Solution for Problem Set 3: Rotations and Hamiltonians

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

1. The Hamiltonians for the most important interactions in solid-state NMR can be described in a general form as

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

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 $\vec{B}$. $\hat{A}$ is a tensor 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

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

With

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

and

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

this gives

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

and consequently

$$\hat{\mathcal{H}}^{(k)}_{CS} = \sigma^{(k)}_{xz}\omega^{(k)}_0 \hat{I}_{kx} + \sigma^{(k)}_{yz}\omega^{(k)}_0 \hat{I}_{ky} + \sigma^{(k)}_{zz}\omega^{(k)}_0 \hat{I}_{kz}.$$

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.

To illustrate this, we do the transformation explicitly for an $\hat{I}_x$ operator

$$\begin{aligned}
\hat{I}_x{}' &= \hat{U}^{-1}\hat{I}_x\hat{U} \\
&= e^{i\omega_0\hat{I}_z t}\cdot\hat{I}_x\cdot e^{-i\omega_0\hat{I}_z t} \\
&= \begin{pmatrix} e^{\frac{i\omega_0 t}{2}} & 0 \\ 0 & e^{\frac{-i\omega_0 t}{2}} \end{pmatrix}\begin{pmatrix} 0 & \frac{1}{2} \\ \frac{1}{2} & 0 \end{pmatrix}\begin{pmatrix} e^{\frac{-i\omega_0 t}{2}} & 0 \\ 0 & e^{\frac{i\omega_0 t}{2}} \end{pmatrix} \\
&= \begin{pmatrix} 0 & \frac{1}{2}\cdot e^{i\omega_0 t} \\ \frac{1}{2}\cdot e^{-i\omega_0 t} & 0 \end{pmatrix} \\
&= \begin{pmatrix} 0 & \frac{1}{2}\cdot(\cos(\omega_0 t) + i\sin(\omega_0 t)) \\ \frac{1}{2}\cdot(\cos(\omega_0 t) - i\sin(\omega_0 t)) & 0 \end{pmatrix} \\
&= \begin{pmatrix} 0 & \frac{1}{2}\cdot\cos(\omega_0 t) \\ \frac{1}{2}\cdot\cos(\omega_0 t) & 0 \end{pmatrix} - \begin{pmatrix} 0 & \frac{-i}{2}\cdot\sin(\omega_0 t) \\ \frac{i}{2}\cdot\sin(\omega_0 t) & 0 \end{pmatrix}
\end{aligned}$$

From the matrix in the last line we can deduce that the $\hat{I}_x$ operator becomes time-dependent and transforms as

$$\hat{I}'_{kx} \rightarrow \hat{I}_{kx}\cos(\omega_0 t) - \hat{I}_{ky}\sin(\omega_0 t).$$

The same calculations for the $\hat{I}_y$ leads to

$$\hat{I}'_{ky} \rightarrow \hat{I}_{ky}\cos(\omega_0 t) + \hat{I}_{kx}\sin(\omega_0 t)$$

making them both time-dependent (see Figure 1). The $\hat{I}_{kz}$ is invariant under rotation and remains time-independent. This arises from the fact that it commutes with itself.

The integration over one rotational period averages the time-dependent contributions to zero, leading to the so called high-field chemical-shift Hamiltonian

$$\hat{\mathcal{H}}^{(k)}_{CS} = \sigma^{(k)}_{zz}\omega^{(k)}_0\hat{I}_{kz}.$$

4. Using the Euler rotation matrix we transform the chemical-shift tensor from the PAS into the laboratory frame.

$$\underset{\sim}{\sigma}^{\mathrm{LAB}} = \boldsymbol{R}(\alpha,\beta,\gamma)\underset{\sim}{\sigma}^{\mathrm{PAS}}\boldsymbol{R}^{-1}(\alpha,\beta,\gamma)$$

We only need to calculate the zz-component. With the given angles this is

$$\underset{\sim}{\sigma}^{\mathrm{LAB}} = \begin{pmatrix} \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \sigma_{11}/2 + \sigma_{33}/2 \end{pmatrix}$$

