

## Lecture 12: Liquid state NMR Hamiltonian

### 1. Zeeman interaction terms

The primary interaction that influences a nuclear spin in a strong magnetic field is the *Zeeman interaction*. Assuming that the field  $\vec{B}$  is directed along the Z axis, the spin Hamiltonian follows from the classical expression for the energy of a magnetic dipole:

$$E = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z \Rightarrow \mathbf{H} = -\gamma B_z \mathbf{S}_z \quad (1)$$

where we have used the fact that  $\mu_z = \gamma \mathbf{S}_z$ . After the chemical shift correction to the *Larmor frequency* is introduced and all nuclei in the system are summed over, we obtain:

$$\mathbf{H}_Z = \sum_k \omega_k \mathbf{S}_z^{(k)}, \quad \omega_k = -\gamma_k (1 + \delta_k) B_z \quad (2)$$

where  $\gamma_k$  is the *magnetogyric ratio* of the  $k$ -th nucleus,  $\delta_k$  is its *chemical shift*, and the index  $k$  runs over all nuclei in the system. Strictly speaking, chemical shift is orientation-dependent, but rapid molecular tumbling in non-viscous liquids averages out the anisotropy. The dependence of the chemical shift on the molecular structure has been covered in your various chemistry courses.

**Example 1:** build the matrix representation of the Zeeman Hamiltonian of a two-spin system using the following basis set:  $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ .

**Solution:** for a two-spin system, the Zeeman Hamiltonian is

$$\mathbf{H}_Z = \omega_1 \mathbf{S}_z^{(1)} + \omega_2 \mathbf{S}_z^{(2)}$$

From the properties of spin operators, we know how  $\mathbf{S}_z$  acts on the individual spin states:

$$\mathbf{S}_z |\alpha\rangle = \frac{1}{2} |\alpha\rangle, \quad \mathbf{S}_z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

We also know that the spin states are orthonormal:

$$\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1 \quad \langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$$

This allows us to calculate all matrix elements of the Hamiltonian:

$$\begin{aligned} \langle\alpha\alpha|\mathbf{H}_Z|\alpha\alpha\rangle &= \frac{\omega_1 + \omega_2}{2} & \langle\alpha\beta|\mathbf{H}_Z|\alpha\beta\rangle &= \frac{\omega_1 - \omega_2}{2} \\ \langle\beta\alpha|\mathbf{H}_Z|\beta\alpha\rangle &= \frac{-\omega_1 + \omega_2}{2} & \langle\beta\beta|\mathbf{H}_Z|\beta\beta\rangle &= \frac{-\omega_1 - \omega_2}{2} \end{aligned}$$

and the rest are zero. The resulting matrix is:

$$\mathbf{H}_Z = \begin{pmatrix} \frac{\omega_1 + \omega_2}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_1 - \omega_2}{2} & 0 & 0 \\ 0 & 0 & \frac{-\omega_1 + \omega_2}{2} & 0 \\ 0 & 0 & 0 & \frac{-\omega_1 - \omega_2}{2} \end{pmatrix}$$

The same Hamiltonian may be more conveniently built using *Kronecker product* relations that use the fact that every possible combination turns up when spins are brought together:

$$\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \otimes \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} \alpha\alpha \\ \alpha\beta \\ \beta\alpha \\ \beta\beta \end{pmatrix} \quad \mathbf{A} \otimes \mathbf{B} = \begin{pmatrix} a_{11}\mathbf{B} & a_{12}\mathbf{B} & \cdots \\ a_{21}\mathbf{B} & a_{22}\mathbf{B} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \quad (3)$$

What makes this useful is the fact that Kronecker product commutes with regular matrix product:

$$(\mathbf{A} \otimes \mathbf{B})(\mathbf{C} \otimes \mathbf{D}) = (\mathbf{AC}) \otimes (\mathbf{BD}) \quad (4)$$

and thus an operator  $\mathbf{A} \otimes \mathbf{B}$  acts with  $\mathbf{A}$  in the first spin and with  $\mathbf{B}$  on the second spin. Therefore, the two-spin Zeeman Hamiltonian is built as follows:

$$\begin{aligned} \mathbf{H}_Z &= \omega_1 (\mathbf{S}_Z \otimes \mathbf{1}) + \omega_2 (\mathbf{1} \otimes \mathbf{S}_Z) = \\ &= \omega_1 \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \omega_2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \end{aligned} \quad (5)$$

from the elementary 2x2 spin operators and the 2x2 unit matrix.

