Spin-spin coupling I
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Spin-interactions

- External interactions
  - Magnetic field $B_0$
  - RF field $B_1$

- Internal Interactions
  - Molecular motions
  - Exchange
  - Chemical shifts
  - $J$-coupling
  - Spin Diffusion
  - Dipolar
  - Quadrupolar
Low resolution spectroscopy
What is the origin of splitting?
Magnetic Equivalence

• A set of spins is magnetically equivalent if
  - The spins have the same chemical shifts
• AND
  - The spins have identical couplings to all other spins in the molecule
  - OR
  - There are no other spins in the molecule
• Ex: CH$_3$CH$_2$Cl
  • Has one group of three magnetically equivalent protons, and one group of two magnetically equivalent protons
Coupling strength

- **Weak coupling**
  - The chemical shift difference $|\nu_1 - \nu_2| >> |J_{12}|$
  - Nomenclature: assign alphabets well separated from each other in the alphabet
  - e.g., AX, AX₂, AX₃ etc.
Spin-spin coupling

- Interaction of the proton magnetic field with bonding electrons.
- Nuclei which are close to one another exert an influence on each other’s effective magnetic field.
- This effect manifests when the nuclei are nonequivalent.
- This effect is observed as spectral line splitting if the distance between the nonequivalent nuclei is less than or equivalent to three bond lengths.
mechanism

Consider a molecule in which two nuclei, A and B are 3 bonds away from each other.
\[ \begin{aligned}
\text{ENERGY} & \quad \beta \beta \\
\beta \alpha & \\
\alpha \beta & \\
\alpha \alpha & \\
\end{aligned} \]
Energies

\[ J_{AB} = 0 \quad J_{AB} \neq 0 \]

\[ \Delta m = \pm 1 \]

\[ m = -1 \]

\[ m = 0 \]

\[ m = +1 \]
Two spin system

- Possible transitions and associated frequencies

<table>
<thead>
<tr>
<th>transition</th>
<th>spin states</th>
<th>frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 → 2 αα → αβ</td>
<td>$-v_{0.2} - \frac{1}{2}J_{12}$</td>
<td></td>
</tr>
<tr>
<td>3 → 4 βα → ββ</td>
<td>$-v_{0.2} + \frac{1}{2}J_{12}$</td>
<td></td>
</tr>
<tr>
<td>1 → 3 αα → βα</td>
<td>$-v_{0.1} - \frac{1}{2}J_{12}$</td>
<td></td>
</tr>
<tr>
<td>2 → 4 αβ → ββ</td>
<td>$-v_{0.1} + \frac{1}{2}J_{12}$</td>
<td></td>
</tr>
</tbody>
</table>
Two spin system
Three spin system
Magnetic field at B
Has two possible values

1

2

Magnetic field at A
Has 4 possible values

1

2

3
Energy level diagram

- bbb
- bba  bab
- baa
- abb
- aba  aab
- aaa
ABC
Methyl isopropyl ether
Splitting tree

Br—CH₂—CH₂—CH₂—OD
Multiplet structure

- The central methylene (CH$_2$) is split by the protons on a into a triplet, J=15 Hz,

- Each of these peaks further split by the protons on carbon c into triplets with J=12 Hz. The spectrum is predicted to be 9 lines.

- At 60 MHz, we see only 5 lines because the central seven peaks are only separated by 2 Hz.
Total lines

- Splitting of a resonance due to coupling with $n$-magnetically equivalent nuclei gives $n+1$ distinct lines.
- The intensity distribution within the $n+1$ lines is given by the binomial coefficients $(1+x)^n$. 
## Intensities

<table>
<thead>
<tr>
<th>N</th>
<th>Relative intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>2</td>
<td>1:2:1</td>
</tr>
<tr>
<td>3</td>
<td>1:3:3:1</td>
</tr>
<tr>
<td>4</td>
<td>1:4:6:4:1</td>
</tr>
<tr>
<td>5</td>
<td>1:5:10:10:5:1</td>
</tr>
</tbody>
</table>
Multidimensional NMR
2D NMR

- Introduction by Jean Jeener (1971)
- Developed by R.R. Ernst
  - J-resolved spectroscopy
  - Correlated spectroscopy
  - Transient NOE
  - NOSEY
Assignment Problem

Consider a mixture of two different compounds with different AX spin system, but with identical J-coupling.
Assignment problem

- Selective decoupling
- Isotope labeling
- OK for small # of spin systems of small molecules
- How about macromolecules?
Consider a $J$-coupled spin system

$A2CCB$
Response to a spin echo sequence

- A2CCB
- Subjected to spin-echo sequence
The time domain data is recorded as a function of TE (t1) and t2(acq).
**J-resolved**

- Time domain data is first FTd in t2 to get F2 dimension (chemical shift) and then in t1 direction to get F1 dimension (J-coupling)
Homonuclear $J$-resolved 2D spectra

- Data display as shaded contours
- Or rotated by 45 degree
Chemical shift correlated spectroscopy (COSY)

- **Pulse sequence**

  Two 90° pulses are applied to a spin system. The FID is collected as a function of t1. The FT of both the dimensions gives us chemical shift and J-coupling information. Cross peaks exist in the 2D COSY whenever there is J-coupling between the spins.

