

Tutorial Session - Exercises

Problem 1: Dipolar Interaction in Water Molecules

The goal of this exercise is to calculate the dipolar ^1H spectrum of the protons in an isolated water molecule which does not move.

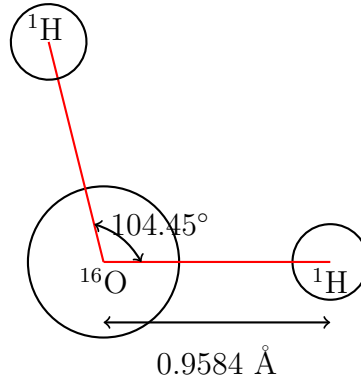


Figure 1: Molecular geometry of the water molecule.

$$\begin{aligned}
 \gamma_H &= 26.75 \cdot 10^7 \text{ rad} \cdot \text{s}^{-1} \text{T}^{-1} \\
 \gamma_T &= 28.53 \cdot 10^7 \text{ rad} \cdot \text{s}^{-1} \text{T}^{-1} \\
 \mu_0 &= 4\pi \cdot 10^{-7} \text{ Vs/Am} \\
 \hbar &= 1.05 \cdot 10^{-34} \text{ Js}
 \end{aligned}$$

The homonuclear dipolar coupling Hamiltonian is given by

$$\hat{H} = \underbrace{-\frac{\mu_0 \gamma_H^2 \hbar}{4\pi r^3}}_{\text{dipolar coupling constant}} \frac{3 \cos^2 \Theta - 1}{2} \left(2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2} (I_k^+ I_n^- + I_k^- I_n^+) \right). \quad (1)$$

1. Start with the single-spin operators in matrix representation and determine the matrix representation of the dipolar Hamiltonian. Calculate the Eigenvalues and allowed transitions. Also calculate the dipolar coupling constant.
2. Which orientation would a single isolated water molecule have to have with respect to an external field to show a maximum dipolar splitting? How big is the maximum splitting?
3. How does the spectrum of a powder-like sample containing water molecules in arbitrary orientations look like?
4. Which would be the longest ^1H - ^1H distance that could be detected by this experiment assuming a minimum spectral resolution of 100 Hz?

5. How large is the dipolar coupling if one of the protons is replaced by a tritium? What does the corresponding spectrum look like with respect to the homonuclear case?
6. Which interactions are present in the liquid state? What would the corresponding spectrum look like?

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

$$\hat{H} = \sum_l \sum_{q=-l}^l (-1)^q A_{l,q} T_{l,-q}$$

Starting from this expression, calculate the dipolar Hamiltonian (Hint: see additional expressions for the spherical tensors at the end of this exercise sheet). Show that the result is equivalent to the “dipolar alphabet” representation given as

$$\hat{H}_D^{(k,n)} = -\frac{\mu_0}{4\pi} \frac{\gamma_k \gamma_n \hbar}{r_{kn}^3} \left(\hat{A} + \hat{B} + \hat{C} + \hat{D} + \hat{E} + \hat{F} \right) \quad (2)$$

with

$$\begin{aligned} \hat{A} &= 2\hat{I}_{kz}\hat{I}_{nz} \frac{3\cos^2\Theta - 1}{2} \\ \hat{B} &= -\frac{1}{2} \left(\hat{I}_k^+ \hat{I}_n^- + \hat{I}_k^- \hat{I}_n^+ \right) \frac{3\cos^2\Theta - 1}{2} \\ \hat{C} &= \left(\hat{I}_k^+ \hat{I}_{nz} + \hat{I}_{kz} \hat{I}_n^+ \right) \frac{3\sin\Theta \cos\Theta e^{-i\varphi}}{2} \\ \hat{D} &= \left(\hat{I}_k^- \hat{I}_{nz} + \hat{I}_{kz} \hat{I}_n^- \right) \frac{3\sin\Theta \cos\Theta e^{i\varphi}}{2} \\ \hat{E} &= \frac{1}{2} \hat{I}_k^+ \hat{I}_n^+ \frac{3\sin^2\Theta e^{-2i\varphi}}{2} \\ \hat{F} &= \frac{1}{2} \hat{I}_k^- \hat{I}_n^- \frac{3\sin^2\Theta e^{2i\varphi}}{2}. \end{aligned} \quad (3)$$

Assign to the components A, B, C, D, E, F the corresponding rank and order of the spin and spatial tensor.

2. Taking into account that only the $q = 0$ components are invariant under z-rotation, give a reason why all components except A and B are neglected in the secular approximation.
3. Calculate $\hat{T}_{2,+2}^{(k,n)} = \frac{1}{2} \left(\hat{I}_k^+ \hat{I}_n^+ \right)$ explicitly in matrix form.

