Magnetic Resonance and its application

Farrokh Sarreshtedari
2018
Topics

• Spin-1/2 Pairs
  • Coupling Regimes
  • Zeeman Product States
  • Spin-1 density matrix
  • Spin-Pair Hamiltonian
  • Pairs of Magnetically Equivalent Spins
  • Weakly Coupled Spin Pairs
Most samples consist of more complex molecules which contain more than one spin. In general, the spin–
spin couplings cannot be ignored.

A simplest possible situation: a large number of identical molecules, each containing only two spins-1/2. In
this case, the set of nuclear spins comprises an ensemble of spin-1/2 pairs:

If the members of the pair are of the same isotopic type, then the spin system consists of a homonuclear spin pair.

If the members of the pair are of different isotopic types, then the term heteronuclear spin pair is used.

We examine the behaviour of spin-1/2 pairs in the presence of dipole–
dipole couplings as well as J-couplings.
The behaviour of homonuclear spin-1/2 pairs depends strongly on the difference in chemical shifts between the spins, as compared to the spin-spin coupling.

**Weakly coupled pairs.** If the difference in chemical shift frequencies is much larger than the spin–spin coupling, then the spin pair is said to be weakly coupled. A weakly coupled spin pair is denoted by the symbol $\text{AX}$.

**Strongly coupled pairs.** If the chemical shift frequency difference has roughly the same magnitude as the spin–spin coupling, then the spin system is said to be strongly coupled. The spin pair is denoted $\text{AB}$ in this case.

**Identical chemical shifts.** If the chemical shifts of the two spins are the same, then the two spins are said to be magnetically equivalent. The spin system in each molecule is denoted by the symbol $\text{A}_2$. An example is given by the protons in water.

Our discussion concentrates on the magnetically equivalent and weakly coupled cases.
The pair of coupled spins-1/2 form a single quantum system. The state of the spin pair is described by a single ket, which has the following general form:

\[
|\psi\rangle = c_{\alpha\alpha}|\alpha\alpha\rangle + c_{\alpha\beta}|\alpha\beta\rangle + c_{\beta\alpha}|\beta\alpha\rangle + c_{\beta\beta}|\beta\beta\rangle
\]

The states $|\alpha\alpha\rangle, |\alpha\beta\rangle, \ldots$ are called Zeeman product states of the two spin-1/2 particles.

In the notation $|\alpha\beta\rangle$, the $\alpha$ symbol indicates that the $z$-angular momentum of spin $I_1$ has the definite value $+1/2$, and the $\beta$ symbol indicates that the $z$-angular momentum of spin $I_2$ has the definite value $-1/2$.

The four Zeeman product states of the spin-1/2 pair obey the following eigenequations:

Physically, the state $|\psi\rangle$ describes a spin pair with both polarizations pointing in some arbitrary direction:
Zeeman Product States

The coefficients $c_{\alpha\alpha}, c_{\alpha\beta}, \ldots$ are complex numbers:

$$|\psi\rangle = c_{\alpha\alpha}|\alpha\alpha\rangle + c_{\alpha\beta}|\alpha\beta\rangle + c_{\beta\alpha}|\beta\alpha\rangle + c_{\beta\beta}|\beta\beta\rangle$$

As usual, the coefficients must be normalized:

$$\langle\psi|\psi\rangle = (c_{\alpha\alpha}^*, c_{\alpha\beta}^*, c_{\beta\alpha}^*, c_{\beta\beta}^*) \cdot \begin{pmatrix} c_{\alpha\alpha} \\ c_{\alpha\beta} \\ c_{\beta\alpha} \\ c_{\beta\beta} \end{pmatrix} = 1 \quad \Rightarrow \quad |c_{\alpha\alpha}|^2 + |c_{\alpha\beta}|^2 + |c_{\beta\alpha}|^2 + |c_{\beta\beta}|^2 = 1$$
Zeeman Product States

Our basis in new Hilbert space:

\[
|\alpha\alpha\rangle = |\alpha\rangle \otimes |\alpha\rangle = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}
\]

\[
|\beta\alpha\rangle = |\beta\rangle \otimes |\alpha\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}
\]

\[
|\alpha\beta\rangle = |\alpha\rangle \otimes |\beta\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}
\]

\[
|\beta\beta\rangle = |\beta\rangle \otimes |\beta\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}
\]
Zeeman Product States

