7– NMR Interactions: Scalar Coupling

7.1 Hamiltonian

The scalar interaction arises between two different nuclear spins, $I_1$ and $I_2$, and is mediated by the electrons surrounding these two spins. Through the Fermi contact, the electrons are polarised in the opposite direction to the nucleus they are interacting with. This polarisation in turn has an effect on the other electrons in close proximity, which in turn affects the neighbouring nuclei.
Unlike the chemical shift, the scalar interaction does not depend strongly on orientation. In some cases though, for particular compounds, the scalar interaction does exhibit a slight anisotropy. For more details, see R.E. Wasylishen, Encyclopedia of NMR, Grant and Harris (eds).

Written in terms of a Hamiltonian, the scalar interaction is

$$\hat{\mathcal{H}}_J = \sum_k \sum_j 2\pi J_{kj} \vec{I}_k \cdot \vec{I}_j$$  \hspace{1cm} (7.1)

where \( k < j \).

As we will see in the next section, this function is analogous to the dipolar Hamiltonian. In fact, the scalar interaction and the dipolar interaction are quite similar in that the interaction occurs between two nuclear spins.

7.2 Spherical Tensor Notation

The spin part of the spherical tensor for J-coupling
can be written as:

\[ T_{10} = -\frac{1}{2\sqrt{2}}(I_+S_- - I_-S_+) \]
\[ T_{1\pm 1} = \frac{1}{2}(I_zS_\pm - I_\pm S_z) \]
\[ T_{20} = \frac{1}{\sqrt{6}}(3I_zS_z - \mathbf{I} \cdot \mathbf{S}) \]
\[ T_{2\pm 1} = \mp\frac{1}{2}(I_zS_\pm + I_\pm S_z) \]
\[ T_{2\pm 2} = \frac{1}{2}I_\pm S_\pm \]

(7.2)

see Mehring for further details

As we will see in the next chapter, the \( T_{2m} \) terms are exactly the same for the scalar and dipolar coupling interaction. **WHAT IS THE PHYSICAL EXPLANATION FOR THAT?** We will not describe the spatial tensors here.

### 7.3 J-coupling in solution

**Types of J-coupling**

There are two “types” of J-coupling:
1. homonuclear coupling - i.e. between like nuclei (e.g. H-...-H)

2. heteronuclear coupling - i.e. between different types of nuclei (e.g. H-C)

**Distance dependence of J-coupling**

The number of interceding bonds between coupled nuclei will effect the absolute value of the coupling constant. The order of the strength of coupling is as follows:

\[ \begin{align*}
1^J & : 110-270 \text{ Hz} \\
2^J & : 9-15 \text{ Hz} \\
3^J & : 6-8 \text{ Hz}
\end{align*} \]

**Line splitting**

As a result of the scalar interaction between the nuclei, the lines in a non-decoupled spectrum are split. The splitting is independent of \( \vec{B}_0 \).

For a two spin 1/2 system (AX), with J-coupling \( J_{AX} \), the resulting spectrum is:
For a three spin 1/2 system (AMX), with J-coupling $J_{AX}$, $J_{AM}$, and $J_{MX}$, the resulting spectrum is:

7.4 J-coupling in the solid state

In the solid state, J-coupling typically does not result in a clear separation of a line into two, as illustrated above. The reason for this is that typical linewidths
obtained in the solid state (100 Hz - 10’s of kHz) are often greater than the J-splitting.

Nonetheless, there are a few cases, where some splitting can be observed, as shown for the spectrum of fully $^{13}C/^{15}N$-labelled arginine below.
1. Determination of angles between nuclei via geminal and vicinal J coupling:
   - Geminal coupling: Geminal coupling or $^2J$ coupling is dependent upon the bond angle between the nuclei. Generally, the smaller the angle the bigger the coupling constant.

Example:

\[ \alpha = 109^\circ \]
\[ ^2J = 12 - 18 \text{ Hz} \]

\[ \alpha = 118^\circ \]
\[ ^2J = 3 - 7 \text{ Hz} \]

\[ \alpha = 120^\circ \]
\[ ^2J = 0 - 3 \text{ Hz} \]
- Vicinal coupling: dihedral angle via the Karplus equation

\[ ^3J = A + B \cos \varphi + C \cos^2 \varphi \quad (7.3) \]

2. Correlation between nuclei (e.g. COSY, TOCSY and analogous experiments in the solid state)