## 2. J-coupling terms

The J-coupling Hamiltonian between two spins has the following form:

$$\mathbf{H}_J = 2\pi J (\mathbf{L}_X \otimes \mathbf{S}_X + \mathbf{L}_Y \otimes \mathbf{S}_Y + \mathbf{L}_Z \otimes \mathbf{S}_Z) \quad (6)$$

where  $\{\mathbf{L}_X, \mathbf{L}_Y, \mathbf{L}_Z\}$  and  $\{\mathbf{S}_X, \mathbf{S}_Y, \mathbf{S}_Z\}$  are single-spin operators of appropriate dimensions. In chemical literature, Kronecker product symbols in this equation are commonly abbreviated away:

$$\mathbf{H}_J = 2\pi J (\mathbf{L}_X \mathbf{S}_X + \mathbf{L}_Y \mathbf{S}_Y + \mathbf{L}_Z \mathbf{S}_Z) \quad (7)$$

The  $\mathbf{L}_X \mathbf{S}_X + \mathbf{L}_Y \mathbf{S}_Y$  part of this Hamiltonian has a non-negligible effect (*strong coupling*) when  $|2\pi J|$  is comparable to the Zeeman frequency separation  $|\omega_L - \omega_S|$ ; in high-field NMR this only happens when the spins belong to the same isotope type and have similar chemical shifts.

When  $|\omega_L - \omega_S| \gg |2\pi J|$  (different isotopes or big chemical shift difference),  $\mathbf{L}_X \mathbf{S}_X + \mathbf{L}_Y \mathbf{S}_Y$  terms have no effect because spins move very rapidly relative to each other in the transverse plane, and these terms average out. In that case, only  $\mathbf{L}_Z \mathbf{S}_Z$  has an influence (*weak coupling*):

$$\mathbf{H}_J = 2\pi J \mathbf{L}_Z \mathbf{S}_Z \quad (8)$$

In Eqs (6)-(8),  $J$  is the coupling coefficient, measured conventionally in Hz. Nuclear spin Hamiltonians use angular frequency units, hence the factor of  $2\pi$  in front.

**Example 2:** build the matrix representation of the liquid state NMR Hamiltonian of a J-coupled two-spin system using the following basis set:  $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ .

**Solution:** for a two-spin system, the liquid state NMR Hamiltonian is

$$\mathbf{H} = \omega_L \mathbf{L}_Z + \omega_S \mathbf{S}_Z + 2\pi J (\mathbf{L}_X \mathbf{S}_X + \mathbf{L}_Y \mathbf{S}_Y + \mathbf{L}_Z \mathbf{S}_Z)$$

Building the matrix element by element would take a long time here, and we shall therefore make use of the direct product formulas for the operators of the two-spin system:

$$\mathbf{H} = \omega_L \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \omega_S \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} +$$

$$+ 2\pi J \begin{bmatrix} \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & 1/2 \\ 1/2 & 0 \end{pmatrix} + \\ \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} \otimes \begin{pmatrix} 0 & -i/2 \\ i/2 & 0 \end{pmatrix} + \\ \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \otimes \begin{pmatrix} 1/2 & 0 \\ 0 & -1/2 \end{pmatrix} \end{bmatrix}$$