Some of the operators in new Hilbert space:

\[
\hat{I}_{1z} = \hat{I}_z \otimes 1 = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}
\]

\[
\hat{I}_{2z} = 1 \otimes \hat{I}_z = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix}
\]

\[
\hat{I}_{1z}\hat{I}_{2z} = \frac{1}{4} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix} = \frac{1}{4} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]
Spin-Pair Hamiltonian

The behaviour of an individual spin pair is treated by constructing the Hamiltonian and solving the Schrödinger equation.

Each of the spins $I_1$ and $I_2$ has a different chemical shift $\delta_1$ and $\delta_2$, leading to chemically shifted Larmor frequencies given by:

$$\omega_1^0 = -\gamma B^0 (1 + \delta_1)$$
$$\omega_2^0 = -\gamma B^0 (1 + \delta_2)$$

The spins have a **mutual J-coupling** $J_{12}$, and also a **secular dipole–dipole coupling** $d_{12}$, as previously described.

The secular spin Hamiltonian is equal to:

$$\hat{\mathcal{H}}^0 = \omega_1^0 \hat{I}_{1z} + \omega_2^0 \hat{I}_{2z} + 2\pi J_{12} \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2 + d_{12}(3\hat{I}_{1z}\hat{I}_{2z} - \hat{\mathbf{I}}_1 \cdot \hat{\mathbf{I}}_2)$$
Spin-Pair Hamiltonian

\[ \hat{H}^0 = \omega_1^0 \hat{I}_{1z} + \omega_2^0 \hat{I}_{2z} + 2\pi J_{12} \hat{I}_1 \cdot \hat{I}_2 + d_{12} (3\hat{I}_{1z} \hat{I}_{2z} - \hat{I}_1 \cdot \hat{I}_2) \]

Our first task is to form the matrix representation of this Hamiltonian in the basis of Zeeman product states \{ |\alpha\alpha>, |\alpha\beta>, |\beta\alpha>, |\beta\beta> \}

\[ \hat{I}_1 \cdot \hat{I}_2 = \hat{I}_{1x} \hat{I}_{2x} + \hat{I}_{1y} \hat{I}_{2y} + \hat{I}_{1z} \hat{I}_{2z} \]

\[ \hat{I}_{1x} \hat{I}_{2x} + \hat{I}_{1y} \hat{I}_{2y} = \frac{1}{2} (\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+) \]

\[ \hat{H}^0 = \hat{H}^0_A + \hat{H}^0_B \]

\[ \hat{H}_A^0 = \omega_1^0 \hat{I}_{1z} + \omega_2^0 \hat{I}_{2z} + \omega_{12}^A 2\hat{I}_{1z} \hat{I}_{2z} \]

\[ \hat{H}_B^0 = \omega_{12}^B \frac{1}{2} (\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+) \]

Where:

\[ \omega_{12}^A = \pi J_{12} + d_{12} \]

\[ \omega_{12}^B = 2\pi J_{12} - d_{12} \]

Review

\[ \hat{I}^+ = \hat{I}_x + i\hat{I}_y \]

\[ \hat{I}^- = \hat{I}_x - i\hat{I}_y \]

For Spin ½:

\[ \hat{I}_z |\alpha\rangle = \pm \frac{1}{2} |\alpha\rangle \]

\[ \hat{I}_z |\beta\rangle = \mp \frac{1}{2} |\beta\rangle \]

\[ \hat{I}^+ |\alpha\rangle = 0 \]

\[ \hat{I}^+ |\beta\rangle = |\alpha\rangle \]

\[ \hat{I}^- |\alpha\rangle = |\beta\rangle \]

\[ \hat{I}^- |\beta\rangle = 0 \]
Spin-Pair Hamiltonian

The matrix representations of the two parts of the Hamiltonian in the Zeeman product basis \{ |\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle \} are given by:

\[
\hat{H}_A^0 = \frac{1}{2} 
\begin{pmatrix}
\omega_1^0 + \omega_2^0 + \omega_{12} & 0 & 0 & 0 \\
0 & \omega_1^0 - \omega_2^0 - \omega_{12} & 0 & 0 \\
0 & 0 & -\omega_1^0 + \omega_2^0 - \omega_{12} & 0 \\
0 & 0 & 0 & -\omega_1^0 - \omega_2^0 + \omega_{12}
\end{pmatrix}
\]

\[
\hat{H}_B^0 = \frac{1}{2} 
\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & \omega_{12}^B & 0 \\
0 & \omega_{12}^B & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix}
\]

