

1. Zeeman interaction terms

The primary interaction that influences the spin that is placed into a strong magnetic field is the Zeeman interaction. Assuming that the field is directed along the Z axis, the Hamiltonian is:

$$\hat{H}_Z = \sum_k \omega_k \hat{S}_Z^{(k)}, \quad \omega_k = -\gamma_k (1 + \delta_k) B_0 \quad (1)$$

where B_0 is the applied magnetic field, γ_k is the magnetogyric ratio of the k -th nucleus, δ_k is its chemical shift, and the index k runs over all nuclei in the system.

Strictly speaking, chemical shift is anisotropic, but the presence of rapid molecular tumbling in liquid state NMR usually averages out the anisotropy. The dependence of the chemical shift on the molecular structure has been well covered in your various organic 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

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

From the properties of spin operators, we know how \hat{S}_Z acts on the individual spin states:

$$\hat{S}_Z |\alpha\rangle = \frac{1}{2} |\alpha\rangle \quad \hat{S}_Z |\beta\rangle = -\frac{1}{2} |\beta\rangle$$

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:

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

and the rest are zero. The resulting matrix is:

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

The same matrix may also be built from Pauli matrices using the direct product structure of the operators that appear in the Hamiltonian:

$$\hat{H}_Z = \omega_1 \hat{\sigma}_Z \otimes \mathbf{1} + \omega_2 \mathbf{1} \otimes \hat{\sigma}_Z$$

2. J -coupling terms

The J -coupling Hamiltonian between spin L and spin S has the following form:

$$\hat{H}_J = 2\pi J \left[\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y + \hat{L}_Z \hat{S}_Z \right] \quad (2)$$

when the interacting spins belong to the same nuclear type (*strong coupling*) and the following form

$$\hat{H}_J = 2\pi J \left[\hat{L}_Z \hat{S}_Z \right] \quad (3)$$

when the interacting spins belong to different nuclear types (*weak coupling*). In both expressions, J is the interaction amplitude, measured conventionally in Hz. Nuclear spin Hamiltonians use angular frequency units, hence the factor of 2π in front. Weak J -coupling appears when the difference in the Zeeman frequencies of the two spins is much greater than J . In that case, the spins move too rapidly relative to one another for the $\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y$ term to have an effect, and it may be dropped.

Example 2: build the matrix representation of the liquid state NMR 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 liquid state NMR Hamiltonian is

$$\hat{H} = \omega_1 \hat{L}_Z + \omega_2 \hat{S}_Z + 2\pi J \left[\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y + \hat{L}_Z \hat{S}_Z \right]$$

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 individual operators:

$$\hat{H}_Z = \omega_1 \hat{\sigma}_Z \otimes \mathbf{1} + \omega_2 \mathbf{1} \otimes \hat{\sigma}_Z + 2\pi J \left[\hat{\sigma}_X \otimes \hat{\sigma}_X + \hat{\sigma}_Y \otimes \hat{\sigma}_Y + \hat{\sigma}_Z \otimes \hat{\sigma}_Z \right]$$

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

$$\hat{H} = \begin{pmatrix} \frac{\omega_A + \omega_X}{2} + \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_A - \omega_X}{2} - \frac{\pi J}{2} & \pi J & 0 \\ 0 & \pi J & \frac{-\omega_A + \omega_X}{2} - \frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{-\omega_A - \omega_X}{2} + \frac{\pi J}{2} \end{pmatrix}$$

and the following matrix for the weak J -coupling:

$$\hat{H} = \begin{pmatrix} \frac{\omega_A + \omega_X}{2} + \frac{\pi J}{2} & 0 & 0 & 0 \\ 0 & \frac{\omega_A - \omega_X}{2} - \frac{\pi J}{2} & 0 & 0 \\ 0 & 0 & \frac{-\omega_A + \omega_X}{2} - \frac{\pi J}{2} & 0 \\ 0 & 0 & 0 & \frac{-\omega_A - \omega_X}{2} + \frac{\pi J}{2} \end{pmatrix}$$

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.