Problem 3: Single Crystals and MAS

The aim of this problem is to calculate the resonance frequency of a ^{13}C spin in the carbonyl group of an Alanine single crystal. The components of the chemical-shift tensor in the principle axis system are $\hat{\sigma}_{xx} = 239$ ppm, $\hat{\sigma}_{yy} = 184$ ppm and $\hat{\sigma}_{zz} = 106$ ppm. The orientation of the crystal is such that the vectors of the principle components lie along the x, y and z axis in the laboratory frame. The static magnetic field is along the laboratory z-axis ($\vec{B} \parallel \vec{e}_z$)

1. Calculate the isotropic chemical shift σ_{iso} .
2. Simplify general Hamiltonian describing the interaction of the chemical-shift tensor and the magnetic field, which is given as,

$$\hat{H} = \gamma \vec{I} \hat{\sigma} \vec{B} \quad (4)$$

and simplify it according to the high-field approximation.

3. The crystal is rotated from its original orientation by an angle γ around a rotation axis that has the polar coordinates $\phi = 0^\circ$ and $\theta = \cos^{-1}(1/\sqrt{3}) = 54.7356^\circ$. The matrix describing this rotation is given as

$$\mathbf{R}(\gamma) = \begin{pmatrix} \frac{1}{3}(2 + \cos \gamma) & -\frac{1}{\sqrt{3}} \sin \gamma & \frac{\sqrt{2}}{3}(1 - \cos \gamma) \\ \frac{1}{\sqrt{3}} \sin \gamma & \cos \gamma & -\sqrt{\frac{2}{3}} \sin \gamma \\ \frac{\sqrt{2}}{3}(1 - \cos \gamma) & \sqrt{\frac{2}{3}} \sin \gamma & \frac{1}{3}(1 + 2 \cos \gamma) \end{pmatrix} \quad (5)$$

Calculate $\hat{\sigma}'_{zz}(\gamma)$ and express the result in the form $\hat{\sigma}'_{zz}(\gamma) = \hat{\sigma}_{iso} + \hat{\sigma}_1 \cos(\gamma) + \hat{\sigma}_2 \cos(2\gamma)$. What does $\hat{\sigma}_{iso}$ correspond to? (Keep in mind that $\hat{\sigma}'(\gamma) = \mathbf{R}(\gamma) \hat{\sigma} \mathbf{R}(-\gamma)$)

4. Plot $\hat{\sigma}'_{zz}(\gamma)$ it as a function of γ . What happens if we rotate the sample continuously around the previously chosen axis (i.e. if $\gamma(t) = 2\pi\omega_r t$ where ω_r is the rotation frequency)?

Problem 4 (Optional): 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{J}_K that follow the relation

$$\begin{aligned}\mathfrak{J}_{KQ}(k, k') &= \sum_{q=-k}^k \sum_{q'=-k'}^{k'} \langle kk'qq'|KQ\rangle A_{kq}B_{k'q'} \\ &= (-1)^{k-k'+Q} \sqrt{2K+1} \sum_{q=-k}^k \sum_{q'=-k'}^{k'} \begin{pmatrix} k & k' & K \\ q & q' & Q \end{pmatrix} A_{kq}B_{k'q'}\end{aligned}\quad (6)$$

with

$$\langle kk'qq'|KQ\rangle A_{kq}B_{k'q'} = (-1)^{k-k'+Q} \sqrt{2K+1} \sum_{q=-k}^k \sum_{q'=-k'}^{k'} \begin{pmatrix} k & k' & K \\ q & q' & Q \end{pmatrix}\quad (7)$$

as the so-called Clebsch-Gordan coefficients and

$$\begin{aligned}(k+k') &\geq K \geq |k-k'| \\ Q &= q+q'\end{aligned}\quad (8)$$

1. Name all components \mathfrak{J}_{KQ} of the product $A_1 \otimes B_1$. How many components would there be for $A_2 \otimes B_2$?
2. As an example, verify that

$$\mathfrak{J}_{00} = \frac{1}{\sqrt{3}} (A_{1,-1}B_{1,1} + A_{1,1}B_{1,-1} - A_{1,0}B_{1,0})\quad (9)$$

$$\mathfrak{J}_{20} = \frac{1}{\sqrt{6}} (2A_{1,0}B_{1,0} + A_{1,1}B_{1,-1} + A_{1,-1}B_{1,1})\quad (10)$$

$$\hat{T}_{00}^{(k,n)} = \frac{-1}{\sqrt{3}}(\hat{I}_{kz}\hat{I}_{nz} + \frac{1}{2}\hat{I}_k^+\hat{I}_n^- + \frac{1}{2}\hat{I}_k^-\hat{I}_n^+) = \frac{-1}{\sqrt{3}}(\hat{\vec{I}}_k \cdot \hat{\vec{I}}_n)$$