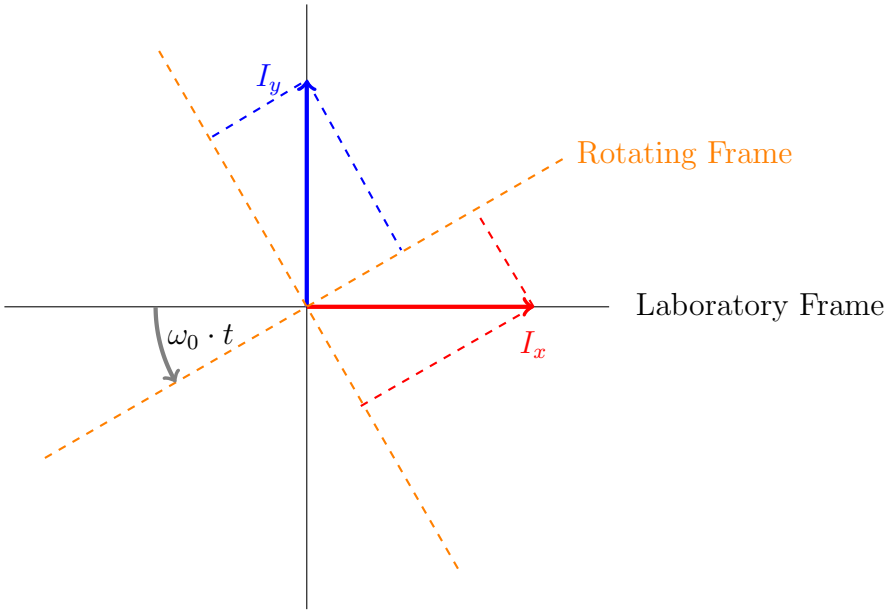

Figure 1: Illustration of the interaction-frame transformation (passive rotation).

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

$$\begin{aligned} A^{(\mathrm{lab})}_{2,m} &= \sum_{m'=-2}^{2} \mathfrak{D}^2_{m',m} \rho^{(\mathrm{PAS})}_{2,m'} \\ &= \mathfrak{D}^2_{-2,m} \rho^{(\mathrm{PAS})}_{2,-2} + \mathfrak{D}^2_{-1,m} \rho^{(\mathrm{PAS})}_{2,-1} + \mathfrak{D}^2_{0,m} \rho^{(\mathrm{PAS})}_{2,0} + \mathfrak{D}^2_{-1,m} \rho^{(\mathrm{PAS})}_{2,-1} + \mathfrak{D}^2_{-2,m} \rho^{(\mathrm{PAS})}_{2,-2} \end{aligned}$$

Note that this formula means that each of the five tensor components in the laboratory frame ($A^{(\mathrm{lab})}_{2,\pm 2}, A^{(\mathrm{lab})}_{2,\pm 1}, A^{(\mathrm{lab})}_{2,0}$) can be written as linear combination of the five tensor components in the principal axis system ($\rho^{(\mathrm{PAS})}_{2,\pm 2}, \rho^{(\mathrm{PAS})}_{2,\pm 1}, \rho^{(\mathrm{PAS})}_{2,0}$), 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 $\rho^{(\mathrm{PAS})}_{2,\pm 1} = 0$, 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 $\rho^{(\mathrm{PAS})}_{2,\pm 2} = -0.5\delta\eta = 0$ and we can drop them from the transformation formula. In summary, the rotation into the lab-frame becomes

$$A^{(\mathrm{lab})}_{2,m} = \mathfrak{D}^2_{0,m} \rho^{(\mathrm{PAS})}_{2,0} = d^2_{0,m}(\beta) e^{-i\gamma m} \sqrt{\frac{3}{2}} \delta \tag{1}$$

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 (1) and looking up the definition of the reduced Wigner rotation matrix elements for rank 2:

$$
\begin{aligned}
A_{2,\pm 2}^{(\mathrm{lab})} &= \frac{3\delta}{4}\sin^2(\beta)e^{\mp i2\gamma} \\
A_{2,\pm 1}^{(\mathrm{lab})} &= \pm\frac{\delta}{4}3\sin(2\beta)e^{\mp i\gamma} = \pm\frac{\delta}{2}3\sin(\beta)\cos(\beta)e^{\mp i\gamma} \\
A_{2,0}^{(\mathrm{lab})} &= \sqrt{\frac{3}{8}}\delta(3\cos^2(\beta)-1)
\end{aligned}
$$

2. The sum

$$
\hat{\mathcal{H}} = \sum_i \sum_l \sum_{m=-l}^{l} = (-1)^m A_{l,m}^{(\mathrm{lab})\ (\mathrm{i})}\hat{\mathfrak{T}}_{l,-m}^{(i)}
$$

can explicitly be written for one interaction i as $(l = 0, 1, 2)$

$$
\begin{aligned}
\hat{\mathcal{H}}^{(i)} =& (-1)^0 A_{0,0}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{0,0} \\
&+(-1)^{-1}A_{1,-1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{1,1} + (-1)^0 A_{1,0}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{1,0} + (-1)^1 A_{1,1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{1,-1} \\
&+(-1)^0 A_{2,0}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,0} + (-1)^{-1}A_{2,-1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,1} + (-1)^1 A_{2,1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,-1} + \\
&\ (-1)^{-2}A_{2,-2}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,2} + (-1)^2 A_{2,2}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,-2}.
\end{aligned}
$$