The term \( \hat{H}_A^0 \) is called the diagonal part of the spin Hamiltonian. The term \( \hat{H}_B^0 \) is called the off-diagonal part of the spin Hamiltonian.
Spin-Pair Hamiltonian

For example, the element in the second row and third column of the matrix representation of $\hat{H}_B^0$ may be calculated as follows:

\[
\langle \alpha\beta|\hat{H}_B^0|\beta\alpha\rangle = \frac{1}{2} \omega_{12}^B \langle \alpha\beta| (\hat{i}_1^+ \hat{i}_2^- + \hat{i}_1^- \hat{i}_2^+) |\beta\alpha\rangle \\
= \frac{1}{2} \omega_{12}^B (\langle \alpha\beta|\hat{i}_1^+ \hat{i}_2^- |\beta\alpha\rangle + \langle \alpha\beta|\hat{i}_1^- \hat{i}_2^+ |\beta\alpha\rangle) \\
= \frac{1}{2} \omega_{12}^B (\langle \alpha\beta|\alpha\beta\rangle + 0) \\
= \frac{1}{2} \omega_{12}^B
\]

We now consider the cases of magnetic equivalence and weak coupling separately.
Pairs of Magnetically Equivalent Spins
Pairs of Magnetically Equivalent Spins

• Singlets and triplets

If the two chemical shifts are the same $\omega_1^0 = \omega_2^0 = \omega^0$, the spins are magnetically equivalent. The matrix representation of the spin Hamiltonian is given by:

$$\hat{H}^0 = \frac{1}{2} \begin{pmatrix} 2\omega^0 + \omega_{12}^A & 0 & 0 & 0 \\ -\omega_{12}^A & -\omega_{12}^A & \omega_{12}^B & 0 \\ 0 & \omega_{12}^B & -\omega_{12}^A & 0 \\ 0 & 0 & 0 & -2\omega^0 + \omega_{12}^A \end{pmatrix}$$

The Hamiltonian matrix may be diagonalized by choosing a different set of four basis states, called the singlet–triplet basis.

Three triplet states, defined as follows:

$$|T_{+1}\rangle = |\alpha\alpha\rangle$$

$$|T_0\rangle = \frac{1}{\sqrt{2}} (|\alpha\beta\rangle + |\beta\alpha\rangle)$$

$$|T_{-1}\rangle = |\beta\beta\rangle$$

and one singlet state, defined as follows:

$$|S_0\rangle = \frac{1}{\sqrt{2}} (|\alpha\beta\rangle - |\beta\alpha\rangle)$$
The matrix elements of the Hamiltonian in the singlet–triplet basis may be derived according to the following example:

\[
\langle S_0 | \hat{H}^0 | T_0 \rangle = \frac{1}{2} (\langle \alpha \beta \rangle - \langle \beta \alpha \rangle) \hat{H}^0 (|\alpha \beta \rangle + |\beta \alpha \rangle)
\]

\[
= \frac{1}{2} \left( \langle \alpha \beta | \hat{H}^0 | \alpha \beta \rangle - \langle \beta \alpha | \hat{H}^0 | \alpha \beta \rangle + \langle \alpha \beta | \hat{H}^0 | \beta \alpha \rangle - \langle \beta \alpha | \hat{H}^0 | \beta \alpha \rangle \right)
\]

\[
= \frac{1}{4} \left( - \omega_{12}^A - \omega_{12}^B + \omega_{12}^B - (\omega_{12}^A) \right) = 0
\]

