Problem Set 3: Rotations and Hamiltonians

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

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

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 corresponding coordinate system 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. Explain which terms can be neglected in the secular approximation.

4. The chemical-shift tensor of a carbon spin in its principal-axis system is given by

$$\underset{\sim}{\sigma}^{\mathrm{PAS}} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}.$$

   Calculate the chemical shift $(\underset{\sim}{\sigma}^{\mathrm{LAB}})_{zz}$ of the spin, if the principal-axis system and the laboratory system are related by the Euler angles $\alpha = 0°$, $\beta = 45°$, $\gamma = 45°$.

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

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

Usually, the spatial part of the spherical-tensor is given in the principal axis 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 ($A_{l,m}^{(\mathrm{lab})}$). A second-rank tensor characterized by the anisotropy δ and the asymmetry η has the following spherical-tensor elements in the PAS: $\rho_{2,0}^{(\mathrm{PAS})} = \sqrt{3/2}\delta$, $\rho_{2,\pm 1}^{(\mathrm{PAS})} = 0$, and $\rho_{2,\pm 2}^{(\mathrm{PAS})} = -0.5\delta\eta$. 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

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

Hint: 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. Starting from the first expression and the results from the previous problem, calculate the dipolar Hamiltonian. Show that the result is equivalent to the "dipolar alphabet" representation given in expression [3.41] in the lecture notes. Assign to the components $\hat{A}, \hat{B}, \hat{C}, \hat{D}, \hat{E}, \hat{F}$ the corresponding rank and order of the spin and spatial tensor.

   Hint: See expressions [3.114] to [3.116] in the lecture notes for spherical spin tensor operators.

3. Taking the transformation behavior of spherical tensors into account, give a reason why all components except $\hat{A}$ and $\hat{B}$ are neglected in the secular approximation.

Problem 3: The Tensor Product

The tensor product of two spherical tensors A_k and $B_{k'}$ of rank k and k' respectively, can be expressed with irreducible tensors $\mathfrak{I}_K$ that follow the relation

$$\begin{aligned} \mathfrak{I}_{KQ}(k,k') &= \sum_{q=-k}^{k} \sum_{q'=-k'}^{k'} \langle kk'qq'|KQ\rangle\, A_{kq}B_{k'q'} \\ &= (-1)^{k-k'+Q}\sqrt{2K+1}\sum_{q=-k}^{k} \sum_{q'=-k'}^{k'} \begin{pmatrix} k & k' & K \\ q & q' & Q \end{pmatrix} A_{kq}B_{k'q'} \end{aligned} \tag{1}$$

with

$$\langle kk'qq'|KQ\rangle\, A_{kq}B_{k'q'} = (-1)^{k-k'+Q}\sqrt{2K+1}\sum_{q=-k}^{k} \sum_{q'=-k'}^{k'} \begin{pmatrix} k & k' & K \\ q & q' & Q \end{pmatrix} \tag{2}$$

as the so-called Clebsch-Gordan coefficients and

$$\begin{gathered} (k+k') \geq K \geq |k-k'| \\ Q = q+q' \end{gathered} \quad . \tag{3}$$

1. Name all components $\mathfrak{I}_{KQ}$ of the product $A_1 \otimes B_1$. How many components would there be for $A_2 \otimes B_2$?

2. Calculate the results for $\mathfrak{I}_{00}$ and $\mathfrak{I}_{20}$ explicitly for a second-rank tensor product as a function of A_1 and B_1.
   Hint: Use the table provided to find the Clebsch-Gordan-coefficients.

36. CLEBSCH-GORDAN COEFFICIENTS, SPHERICAL HARMONICS, AND d FUNCTIONS

Note: A square-root sign is to be understood over *every* coefficient, *e.g.*, for $-8/15$ read $-\sqrt{8/15}$.

Notation:

		J	J	...
		M	M	...
m_1	m_2	Coefficients		
m_1	m_2			
.	.			