As discussed in the previous subproblem, only the contributions of the second-rank components need to be taken into account. Combining the spatial-part with the spin-part given in expression [3.116] in the lecture notes, one obtains:

$$
\begin{aligned}
\hat{\mathcal{H}} =& \sqrt{\frac{3}{8}}\delta(3\cos^2(\beta)-1)\frac{1}{\sqrt{6}}(2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y}) \\
&+ \frac{\delta}{2}3\sin(\beta)\cos(\beta)e^{i\gamma}\Big(-\frac{1}{2}(\hat{I}_1^+\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+)\Big) \\
&- \frac{\delta}{2}3\sin(\beta)\cos(\beta)e^{-i\gamma}\Big(\frac{1}{2}(\hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^-)\Big) \\
&+ \frac{3\delta}{4}\sin^2(\beta)e^{i2\gamma}\frac{1}{2}(\hat{I}_1^+\hat{I}_2^+) \\
&+ \frac{3\delta}{4}\sin^2(\beta)e^{-i2\gamma}\frac{1}{2}(\hat{I}_1^-\hat{I}_2^-)
\end{aligned}
$$

Using $\delta = -2\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r_{12}^3}$ this can be simplified:

$$\hat{\mathcal{H}} = -\frac{\mu_0\gamma_1\gamma_2\hbar}{4\pi r_{12}^3}\Big(\frac{3\cos^2(\beta)-1}{2}(2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y}) \\ - \frac{3\sin(\beta)\cos(\beta)e^{i\gamma}}{2}(\hat{I}_1^+\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^+) \\ - \frac{3\sin(\beta)\cos(\beta)e^{-i\gamma}}{2}(\hat{I}_1^-\hat{I}_{2z} + \hat{I}_{1z}\hat{I}_2^-) \\ + \frac{3\sin^2(\beta)e^{i2\gamma}}{2}(\frac{1}{2}\hat{I}_1^+\hat{I}_2^+) \\ + \frac{3\sin^2(\beta)e^{-i2\gamma}}{2}(\frac{1}{2}\hat{I}_1^-\hat{I}_2^-)\Big)$$

Care has to be taken when comparing this expression with the dipolar alphabet in the script since the dipolar alphabet is expressed in terms of θ and φ. The expressions in the script were obtained by passive rotation of the coordinate system while we actively rotated the tensor into the lab frame. This leads to a sign change in the rotation angles and, therefore, $\theta = -\beta$ and $\varphi = -\gamma$. Keeping that in mind, the expressions in the second and third line can be identified as the terms $\hat{C}$ and $\hat{D}$ of the dipolar alphabet and originate from the ±1-components of the second-rank interaction. In the last two rows, the ±2-components can be identified as the $\hat{E}$ and $\hat{F}$ terms of the dipolar alphabet.
The spin part of the remaining contribution to $\hat{\mathcal{H}}$, originating from the $q = 0$ components can be rewritten as

$$2\hat{I}_{1z}\hat{I}_{2z} - \hat{I}_{1x}\hat{I}_{2x} - \hat{I}_{1y}\hat{I}_{2y} = 2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2}(\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+)$$

yielding the remaining $\hat{A}$ and $\hat{B}$ terms of the alphabet.

Table 1: The dipolar alphabet and its relation to spherical tensor representation.

dipolar alphabet	origin
$\hat{A}$	$A_{2,0}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,0}$
$\hat{B}$	$A_{2,0}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,0}$
$\hat{C}$	$A_{2,-1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,1}$
$\hat{D}$	$A_{2,1}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,-1}$
$\hat{E}$	$A_{2,-2}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,2}$
$\hat{F}$	$A_{2,2}^{(\mathrm{lab})}\hat{\mathfrak{T}}_{2,-2}$

3. Mathematically, a transformation into the rotating frame involves a rotation about $\hat{F}_z = \sum_k \hat{I}_{kz}$. Only the terms $\hat{A}$ and $\hat{B}$ are proportional to the $\hat{\mathfrak{T}}_{2,0}$-spin tensor operator, which is invariant under such a rotation. Consequently, $\hat{A}$ and $\hat{B}$ do not become time-dependent in the rotating frame. All the other components $\hat{\mathfrak{T}}_{2,q}$, with $q = \pm1, \pm2$, will be modulated with a frequency $q\omega_0$ and are averaged out over one

period of ω_0.
This fact only holds true for a homonuclear dipolar-coupled system where we can replace the spin tensor operator $\hat{\mathfrak{T}}_{2,0}$ with $\hat{T}_{2,0}$. In the case of a heteronuclear dipolar-coupled system only the $\hat{T}^{(k)}_{1,0}$ and $\hat{T}^{(n)}_{1,0}$ are time-independent in the rotating frame and the $\hat{\mathfrak{T}}_{2,0}$ reduces to $\hat{T}^{(1)}_{1,0}\hat{T}^{(2)}_{1,0}$ which is equal to $\hat{I}_{1z}\hat{I}_{2z}$.