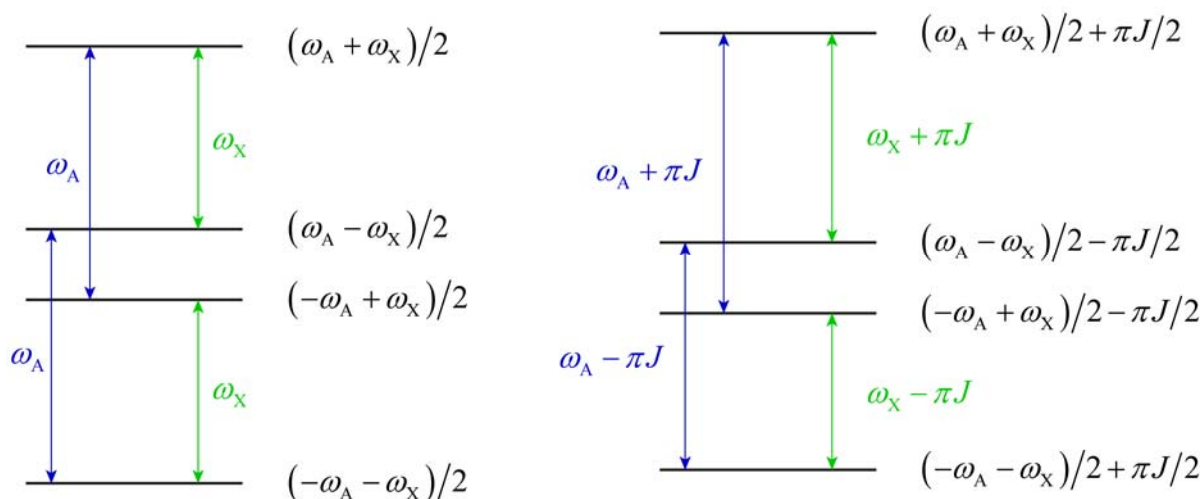


Figure 1. Energy level diagrams for an uncoupled (left) weakly J-coupled (right) AX spin systems.

3. Roof effect

The presence of $\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y$ 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 referred to as the *roof effect*.