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\phi}$$

$$Y_2^0 = \sqrt{\frac{5}{4\pi}}\Big(\frac{3}{2}\cos^2\theta - \frac{1}{2}\Big)$$

$$Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\, e^{i\phi}$$

$$Y_2^2 = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{2i\phi}$$

$$Y_\ell^{-m} = (-1)^m Y_\ell^{m*}$$

$$d^\ell_{m,0} = \sqrt{\frac{4\pi}{2\ell+1}}\, Y_\ell^m\, e^{-im\phi}$$

$$\langle j_1 j_2 m_1 m_2 | j_1 j_2 J M\rangle = (-1)^{J-j_1-j_2}\langle j_2 j_1 m_2 m_1 | j_2 j_1 J M\rangle$$

1/2×1/2

m_1	m_2	1 +1
+1/2	+1/2	1

m_1	m_2	1 0	0 0
+1/2	−1/2	1/2	1/2
−1/2	+1/2	1/2	−1/2

m_1	m_2	1 −1
−1/2	−1/2	1

1×1/2

m_1	m_2	3/2 +3/2
+1	+1/2	1

m_1	m_2	3/2 +1/2	1/2 +1/2
+1	−1/2	1/3	2/3
0	+1/2	2/3	−1/3

m_1	m_2	3/2 −1/2	1/2 −1/2
0	−1/2	2/3	1/3
−1	+1/2	1/3	−2/3

m_1	m_2	3/2 −3/2
−1	−1/2	1

2×1

m_1	m_2	3 +3
+2	+1	1

m_1	m_2	3 +2	2 +2
+2	0	1/3	2/3
+1	+1	2/3	−1/3

m_1	m_2	3 +1	2 +1	1 +1
+2	−1	1/15	1/3	3/5
+1	0	8/15	1/6	−3/10
0	+1	2/5	−1/2	1/10

m_1	m_2	3 0	2 0	1 0
+1	−1	1/5	1/2	3/10
0	0	3/5	0	−2/5
−1	+1	1/5	−1/2	3/10

m_1	m_2	3 −1	2 −1	1 −1
0	−1	2/5	1/2	1/10
−1	0	8/15	−1/6	−3/10
−2	+1	1/15	−1/3	3/5

m_1	m_2	3 −2	2 −2
−1	−1	2/3	1/3
−2	0	1/3	−2/3

m_1	m_2	3 −3
−2	−1	1

1×1

m_1	m_2	2 +2
+1	+1	1

m_1	m_2	2 +1	1 +1
+1	0	1/2	1/2
0	+1	1/2	−1/2

m_1	m_2	2 0	1 0	0 0
+1	−1	1/6	1/2	1/3
0	0	2/3	0	−1/3
−1	+1	1/6	−1/2	1/3

m_1	m_2	2 −1	1 −1
0	−1	1/2	1/2
−1	0	1/2	−1/2

m_1	m_2	2 −2
−1	−1	1

2×1/2

m_1	m_2	5/2 +5/2
+2	+1/2	1

m_1	m_2	5/2 +3/2	3/2 +3/2
+2	−1/2	1/5	4/5
+1	+1/2	4/5	−1/5

m_1	m_2	5/2 +1/2	3/2 +1/2
+1	−1/2	2/5	3/5
0	+1/2	3/5	−2/5

m_1	m_2	5/2 −1/2	3/2 −1/2
0	−1/2	3/5	2/5
−1	+1/2	2/5	−3/5

m_1	m_2	5/2 −3/2	3/2 −3/2
−1	−1/2	4/5	1/5
−2	+1/2	1/5	−4/5

m_1	m_2	5/2 −5/2
−2	−1/2	1

3/2×1/2

m_1	m_2	2 +2
+3/2	+1/2	1

m_1	m_2	2 +1	1 +1
+3/2	−1/2	1/4	3/4
+1/2	+1/2	3/4	−1/4

m_1	m_2	2 0	1 0
+1/2	−1/2	1/2	1/2
−1/2	+1/2	1/2	−1/2

m_1	m_2	2 −1	1 −1
−1/2	−1/2	3/4	1/4
−3/2	+1/2	1/4	−3/4

m_1	m_2	2 −2
−3/2	−1/2	1

3/2×1

m_1	m_2	5/2 +5/2
+3/2	+1	1

m_1	m_2	5/2 +3/2	3/2 +3/2
+3/2	0	2/5	3/5
+1/2	+1	3/5	−2/5

m_1	m_2	5/2 +1/2	3/2 +1/2	1/2 +1/2
+3/2	−1	1/10	2/5	1/2
+1/2	0	3/5	1/15	−1/3
−1/2	+1	3/10	−8/15	1/6