Problem 3: The Tensor Product

1. From
$$(k + k') \geq K \geq |k - k'|$$
$$Q = q + q'$$
we can see that for a product of rank one tensors $A_1 \otimes B_1$ one has to calculate nine components: $\mathfrak{I}_{00}, \mathfrak{I}_{10}, \mathfrak{I}_{1,\pm1}, \mathfrak{I}_{20}, \mathfrak{I}_{2,\pm1}, \mathfrak{I}_{2,\pm2}$. For $A_2 \otimes B_2$ there would be 25 elements to calculate.

2. We start by calculating the tensor component $\mathfrak{I}_{00}$ from the tensor product $A_1 \otimes B_1$. Inserting the component indices $K = 0$ and $Q = 0$ into the relation given on the exercise sheet, we can see that we have to calculate
$$\mathfrak{I}_{00}(1,1) = \sum_{q=-1}^{1} \sum_{q'=-1}^{1} \langle 11qq'|00\rangle \, A_{1q} B_{1q'}$$
In principle ,the sum of products gives nine possible combinations between A_{kq} and $B_{k'q'}$. However, keeping in mind that $Q = 0 = q + q'$, only the elements $A_{1,-1}B_{1,1}$, $A_{1,1}B_{1,-1}$ and $A_{1,0}B_{1,0}$ can remain, *i.e.*
$$\mathfrak{I}_{00}(1,1) = \langle 111-1|00\rangle \, A_{11}B_{1-1} + \langle 1100|00\rangle \, A_{10}B_{10} + \langle 11-11|00\rangle \, A_{1-1}B_{11}$$
The prefactors $\langle 11qq'|00\rangle$ are the Clebsch-Gordan coefficients, which can be taken from the provided table. The relevant part of the table for the $A_1 \otimes B_1$ is shown in Figure 2, which also illustrates the procedure to obtain the Clebsch-Gordan coefficients for the $\mathfrak{I}_{00}$ component, which are $1/\sqrt{3}, 1/\sqrt{3}$ and $-1/\sqrt{3}$, respectively.
Combining all results, we obtain the linear combination:
$$\mathfrak{I}_{00}(1,1) = \sqrt{\frac{1}{3}} A_{11}B_{1-1} - \sqrt{\frac{1}{3}} A_{10}B_{10} + \sqrt{\frac{1}{3}} A_{1-1}B_{11}$$
The same procedure can be used for
$$\mathfrak{I}_{20}(1,1) = \sum_{q=-1}^{1} \sum_{q'=-1}^{1} \langle 11qq'|20\rangle \, A_{1q} B_{1q'}$$
Also in this case, due to the $Q = 0 = q + q'$ condition, the sum reduces to:
$$\mathfrak{I}_{20}(1,1) = \langle 111-1|20\rangle \, A_{11}B_{1-1} + \langle 1100|20\rangle \, A_{10}B_{10} + \langle 11-11|20\rangle \, A_{1-1}B_{11}.$$

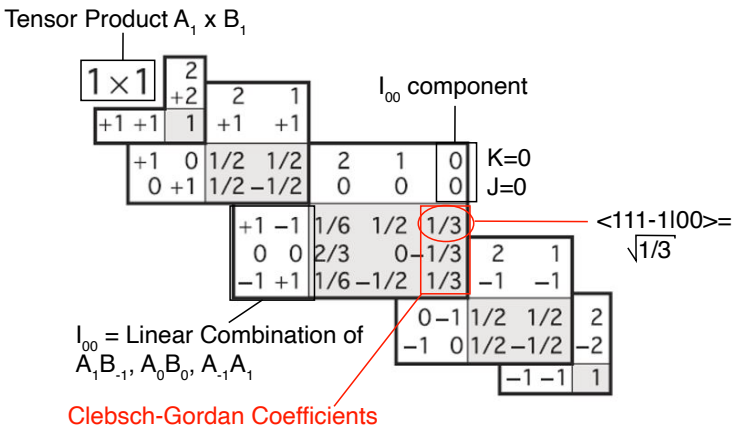

Figure 2: Table of relevant Clebsch-Gordon coefficients in order to create the second-rank tensor product $A_1 \otimes B_1$ and procedure to obtain the Clebsch-Gordan coefficients for the tensor component $\mathfrak{I}_{00}$.

The prefactors for the $A_{1,-1}B_{1,1}$, $A_{1,1}B_{1,-1}$ and $A_{1,0}B_{1,0}$ terms are again extracted from the Clebsch-Gordan table and we find:

$$\mathfrak{I}_{20}(1,1) = \sqrt{\frac{1}{6}}A_{11}B_{1-1} + \sqrt{\frac{2}{3}}A_{10}B_{10} + \sqrt{\frac{1}{6}}A_{1-1}B_{11}.$$