^{(k)} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} = (\hat{I}_{kx}, \hat{I}_{ky}, \hat{I}_{kz}) \cdot \begin{pmatrix} -\gamma^{(k)} \sigma_{xz}^{(k)} B_0 \\ -\gamma^{(k)} \sigma_{yz}^{(k)} B_0 \\ -\gamma^{(k)} \sigma_{zz}^{(k)} B_0 \end{pmatrix}$$

and consequently

$$\hat{\mathcal{H}}_{CS}^{(k)} = \sigma_{xz}^{(k)} \omega_0^{(k)} \hat{I}_{kx} + \sigma_{yz}^{(k)} \omega_0^{(k)} \hat{I}_{ky} + \sigma_{zz}^{(k)} \omega_0^{(k)} \hat{I}_{kz}.$$

We have in the end three different terms in the LABoratory-frame Hamiltonian that contain the three Cartesian spin operators $\hat{I}_{\{x,y,z\}}$ and the elements of the last column of the chemical-shift tensor.

3. In general, any operator \hat{A}' in a rotating frame of reference is related to the operator \hat{A} in the LAB frame by

$$\hat{A}' = \hat{U}^{-1} \hat{A} \hat{U}$$

Note that we use the transformation formula $\hat{A}' = \hat{U}^{-1} \hat{A} \hat{U}$ rather than $\hat{A}' = \hat{U} \hat{A} \hat{U}^{-1}$ because the interaction-frame transformation is a *passive* rotation.

We obtain for the three operators:

$$\begin{aligned}\hat{U}^{-1} \hat{I}_x \hat{U} &= \hat{I}_x \cos(\omega_0 t) - \hat{I}_y \sin(\omega_0 t) \\ \hat{U}^{-1} \hat{I}_y \hat{U} &= \hat{I}_y \cos(\omega_0 t) + \hat{I}_x \sin(\omega_0 t) \\ \hat{U}^{-1} \hat{I}_z \hat{U} &= \hat{I}_z\end{aligned}$$

Therefore, \hat{I}_x and \hat{I}_y become time dependent with the Larmor frequency of the spin while \hat{I}_z is invariant under rotation and remains time independent. This arises from the fact that it commutes with itself.

The time-dependent chemical-shift Hamiltonian in the rotating frame is then given by:

$$\hat{\mathcal{H}}_{CS}^{(k)} = \sigma_{xz}^{(k)} \omega_0^{(k)} (\hat{I}_x \cos(\omega_0 t) - \hat{I}_y \sin(\omega_0 t)) + \sigma_{yz}^{(k)} \omega_0^{(k)} (\hat{I}_y \cos(\omega_0 t) + \hat{I}_x \sin(\omega_0 t)) + \sigma_{zz}^{(k)} \omega_0^{(k)} \hat{I}_{kz}.$$

4. The \hat{I}_x and \hat{I}_y operators are time dependent in the rotating frame with the Larmor frequency and can be neglected. Therefore, the secular high-field rotating-frame Hamiltonian has only a single term

$$\hat{\mathcal{H}}_{CS}^{(k)} = \sigma_{zz}^{(k)} \omega_0^{(k)} \hat{I}_{kz}.$$

This implies that we measure a single matrix element of the chemical-shift tensor, namely the σ_{zz} element. Of course, it will depend on all three elements in the principal-axis system.

Problem 2: Dipolar Coupling and the Spherical Tensor Notation

1. The dipolar coupling Hamiltonian is a second-rank tensor ($l = 2$). The formula to transform its tensor components from the principal-axis system into the LABoratory frame, therefore becomes

$$\begin{aligned} A_{2,m}^{(\text{LAB})} &= \sum_{m'=-2}^2 \mathfrak{D}_{m',m}^2 \rho_{2,m'}^{(\text{PAS})} \\ &= \mathfrak{D}_{-2,m}^2 \rho_{2,-2}^{(\text{PAS})} + \mathfrak{D}_{-1,m}^2 \rho_{2,-1}^{(\text{PAS})} + \mathfrak{D}_{0,m}^2 \rho_{2,0}^{(\text{PAS})} + \mathfrak{D}_{1,m}^2 \rho_{2,1}^{(\text{PAS})} + \mathfrak{D}_{2,m}^2 \rho_{2,2}^{(\text{PAS})} \end{aligned}$$

Note that this formula means that each of the five tensor components in the laboratory frame ($A_{2,\pm 2}^{(\text{LAB})}, A_{2,\pm 1}^{(\text{LAB})}, A_{2,0}^{(\text{LAB})}$) can be written as linear combination of the five tensor components in the principal-axis system ($\rho_{2,\pm 2}^{(\text{PAS})}, \rho_{2,\pm 1}^{(\text{PAS})}, \rho_{2,0}^{(\text{PAS})}$), where the weights of the combination are given by the Wigner rotation elements.