Doing the necessary arithmetic yields the following matrix for the strong  $J$ -coupling:

$$\mathbf{H} = \begin{pmatrix} \frac{\omega_L + \omega_S}{2} + \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_L - \omega_S}{2} - \frac{\pi J}{2} & \pi J & 0 \\ 0 & \pi J & \frac{-\omega_L + \omega_S}{2} - \frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{-\omega_L - \omega_S}{2} + \frac{\pi J}{2} \end{pmatrix}$$

and the following matrix for the weak  $J$ -coupling:

$$\mathbf{H} = \begin{pmatrix} \frac{\omega_L + \omega_S}{2} + \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_L - \omega_S}{2} - \frac{\pi J}{2} & 0 & 0 \\ 0 & 0 & \frac{-\omega_L + \omega_S}{2} - \frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{-\omega_L - \omega_S}{2} + \frac{\pi J}{2} \end{pmatrix}$$

The energy level diagrams for a two-spin system without  $J$ -coupling (left) and with a weak  $J$ -coupling (right) are shown in Figure 1.

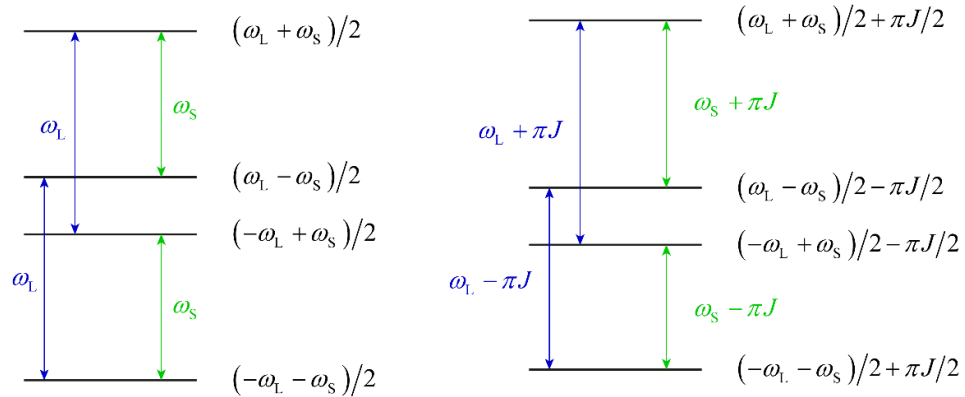


**Figure 1.** Energy level diagrams for an uncoupled (*left*) and weakly  $J$ -coupled (*right*) two-spin systems.

### 3. Roof effect in strong $J$ -coupling

The presence of  $\mathbf{L}_X\mathbf{S}_X + \mathbf{L}_Y\mathbf{S}_Y$  component leaves the outer energy levels unchanged, but the inner two levels mix. The result (after a lot of mathematics that we shall skip) is a change in the intensity of the four transitions (Figure 2). This is colloquially called the *roof effect*.

