Advanced Magnetic Resonance HS 2025

Problem Set 1: PCIV Recapitulation

Pre-Discussion: 17.09.2025
Post-Discussion: 24.09.2025

Goal: The goal of this excercise is to recapitulate some of the main concepts from the lecture *PCIV: Magnetic Resonance*, which will be used and discussed in much more detail during the AMR course. The material treated can be found in chapters 4.7, 4.8, 4.9, 5.2, 5.3, 5.4.4-5.4.5, 5.6, 5.8, 8.2, 8.3 of the PCIV script and chapter 1 of the AMR script.

Problem 1: General Repetition Questions

1. Give two advantages of going into an interaction frame with respect to the Zeeman interaction. What is the secular approximation? Can we always perform it? Write down the expression of the Hamiltonian of a homonuclear J-coupled two-spin system with chemical shifts Ω_1, Ω_2 in the liquid state both in the lab frame and in the interaction frame under the high-field approximation. Are homonuclear and heteronuclear spin systems identical?
2. Assuming that the high-field approximation holds exactly. Write down the expression for the heteronuclear and the homonuclear dipolar Hamiltonian using the dipolar alphabet. Why does the heteronuclear case involve only $\hat{A}$, while the homonuclear case involves both terms $\hat{A} + \hat{B}$? (hint: look at the definitions of $\hat{A}, \hat{B}, \hat{C}, \hat{D}, \hat{E}, \hat{F}$).
3. Why is it convenient to introduce the density operator $\hat{\rho}$ in NMR instead of using a wavefunction formulation?
4. Write down the Liouville von-Neumann equation. What does it describe? We can always find an easy solution to the Liouville von-Neumann equation, when the Hamiltonian describing the system is *time-independent*. Give an example of a Hamiltonian which is not time-independent.

Problem 2: Dipolar Interaction in Water Molecules

In this exercise our final goal is to calculate the dipolar ^{1}H spectrum of the protons in an isolated water molecule which is fixed in space.
Useful constants:

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

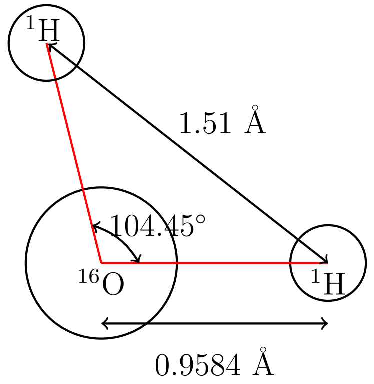

Figure 1: Molecular geometry of the water molecule.

The homonuclear dipolar coupling Hamiltonian (under the high-field approximation) is given by

$$\hat{H} = -\underbrace{\frac{\mu_0 \gamma^2 \hbar}{4\pi r^3}}_{=d} \frac{3\cos^2\Theta - 1}{2} \underbrace{\left(2\hat{I}_{1z}\hat{I}_{2z} - \frac{1}{2}\left(\hat{I}_1^+\hat{I}_2^- + \hat{I}_1^-\hat{I}_2^+\right)\right)}_{\text{spin part}}, \tag{1}$$

where γ denotes the gyromagnetic ratio of the interacting spin, r the internuclear distance, θ the angle between the internuclear vector and the external magnetic field.

1. Start with the single-spin operators in matrix representation (2×2 Pauli matrices for $\hat{I}_x, \hat{I}_y, \hat{I}_z$) in the uncoupled basis and determine the 4×4 matrix representation of the spin part of the dipolar Hamiltonian.
   Rmk: - Remember that the raising and lowering operators can be constructed according to $\hat{I}^+ = \hat{I}_x + i\hat{I}_y$ and $\hat{I}^- = \hat{I}_x - i\hat{I}_y$.
   - The matrix representation of a two-spin operator of the form $\hat{I}_{1z}\hat{I}_{2z}$ is obtained, by calculating the direct product between the matrices of the single-spin operators $\hat{I}_{1z} \otimes \hat{I}_{2z}$ (the simple rule for calculating a direct product between matrices can be found in chapter 5.6 of the PCIV script).

2. Calculate the Eigenvalues λ_i of the Hamiltonian by diagonalizing the obtained matrix. The resonance frequencies of the NMR transitions between states i and k can be computed by taking differences between the corresponding Eigenvalues $\omega_{ik} = \lambda_i - \lambda_k$. Calculate the frequencies for all *allowed* transitions. How much is the splitting between the two lines calculated in the previous exercise? How is it related to the dipolar coupling constant? Calculate the dipolar coupling constant. Use units of Hertz and note that the Hamiltonian is in Hertz·rad.

   Hint 1: The Eigenfunctions of the Hamiltonian are given by:

$$\phi_1 = |\alpha\alpha\rangle, \quad \phi_2 = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle + |\beta\alpha\rangle), \quad \phi_4 = |\beta\beta\rangle$$

$$\phi_3 = \frac{1}{\sqrt{2}}(|\alpha\beta\rangle - |\beta\alpha\rangle) \tag{2}$$

   Only transitions between states $1 \rightarrow 2$ *and* $2 \rightarrow 4$ *are allowed in this specific case.*

Hint 2: Diagonalizing the matrix, one should find the eigenvalues $1/2, -1, 1/2, 0$, which correspond to states 1,2,4 and 3 respectively.

3. Show that the $1 \to 2$ and $2 \to 4$ transitions are indeed the only allowed transitions. To do that, take the matrix representation of the detection operator $\hat{F}_x = \hat{I}_{1x} + \hat{I}_{2x}$ and transform it into the eigenbasis of the Hamiltonian: $\hat{F}'_x = \hat{U}\hat{F}_x\hat{U}^{-1}$. The allowed transitions correspond to non-vanishing off-diagonal elements. The transformation matrix $\hat{U}$ has as columns the eigenvectors given in equation (2).

   Can you find simple arguments for these selection rules by using the coupled basis of the group spin? (without needing to perform the lengthy matrix multiplication)

4. Which orientation would a single isolated water molecule have with respect to an external field to show a maximum dipolar splitting? How big is the maximum splitting?

5. How does the spectrum of a powder-like sample containing many water molecules in arbitrary orientation look like?

6. 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?

7. Now the molecules tumble fast and isotropically. How does the spectrum look like? (ignore effects coming from any form of J-coupling)

Problem 3: In-Phase/Anti-Phase

The terms 'In-Phase' and 'Anti-Phase' are often used to describe certain operator products in two-spin systems. In such a system the states evolve under the Hamiltonian $\mathscr{H}'' = \Omega_1\hat{I}_{1z} + \Omega_2\hat{I}_{2z} + 2\pi J_{12}\hat{I}_{1z}\hat{I}_{2z}$.

1. Calculate by product operator formalism what happens if you let the state $\hat{I}_{1x}$ evolve for a time t under such a Hamiltonian. How does the magnetisation in x- and y-direction behave? Give an expression for the signal after the evolution time t.

   Hint: Our detection operator is $\hat{I}_1^+ = \hat{I}_{1x} + i\hat{I}_{1y}$. Furthermore the identities $\cos(x) + i\sin(x) = e^{ix}$ and $\cos(x) = \frac{1}{2}[e^{ix} + e^{-ix}]$ will be useful.

2. Repeat these steps for the term $2\hat{I}_{1x}\hat{I}_{2z}$.

3. Why is the term $2\hat{I}_{1x}\hat{I}_{2z}$ called 'Anti-phase' while $\hat{I}_{1x}$ is called 'In-phase'?

   Hint: Remember what happens to the signal upon Fourier Transformation.

4. In which case is it not possible to apply the product operator formalism and why not? Give an example of such a spin system.