m_1	m_2	5/2 −1/2	3/2 −1/2	1/2 −1/2
+1/2	−1	3/10	8/15	1/6
−1/2	0	3/5	−1/15	−1/3
−3/2	+1	1/10	−2/5	1/2

m_1	m_2	5/2 −3/2	3/2 −3/2
−1/2	−1	3/5	2/5
−3/2	0	2/5	−3/5

m_1	m_2	5/2 −5/2
−3/2	−1	1

$$d^j_{m',m} = (-1)^{m-m'} d^j_{m,m'} = d^j_{-m,-m'}$$

2×3/2

m_1	m_2	7/2 +7/2
+2	+3/2	1

m_1	m_2	7/2 +5/2	5/2 +5/2
+2	+1/2	3/7	4/7
+1	+3/2	4/7	−3/7

m_1	m_2	7/2 +3/2	5/2 +3/2	3/2 +3/2
+2	−1/2	1/7	16/35	2/5
+1	+1/2	4/7	1/35	−2/5
0	+3/2	2/7	−18/35	1/5

m_1	m_2	7/2 +1/2	5/2 +1/2	3/2 +1/2	1/2 +1/2
+2	−3/2	1/35	6/35	2/5	2/5
+1	−1/2	12/35	5/14	0	−3/10
0	+1/2	18/35	−3/35	−1/5	1/5
−1	+3/2	4/35	−27/70	2/5	−1/10

m_1	m_2	7/2 −1/2	5/2 −1/2	3/2 −1/2	1/2 −1/2
+1	−3/2	4/35	27/70	2/5	1/10
0	−1/2	18/35	3/35	−1/5	−1/5
−1	+1/2	12/35	−5/14	0	3/10
−2	+3/2	1/35	−6/35	2/5	−2/5

m_1	m_2	7/2 −3/2	5/2 −3/2	3/2 −3/2
0	−3/2	2/7	18/35	1/5
−1	−1/2	4/7	−1/35	−2/5
−2	+1/2	1/7	−16/35	2/5

m_1	m_2	7/2 −5/2	5/2 −5/2
−1	−3/2	4/7	3/7
−2	−1/2	3/7	−4/7

m_1	m_2	7/2 −7/2
−2	−3/2	1

3/2×3/2

m_1	m_2	3 +3
+3/2	+3/2	1

m_1	m_2	3 +2	2 +2
+3/2	+1/2	1/2	1/2
+1/2	+3/2	1/2	−1/2

m_1	m_2	3 +1	2 +1	1 +1
+3/2	−1/2	1/5	1/2	3/10
+1/2	+1/2	3/5	0	−2/5
−1/2	+3/2	1/5	−1/2	3/10

m_1	m_2	3 0	2 0	1 0	0 0
+3/2	−3/2	1/20	1/4	9/20	1/4
+1/2	−1/2	9/20	1/4	−1/20	−1/4
−1/2	+1/2	9/20	−1/4	−1/20	1/4
−3/2	+3/2	1/20	−1/4	9/20	−1/4

m_1	m_2	3 −1	2 −1	1 −1
+1/2	−3/2	1/5	1/2	3/10
−1/2	−1/2	3/5	0	−2/5
−3/2	+1/2	1/5	−1/2	3/10

m_1	m_2	3 −2	2 −2
−1/2	−3/2	1/2	1/2
−3/2	−1/2	1/2	−1/2

m_1	m_2	3 −3
−3/2	−3/2	1

2×2

m_1	m_2	4 +4
+2	+2	1

m_1	m_2	4 +3	3 +3
+2	+1	1/2	1/2
+1	+2	1/2	−1/2

m_1	m_2	4 +2	3 +2	2 +2
+2	0	3/14	1/2	2/7
+1	+1	4/7	0	−3/7
0	+2	3/14	−1/2	2/7

m_1	m_2	4 +1	3 +1	2 +1	1 +1
+2	−1	1/14	3/10	3/7	1/5
+1	0	3/7	1/5	−1/14	−3/10
0	+1	3/7	−1/5	−1/14	3/10
−1	+2	1/14	−3/10	3/7	−1/5