  Heteronuclear correlated 2-D NMR is also possible and useful.
Right after the second pulse in COSY sequence
Terms corresponding to spin 1 are given by

\[ -\cos \pi J_{12} t_1 \cos \Omega_1 t_1 I_{1y} \xrightarrow{\pi/2 I_{1x}} \xrightarrow{\pi/2 I_{1z}} -\cos \pi J_{12} t_1 \cos \Omega_1 t_1 I_{1z} \quad \{1\} \]
\[ \sin \pi J_{12} t_1 \cos \Omega_1 t_1 2I_{1x} I_{2z} \xrightarrow{\pi/2 I_{1x}} \xrightarrow{\pi/2 I_{1z}} -\sin \pi J_{12} t_1 \cos \Omega_1 t_1 2I_{1x} I_{2y} \quad \{2\} \]
\[ \cos \pi J_{12} t_1 \sin \Omega_1 t_1 I_{1x} \xrightarrow{\pi/2 I_{1z}} \xrightarrow{\pi/2 I_{1y}} \cos \pi J_{12} t_1 \sin \Omega_1 t_1 I_{1x} \quad \{3\} \]
\[ \sin \pi J_{12} t_1 \sin \Omega_1 t_1 2I_{1y} I_{2z} \xrightarrow{\pi/2 I_{1y}} \xrightarrow{\pi/2 I_{1z}} -\sin \pi J_{12} t_1 \sin \Omega_1 t_1 2I_{1y} I_{2y} \quad \{4\} \]

Terms \{1\} and \{2\} are unobservable. Term \{3\} corresponds to in-phase magnetization of spin 1, aligned along the \(x\)-axis. The \(t_1\) modulation of this term depends on the offset of spin 1, so a diagonal peak centred at \((\Omega_1, \Omega_1)\) is predicted. Term \{4\} is the really interesting one. It shows that anti-phase magnetization on spin 1, \(2I_{1y} I_{2z}\), is transferred to anti-phase magnetization on spin 2, \(2I_{1z} I_{2y}\); this is an example of coherence transfer. Term \{4\} appears as observable magnetization on spin 2, but it is modulated in \(t_1\) with the offset of spin 1, thus it gives rise to a cross-peak centred at \((\Omega_1, \Omega_2)\). It has been shown, therefore, how cross- and diagonal-peaks arise in a COSY spectrum.
Diagonal peaks

\[
\cos \pi J_{12} t_1 \sin \Omega_1 t_1 \rightarrow \pi f_{1x} \rightarrow \pi f_{2x} \rightarrow \cos \pi J_{12} t_1 \sin \Omega_1 t_1
\]

\[
\cos \pi J_{12} t_1 \sin \Omega_1 t_1 = \frac{1}{2} \left\{ \sin (\Omega_1 t_1 + \pi J_{12} t_1) + \sin (\Omega_1 t_1 - \pi J_{12} t) \right\}
\]

The Fourier transform of a decaying sine function \( \sin \Omega t \exp(-t/T_2) \) is a dispersion mode Lorentzian centred at frequency \( \Omega \).

Schematic view of the diagonal peak from a COSY spectrum. The squares are supposed to indicate the two-dimensional double dispersion lineshape illustrated below.
Diagonal peak-line shape

- Double dispersion

The double dispersion lineshape seen in pseudo 3D and as a contour plot, negative contours are indicated by dashed lines.
Cross peaks

\[
\sin \pi J_{12} t_1 \sin \Omega_1 t_1 2 I_{1y} I_{2z} \xrightarrow{\pi J_{12} t_1} \xrightarrow{\pi J_{12} t_1} -\sin \pi J_{12} t_1 \sin \Omega_1 t_1 2 I_{1z} I_{2y} \quad (4)
\]

\[
\sin \pi J_{12} t_1 \sin \Omega_1 t = \frac{1}{2} \left\{ -\cos(\Omega_1 t_1 + \pi J_{12} t_1) + \cos(\Omega_1 t_1 - \pi J_{12} t_1) \right\}
\]

The Fourier transform of a decaying cosine function \( \cos \tilde{\Omega} t \exp(-t/T_2) \) is an absorption mode Lorentzian centred at frequency \( \Omega \).

Schematic view of the cross-peak multiplet from a COSY spectrum. The circles are supposed to indicate the two-dimensional double absorption lineshape illustrated below; filled circles represent positive intensity, open represent negative intensity.
Cross Peak-line shape

- Double absorption

The double absorption lineshape seen in pseudo 3D and as a contour plot.
There are cross peaks between OH and CH2 hydrogens, and also between CH3 and CH2 hydrogens. There are no cross peaks between the CH3 and OH hydrogens because there is no coupling between them.
COSY of Ethanol
1-Propanol COSY

- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \)
Ethyl benzene COSY
Two-dimensional $^1$H-$^1$H COSY NMR Spectroscopy

2D NMR of Ligand 16-Crown4
**COSY Signals**

- \( S(t_1,t_2)_{\text{cross}} \sim \sin(2\pi Jt_1) \sin(2\pi Jt_2) \exp(-2\pi i \delta_A t_1) \exp(+2\pi i \delta_x t_2) \)

- \( S(t_1,t_2)_{\text{diag}} \sim \cos(2\pi Jt_1) \cos(2\pi Jt_2) \exp(-2\pi i \delta_A t_1) \exp(+2\pi i \delta_A t_2) \)
Magnetic inequivalence

• Each of the two protons have different coupling with each of the F.
• One coupling is in *cis* and the other in *trans* geometry
  • Two protons are chemically equivalent but not magnetically equivalent
  • The same is true for two Fs.
Magnetic equivalence

- Two protons $H_a$ and $H_a'$ are chemically equivalent but magnetically inequivalent. The same is true for $H_b$ and $H_b'$.