Repetition for all elements generates the following matrix representation in the singlet–triplet basis:

\[
\hat{H}^0 = \frac{1}{2} \begin{pmatrix}
\omega^0 + \frac{1}{2} \pi J_{12} + \frac{1}{2} d_{12} & 0 & 0 & 0 \\
0 & -d_{12} + \frac{1}{2} \pi J_{12} & 0 & 0 \\
0 & 0 & -\omega^0 + \frac{1}{2} \pi J_{12} + \frac{1}{2} d_{12} & 0 \\
0 & 0 & 0 & -\frac{3}{2} \pi J_{12}
\end{pmatrix}
\]

So, the singlet–triplet basis states \( \{|T_{+1}\}, |T_0\rangle, |T_{-1}\rangle, |S_0\rangle \) are the energy eigenstates of the magnetically equivalent spin pair.
The three triplet states of the spin-1/2 pair behave in a similar way to the three states of a *single* nuclear spin with \( I = 1 \)

The analogy may be emphasized by constructing *total* angular momentum operators by adding together the angular momentum operators of the two spins:

\[
\hat{I}_x = \hat{I}_{1x} + \hat{I}_{2x} \\
\hat{I}_y = \hat{I}_{1y} + \hat{I}_{2y} \\
\hat{I}_z = \hat{I}_{1z} + \hat{I}_{2z}
\]

The total square angular momentum operator may be constructed as follows:

\[
\hat{I}^2 = \hat{I}^2_x + \hat{I}^2_y + \hat{I}^2_z
\]

The three triplet states obey the following eigen equations:

\[
\begin{align*}
\hat{I}_z |T_M\rangle &= M |T_M\rangle \\
\hat{I}^2 |T_M\rangle &= 2 |T_M\rangle
\end{align*}
\]

The singlet state \( |S_0\rangle \) behaves in the same way as the state of a spin \( I = 0 \) nucleus.
Pairs of Magnetically Equivalent Spins

- **Energy levels**

\[
\hat{\mathcal{H}}^0 |T_{+1}\rangle = \left(\omega^0 + \frac{1}{2}\pi J_{12} + \frac{1}{2}d_{12}\right) |T_{+1}\rangle
\]

\[
\hat{\mathcal{H}}^0 |T_0\rangle = \left(\frac{1}{2}\pi J_{12} - d_{12}\right) |T_0\rangle
\]

\[
\hat{\mathcal{H}}^0 |T_{-1}\rangle = \left(-\omega^0 + \frac{1}{2}\pi J_{12} + \frac{1}{2}d_{12}\right) |T_{-1}\rangle
\]

\[
\hat{\mathcal{H}}^0 |S_0\rangle = \left(-\frac{3}{2}\pi J_{12}\right) |S_0\rangle
\]

Energy levels for a pair of magnetically equivalent spins-1/2. The singlet state is shown in grey. The $J$-coupling and dipole–dipole (DD) coupling are assumed to have opposite signs.
The energy levels of the triplet states, are the same as for a spin-1 nucleus, but with the first-order quadrupolar coupling $\omega_Q^{(1)}$ replaced by three times the dipole–dipole coupling $d_{12}$. 

Energy levels of a spin-1 nucleus. 

Singlet and triplet energy levels for a pair of magnetically equivalent spins-1/2.
Pairs of Magnetically Equivalent Spins

- **NMR spectra**

Since there are two (-1)-quantum coherences within the triplet manifold, the spectrum consists of a doublet, in the general case:

![Diagram showing NMR doublet spectrum](image-url)

Doublet NMR spectrum generated by magnetically equivalent spin-1/2 pairs.
• **NMR spectra**

Since there are two (-1)-quantum coherences within the triplet manifold, the spectrum consists of a doublet, in the general case:

\[
\text{Doublet NMR spectrum generated by magnetically equivalent spin-1/2 pairs.}
\]

**Note:**

*Isotropic liquids.* Since the secular dipole–dipole coupling \( d_{12} \) vanishes in isotropic liquids, the two peaks coincide. This is why the NMR spectrum of *liquid water* is a singlet.
Weakly Coupled Spin Pairs
Weakly Coupled Spin Pairs

The spin-pair system is said to be **weakly coupled** if the following general **condition** is satisfied:

\[
\frac{1}{2} |\omega_{12}^B| << |\omega_1^0 - \omega_2^0|
\]

An example of a $^1$H AX system:

![Dichloroacetaldehyde](image)

The two protons have very different chemical shifts due to the strong electronegativity of the Cl atoms. The chemical shift difference between the two protons is $\delta_1 - \delta_2 = 3.28$ ppm and their isotropic $J$-coupling is $J_{12} = 2.9$ Hz.