We now use our specific knowledge about the dipolar coupling. We first note that the $\rho_{2,\pm 1}^{(\text{PAS})} = 0$, meaning that we can drop these terms from the transformation formula. The dipolar coupling has the additional characteristic that it is an axially symmetric rank 2 tensor, meaning that it has a vanishing asymmetry parameter $\eta = 0$. As a direct consequence, also the elements $\rho_{2,\pm 2}^{(\text{PAS})} = -0.5\delta\eta = 0$ and we can drop them from the transformation formula. In summary, the rotation into the lab-frame becomes

$$A_{2,m}^{(\text{LAB})} = \mathfrak{D}_{0,m}^2(\alpha, \beta, \gamma) \rho_{2,0}^{(\text{PAS})} = d_{0,m}^2(\beta) e^{-i\gamma m} \sqrt{\frac{3}{2}} \delta \quad (1)$$

We finally find the five $A_{2,m}$ tensor elements for the spatial-part of the dipolar interaction in the LABoratory frame, by inserting the respective m index in equation (??) and looking up the definition of the reduced Wigner rotation matrix elements for rank 2:

$$\begin{aligned} A_{2,\pm 2}^{(\text{LAB})} &= \frac{3\delta}{4} \sin^2(\beta) e^{\mp i 2\gamma} \\ A_{2,\pm 1}^{(\text{LAB})} &= \pm \frac{\delta}{4} 3 \sin(2\beta) e^{\mp i \gamma} = \pm \frac{\delta}{2} 3 \sin(\beta) \cos(\beta) e^{\mp i \gamma} \\ A_{2,0}^{(\text{LAB})} &= \sqrt{\frac{3}{8}} \delta (3 \cos^2(\beta) - 1) \end{aligned}$$

2. Transforming the dipolar Hamiltonian

$$\hat{\mathcal{H}} = \sum_{m=-2}^2 = (-1)^m A_{2,m}^{(\text{LAB})} \hat{T}_{2,-m}$$

into the rotating frame implies a rotation about the z axis with the Larmor frequency of the spin. The spherical-tensor operators $\hat{T}_{2,m}$ transform according to

$$\hat{U}^{-1}\hat{T}_{2,m}\hat{U} = \hat{T}_{2,m}e^{im\omega_0 t}$$

where \hat{U} is defined as in Ex. 1. Therefore, all terms except $\hat{T}_{2,0}$ become time dependent while $\hat{T}_{2,0}$ remains time independent.

3. The dipolar-coupling high-field rotating-frame Hamiltonian under the secular approximation becomes quite simple and is given by

$$\begin{aligned}\hat{\mathcal{H}} &= A_{2,0}^{(\text{LAB})}\hat{T}_{2,0} = \sqrt{\frac{3}{8}}\delta(3\cos^2(\beta) - 1)\frac{1}{\sqrt{6}}(2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y}) \\ &= \frac{\delta}{4}(3\cos^2(\beta) - 1)(2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y})\end{aligned}$$

4. For magic-angle spinning we do two consecutive rotations. In the case of the dipolar coupling, the transformation is simplified by the fact that in the PAS only the $m = 2$ component exists and we only need the $m = 0$ component in the LABoratory frame since we are only interested in the $A_{2,0}^{(\text{ALB})}$ term. Therefore, the $A_{2,0}^{(\text{LAB})}$ term can be written as

$$\begin{aligned}A_{2,0}^{(\text{LAB})}(t) &= \sum_{m=-2}^2 \mathfrak{D}_{m,0}^2(-\omega_r t, -\theta_m, 0) \mathfrak{D}_{0,m}^2(\alpha, \beta, \gamma) \rho_{2,0}^{(\text{PAS})} \\ &= \sum_{m=-2}^2 \mathfrak{D}_{m,0}^2(-\omega_r t, -\theta_m, 0) A_{2,m}^{(\text{ROT})} \\ &= \sum_{m=-2}^2 d_{m,0}^2(-\theta_m) A_{2,m}^{(\text{ROT})} e^{im\omega_r t}\end{aligned}$$

The complete Hamiltonian is then given by the product of the spatial and spin tensor components and we obtain:

$$\begin{aligned}\hat{\mathcal{H}}(t) &= A_{2,0}^{(\text{LAB})}(t)\hat{T}_{2,0} = \sum_{m=-2}^2 d_{m,0}^2(-\theta_m) A_{2,m}^{(\text{ROT})} e^{im\omega_r t} \frac{1}{\sqrt{6}}(2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y}) \\ &= \sum_{m=-2}^2 \omega_D^{(n)} e^{im\omega_r t} (2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y})\end{aligned}$$

5. The Hamiltonian contains frequencies from $-2\omega_r$ to $2\omega_r$. No higher frequencies can appear in this Hamiltonian. Note that there is no time independent part because $d_{0,0}^2(-\theta_m) = 0$ and the dipolar coupling has no isotropic component.