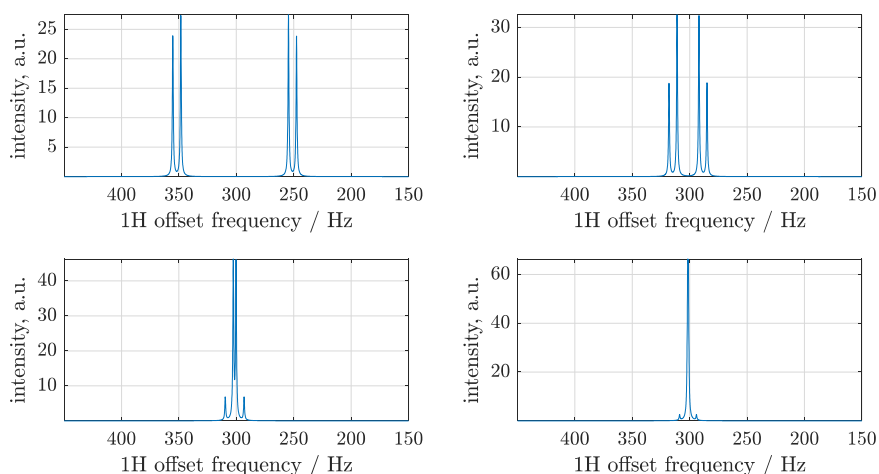


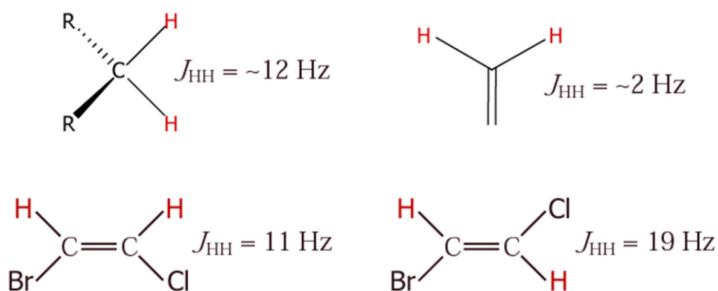
**Figure 2.** Spinach simulation of the effect of the  $XX$  and the  $YY$  terms in Equation (6) on the relative intensities of the NMR lines in a strongly coupled  $AB$  spin system. The system contains two protons with a  $J$ -coupling of 7.0 Hz in a 250 MHz NMR magnet. The difference in chemical shifts is: (**top left**) 0.2 ppm, (**top right**) 0.05 ppm, (**bottom left**) 0.0125 ppm, (**bottom right**) 0.00625 ppm.

### 4. Spin system classification

Because the pattern of  $J$ -couplings depends on the frequency separation between the spins, spin systems are classified by the frequency separation between their constituent spins. Any spins that are close together in frequency are denoted by letters that are close together in the alphabet, *e.g.*  $AB$  designates a strongly coupled spin system and  $AX$  a weakly coupled one.

### 5. $J$ -couplings and chemical structure

Because  $J$ -couplings are mediated by electrons, they are sensitive to the local molecular structure and depend on the number of chemical bonds that separates the atoms. The amplitude of  $J$ -coupling generally decreases with the number of bonds; they are rarely measurable across more than five bonds.



Systems with heavier nuclei tend to have larger  $J$ -couplings:

| $^1J$                             |                        | $^1J_{CH}$             |        |
|-----------------------------------|------------------------|------------------------|--------|
| $^{195}\text{Pt}-^{195}\text{Pt}$ | $\sim 9000 \text{ Hz}$ | $\text{C}_2\text{H}_6$ | 125 Hz |
| $^{195}\text{Pt}-^1\text{H}$      | $\sim 1000 \text{ Hz}$ | $\text{C}_2\text{H}_4$ | 156 Hz |
| $^{13}\text{C}-^1\text{H}$        | $\sim 150 \text{ Hz}$  | $\text{C}_2\text{H}_2$ | 249 Hz |

In flexible molecules, the extent of orbital overlap depends on the conformation, and therefore three-bond  $J$ -couplings in aliphatic chains depend on dihedral angles (*Karplus relation*):

$$J(\theta) = A \cos 2\theta + B \cos \theta + C \quad (9)$$

where  $\theta$  is the dihedral angle and  $\{A, B, C\}$  are parameters that depend on the substituents and other features of the local chemical environment.

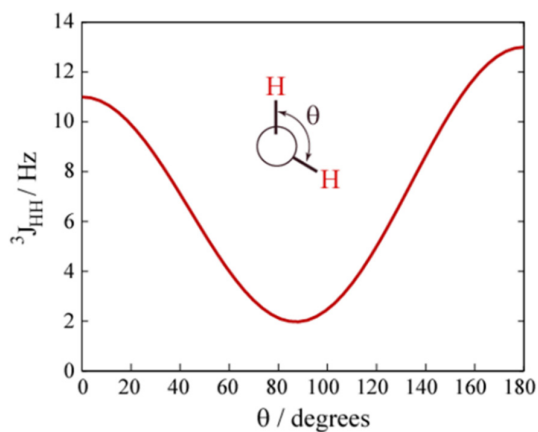


**Figure 3.** A plot of the dihedral angle dependence of the three-bond inter-proton  $J$ -coupling in an H-C-C-H fragment of an aliphatic chain.