The weak-coupling condition is satisfied at all reasonable magnetic fields. For example, if the proton Larmor frequency is $|\omega_0/2\pi| = 500$ MHz, then the chemical shift frequency difference is $3.28$ ppm $\times$ $500$ MHz $= 1.64$ kHz, which is three orders of magnitude larger than $1/2J_{12} = 1.45$ Hz.
If the general form of the weak-coupling condition is satisfied, then the secular approximation may be used to discard the Hamiltonian term of $\hat{H}_B^0$. The spin Hamiltonian may be approximated by the $\hat{H}_A^0$ part alone:

$$\hat{\mathcal{H}}_A^0 = \frac{1}{2} \begin{pmatrix} \omega_1^0 + \omega_2^0 + \omega_{12}^A & 0 & 0 & 0 \\ 0 & \omega_1^0 - \omega_2^0 - \omega_{12}^A & 0 & 0 \\ 0 & 0 & -\omega_1^0 + \omega_2^0 - \omega_{12}^A & 0 \\ 0 & 0 & 0 & -\omega_1^0 - \omega_2^0 + \omega_{12}^A \end{pmatrix}$$

$$\hat{\mathcal{H}}_B^0 = \frac{1}{2} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & \omega_{12}^B & 0 \\ 0 & \omega_{12}^B & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\hat{\mathcal{H}}_A^0 = \omega_1^0 \hat{I}_{1z} + \omega_2^0 \hat{I}_{2z} + \omega_{12}^A 2\hat{I}_{1z} \hat{I}_{2z}$$

$$\hat{\mathcal{H}}_A^0 |\alpha\alpha\rangle = \omega_{\alpha\alpha} |\alpha\alpha\rangle \quad \hat{\mathcal{H}}_A^0 |\alpha\beta\rangle = \omega_{\alpha\beta} |\alpha\beta\rangle$$

$$\hat{\mathcal{H}}_A^0 |\beta\alpha\rangle = \omega_{\beta\alpha} |\beta\alpha\rangle \quad \hat{\mathcal{H}}_A^0 |\beta\beta\rangle = \omega_{\beta\beta} |\beta\beta\rangle$$

$$\omega_{\alpha\alpha} = \frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 + \frac{1}{2} \omega_{12}^A$$

$$\omega_{\alpha\beta} = \frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 - \frac{1}{2} \omega_{12}^A$$

$$\omega_{\beta\alpha} = -\frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 - \frac{1}{2} \omega_{12}^A$$

$$\omega_{\beta\beta} = -\frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 + \frac{1}{2} \omega_{12}^A$$

$\omega_{12}^A = \pi J_{12} + d_{12}$

$\omega_{12}^B = 2\pi J_{12} - d_{12}$
Energy levels for a weakly coupled spin-1/2 pair.

\[
\begin{align*}
\omega_{\alpha\alpha} &= \frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 + \frac{1}{2} \omega_{12}^A \\
\omega_{\alpha\beta} &= \frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 - \frac{1}{2} \omega_{12}^A \\
\omega_{\beta\alpha} &= -\frac{1}{2} \omega_1^0 + \frac{1}{2} \omega_2^0 - \frac{1}{2} \omega_{12}^A \\
\omega_{\beta\beta} &= -\frac{1}{2} \omega_1^0 - \frac{1}{2} \omega_2^0 + \frac{1}{2} \omega_{12}^A
\end{align*}
\]
AX spectrum

The NMR spectrum of an AX system contains four peaks, corresponding to the four different (-1)-quantum coherences in the AX spin ensemble:

In the next chapter, we will derive the exact NMR spectrum of the AX system.

The proton spectrum of dichloroacetaldehyde in solution is shown below. Note the splitting of 2.9 Hz in each doublet:

Proton spectrum of dichloroacetaldehyde, in a field of 4.7 T.