m_1	m_2	4 0	3 0	2 0	1 0	0 0
+2	−2	1/70	1/10	2/7	2/5	1/5
+1	−1	8/35	2/5	1/14	−1/10	−1/5
0	0	18/35	0	−2/7	0	1/5
−1	+1	8/35	−2/5	1/14	1/10	−1/5
−2	+2	1/70	−1/10	2/7	−2/5	1/5

m_1	m_2	4 −1	3 −1	2 −1	1 −1
+1	−2	1/14	3/10	3/7	1/5
0	−1	3/7	1/5	−1/14	−3/10
−1	0	3/7	−1/5	−1/14	3/10
−2	+1	1/14	−3/10	3/7	−1/5

m_1	m_2	4 −2	3 −2	2 −2
0	−2	3/14	1/2	2/7
−1	−1	4/7	0	−3/7
−2	0	3/14	−1/2	2/7

m_1	m_2	4 −3	3 −3
−1	−2	1/2	1/2
−2	−1	1/2	−1/2

m_1	m_2	4 −4
−2	−2	1

$$d^1_{0,0} = \cos\theta \qquad d^{1/2}_{1/2,1/2} = \cos\frac{\theta}{2} \qquad d^1_{1,1} = \frac{1+\cos\theta}{2}$$

$$d^{1/2}_{1/2,-1/2} = -\sin\frac{\theta}{2} \qquad d^1_{1,0} = -\frac{\sin\theta}{\sqrt{2}}$$

$$d^1_{1,-1} = \frac{1-\cos\theta}{2}$$

$$d^{3/2}_{3/2,3/2} = \frac{1+\cos\theta}{2}\cos\frac{\theta}{2}$$

$$d^{3/2}_{3/2,1/2} = -\sqrt{3}\frac{1+\cos\theta}{2}\sin\frac{\theta}{2} \qquad d^2_{2,2} = \Big(\frac{1+\cos\theta}{2}\Big)^2$$

$$d^{3/2}_{3/2,-1/2} = \sqrt{3}\frac{1-\cos\theta}{2}\cos\frac{\theta}{2} \qquad d^2_{2,1} = -\frac{1+\cos\theta}{2}\sin\theta$$

$$d^{3/2}_{3/2,-3/2} = -\frac{1-\cos\theta}{2}\sin\frac{\theta}{2} \qquad d^2_{2,0} = \frac{\sqrt{6}}{4}\sin^2\theta \qquad d^2_{1,1} = \frac{1+\cos\theta}{2}(2\cos\theta - 1)$$

$$d^{3/2}_{1/2,1/2} = \frac{3\cos\theta - 1}{2}\cos\frac{\theta}{2} \qquad d^2_{2,-1} = -\frac{1-\cos\theta}{2}\sin\theta \qquad d^2_{1,0} = -\sqrt{\frac{3}{2}}\sin\theta\cos\theta$$

$$d^{3/2}_{1/2,-1/2} = -\frac{3\cos\theta + 1}{2}\sin\frac{\theta}{2} \qquad d^2_{2,-2} = \Big(\frac{1-\cos\theta}{2}\Big)^2 \qquad d^2_{1,-1} = \frac{1-\cos\theta}{2}(2\cos\theta + 1) \qquad d^2_{0,0} = \Big(\frac{3}{2}\cos^2\theta - \frac{1}{2}\Big)$$

Figure 36.1: The sign convention is that of Wigner (*Group Theory*, Academic Press, New York, 1959), also used by Condon and Shortley (*The Theory of Atomic Spectra*, Cambridge Univ. Press, New York, 1953), Rose (*Elementary Theory of Angular Momentum*, Wiley, New York, 1957), and Cohen (*Tables of the Clebsch-Gordan Coefficients*, North American Rockwell Science Center, Thousand Oaks, Calif., 1974).