$$A_{00} = -\sqrt{3}\bar{a}$$

$$A_{10} = -i\sqrt{2}[a_{xy}\cos\beta - (a_{xz}\sin\alpha - a_{yz}\cos\alpha)\sin\beta]$$

$$\hat{T}_{10}^{(k,n)} = \frac{-1}{2\sqrt{2}}(\hat{I}_k^+\hat{I}_n^- - \hat{I}_k^-\hat{I}_n^+)$$

$$A_{1,\pm 1} = e^{\mp i\gamma}[(a_{xz} \pm ia_{yz}\cos\beta)\cos\alpha + (a_{yz} \mp ia_{xz}\cos\beta)\sin\alpha \mp ia_{xy}\sin\beta]$$

$$\hat{T}_{1,\pm 1}^{(k,n)} = \frac{-1}{2}(\hat{I}_k^{\pm}\hat{I}_{nz} - \hat{I}_{kz}\hat{I}_n^{\pm})$$

$$A_{20} = \sqrt{\frac{3}{8}}\delta[(3\cos^2\beta - 1) - \eta\sin^2\beta\cos(2\alpha)]$$

$$\hat{T}_{20}^{(k,n)} = \frac{1}{\sqrt{6}}[3\hat{I}_{kz}\hat{I}_{nz} - (\hat{\vec{I}}_k \cdot \hat{\vec{I}}_n)]$$

$$A_{2,\pm 1} = \pm \frac{\delta}{2}\sin\beta e^{\mp i\gamma}[(3 + \eta\cos(2\alpha))\cos\beta \mp i\eta\sin(2\alpha)]$$

$$\hat{T}_{2,\pm 1}^{(k,n)} = \frac{1}{\mp 2}(\hat{I}_k^{\pm}\hat{I}_{nz} + \hat{I}_{kz}\hat{I}_n^{\pm})$$

$$A_{2,\pm 2} = \frac{\delta}{2}e^{\mp i2\gamma}\left[\frac{3}{2}\sin^2\beta - \frac{\eta}{2}(1 + \cos^2\beta)\cos(2\alpha) \pm i\eta\cos\beta\sin(2\alpha)\right]$$

$$\hat{T}_{2,\pm 2}^{(k,n)} = \frac{1}{2}(\hat{I}_k^{\pm}\hat{I}_n^{\pm})$$

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	
\vdots	\vdots	
\vdots	\vdots	

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

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

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

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

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

$2 \times 1/2$

$3/2 \times 1/2$

2×1

1×1

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

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

$(j_1 j_2 m_1 m_2 j_1 j_2 J M)$	
$= (-1)^{J-j_1-j_2} (j_2 j_1 m_2 m_1 j_2 j_1 J M)$	

$d_{m',m}^j = (-1)^{m-m'} d_{m,m'}^j = d_{-m,-m'}^j$

$d_{0,0}^1 = \cos \theta$

$d_{1/2,1/2}^{1/2} = \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{1/2} = -\sin \frac{\theta}{2}$

$d_{1,1}^1 = \frac{1 + \cos \theta}{2}$

$d_{1,0}^1 = -\frac{\sin \theta}{\sqrt{2}}$

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

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

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

$d_{3/2,-1/2}^{3/2} = \sqrt{3} \frac{1 - \cos \theta}{2} \cos \frac{\theta}{2}$

$d_{3/2,-3/2}^{3/2} = -\frac{1 - \cos \theta}{2} \sin \frac{\theta}{2}$

$d_{1/2,1/2}^{3/2} = \frac{3 \cos \theta - 1}{2} \cos \frac{\theta}{2}$

$d_{1/2,-1/2}^{3/2} = -\frac{3 \cos \theta + 1}{2} \sin \frac{\theta}{2}$

$d_{2,2}^2 = \left(\frac{1 + \cos \theta}{2} \right)^2$

$d_{2,1}^2 = -\frac{1 + \cos \theta}{2} \sin \theta$

$d_{2,0}^2 = \frac{\sqrt{6}}{4} \sin^2 \theta$

$d_{2,-1}^2 = -\frac{1 - \cos \theta}{2} \sin \theta$

$d_{2,-2}^2 = \left(\frac{1 - \cos \theta}{2} \right)^2$

$d_{1,1}^2 = \frac{1 + \cos \theta}{2} (2 \cos \theta - 1)$

$d_{1,0}^2 = -\sqrt{\frac{3}{2}} \sin \theta \cos \theta$

$d_{1,-1}^2 = \frac{1 - \cos \theta}{2} (2 \cos \theta + 1)$

$d_{0,0}^2 = \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)$

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).