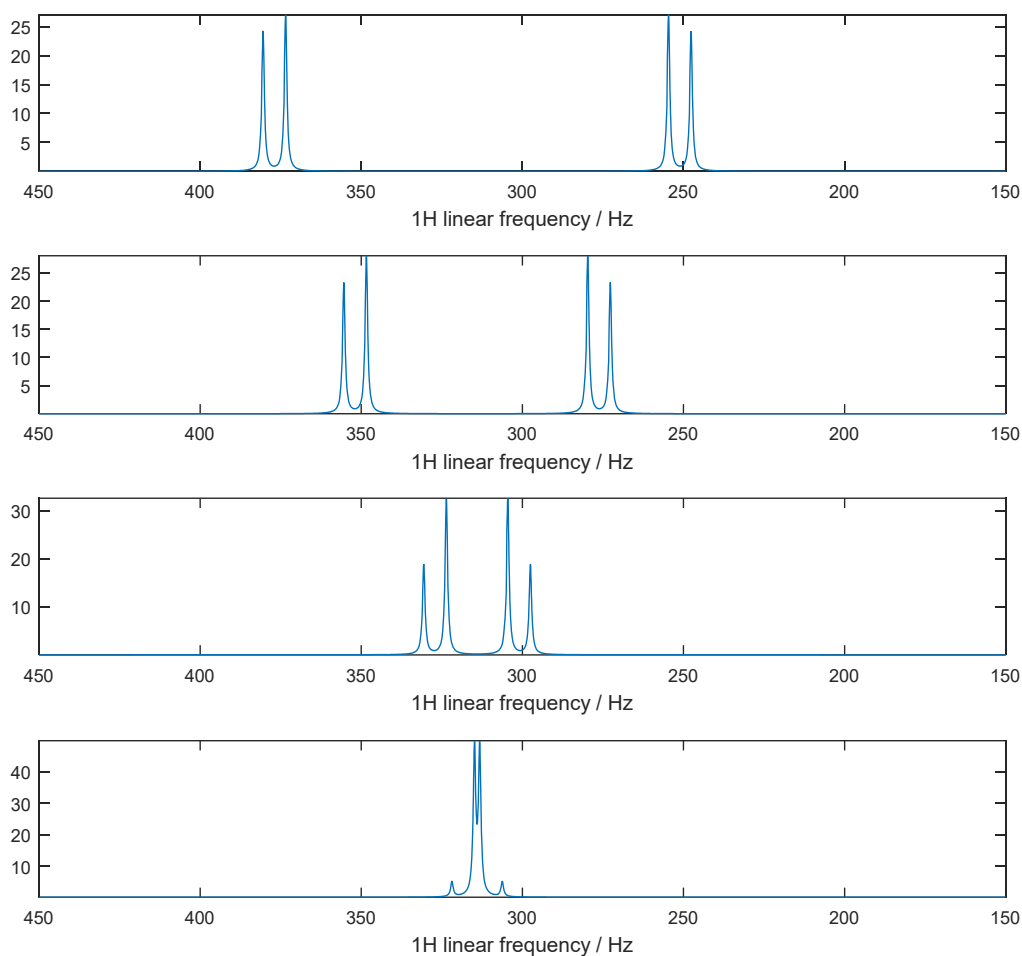


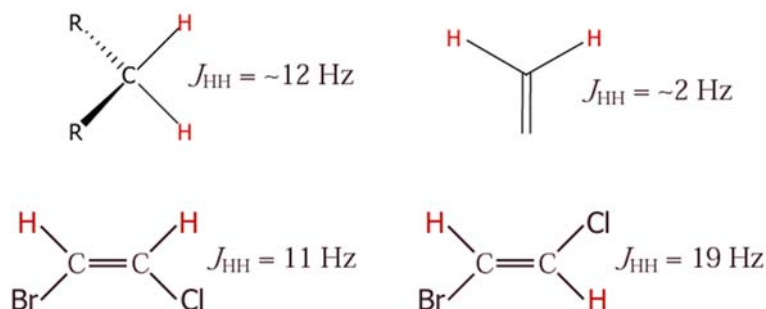
Figure 2. An illustration of the effect of the XX and the YY terms in Equation (2) on the relative intensities of the spectral lines in a strongly coupled AB spin system.

4. Spin system classification

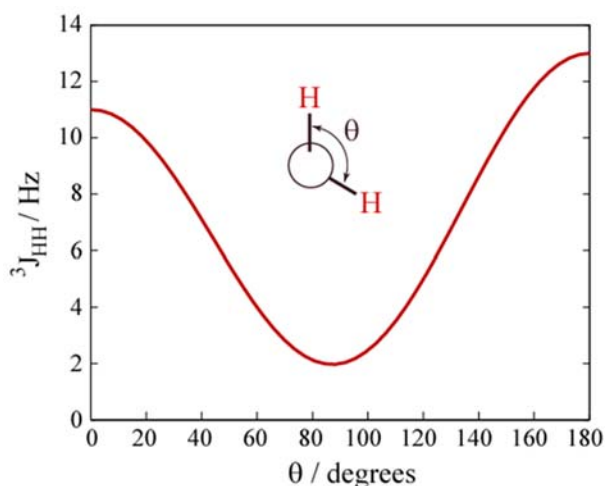
Because the pattern of J -couplings depends on the frequency separation between the spins, spin systems are classified according to the frequency separation between their constituent spins. Any spins that are close together in frequency are denoted by letters that are close together in the alphabet, 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 four bonds.



Three-bond J -couplings are sensitive to the dihedral angle between the bonds (*Karplus relation*):



$$J(\theta) = A \cos 2\theta + B \cos \theta + C \quad (4)$$

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

	1J		$^1J_{CH}$
$^{195}\text{Pt}-^{195}\text{Pt}$	~9000 Hz	C_2H_6	125 Hz
$^{195}\text{Pt}-^1\text{H}$	~1000 Hz	C_2H_4	156 Hz
$^{13}\text{C}-^1\text{H}$	~150 Hz	C_2H_2	249 Hz