Traditional View of Scalar Coupling

Dipole Model: Two equal intensity lines from each interaction for each spin

Reasons to understand couplings:
- magnetization transfer (COSY, HSQC)
- structural information

Measurement: directly as above, 2D J-resolved, intensity based

Problem: dipolar interactions average to zero in solution
Multiple sets of spins

Multiplet structure: as many as $n^2(n-1)$ lines in non-equivalent first order sets, $2^2 \times 3 = 12$ lines for previous example.

Unequal intensities in equivalent cases; proton next to a methylene, has states $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$; a 1:2:1 triplet.
The Origin of Scalar Coupling Constants

\[ E_J = \sum_{i \neq j} J_{ij} I_i \cdot I_j \approx \sum_{i \neq j} J_{ij} I_{zi} I_{zj} \]

Mechanism:
not through space, but Fermi contact
\[ E \propto (3\cos^2\theta - 1) / r^3 \]
\[ E \propto s_A \times s_B \]

Low E
\[
\begin{array}{c}
\mu_B \downarrow \quad e^- \downarrow \quad \mu_A \\
\mu_B \uparrow \quad \mu_A
\end{array}
\]

High E
\[
\begin{array}{c}
\mu_B \downarrow \quad e^- \downarrow \quad e^- \downarrow \quad \mu_A \\
\mu_B \uparrow \quad \mu_A
\end{array}
\]

J is positive
Fermi-Contact Expression for Scalar Coupling

• Expression comes from second order perturbation treatment of spin contribution to electronic energy

\[ E = (4g \beta \gamma N h/3)^2 \sum_{jk} \langle \psi_0 | \delta(r_{kA}) \delta(r_{jB}) \, S_{jz} S_{kz} \, \psi_0 \rangle \, I_{zA} I_{zB} \]

• \( I_{zA} I_{zX} \) dependence as expected for \( H_J \)

• \( \gamma_A \gamma_X \) dependence as expected for \( H_J \)

• Depends on electron density at pair of nuclei \( (\delta(r_{kA}) \delta(r_{jB}) \, S_{jz} S_{kz}) \) and spins must be correlated – hence bonded

\[ (\int S_{jz} S_{kz} = 0 \text{ if spins are uncorrelated}) \]

• Depends on “s” character of bond

\( (\delta(r_{kA}) \text{ is only finite for an s orbital}) \)
Predictions about Scalar Couplings

• Wave functions (electronic) for $^1$H-$^1$H can be calculated at a high level of theory – even at VB prediction of 200Hz is good.

• Experimental $^1$H-$^2$H is 44 Hz; correcting for $\gamma$s, $J_{H-H} = \gamma_{1H}/\gamma_{2H} \times 44 = 6.5 \times 44 = 265$Hz

• Directly bonded pairs should have much larger couplings:

$$\begin{array}{c}
\text{R} \\
\text{1H} \quad 11.6 \text{ Hz} \\
\text{1H} \\
\end{array} \quad \text{2.5 Hz} \quad \text{vs} \quad 265 \text{ Hz}$$
Some predictions for one-bond couplings

Couplings are short range and depend on electron densities at the coupled nuclei (ie, the product of “s characters”) as well as γs.

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<tr>
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<tbody>
<tr>
<td>C-C</td>
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<tr>
<td>C-H</td>
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### C-C

<table>
<thead>
<tr>
<th>Bond</th>
<th>Frequency</th>
<th>Hybridization</th>
<th>Product</th>
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</thead>
<tbody>
<tr>
<td>C-H</td>
<td>35 Hz</td>
<td>sp³ - sp³</td>
<td>1/4 x 1/4 = 1/16</td>
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<tr>
<td>CH₃-CH₃</td>
<td>67 Hz</td>
<td>sp² - sp²</td>
<td>1/3 x 1/3 = 1/9</td>
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<tr>
<td>C₆H₆</td>
<td>57 Hz</td>
<td>sp² - sp²</td>
<td>1/3 x 1/3 = 1/9</td>
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<tr>
<td>HC≡CH</td>
<td>171 Hz</td>
<td>sp-sp</td>
<td>1/2 x 1/2 = 1/4</td>
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### C-H

<table>
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<tr>
<th>Bond</th>
<th>Frequency</th>
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<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-CH₃</td>
<td>125 Hz</td>
<td>s - sp³</td>
<td>1 x 1/4 = 1/4</td>
</tr>
<tr>
<td>CH₂=CH₂</td>
<td>156 Hz</td>
<td>s - sp²</td>
<td>1 x 1/3 = 1/3</td>
</tr>
<tr>
<td>C₆H₆</td>
<td>158 Hz</td>
<td>s - sp²</td>
<td>1 x 1/3 = 1/3</td>
</tr>
<tr>
<td>HC≡CH</td>
<td>249 Hz</td>
<td>s-sp</td>
<td>1 x 1/2 = 1/2</td>
</tr>
</tbody>
</table>
A two-bond coupling is small and sometimes negative – why?

1H

1H

1H

1H

Shared on central carbon

Parallel H and e contributes low energy

Anti parallel H and e contributes high energy

The two terms cancel

Coupling goes up again for a three-bond coupling
Vicinal Couplings ($^3J_{HH}$)

• Originally for H-C-C-H
• M. Karplus (1959) JCP 30 11 - Karplus Equation
• $J_{HNHA} = 7.0 \cos^2(\phi) - 1.4 \cos(\phi) + 1.7$ for peptides
• (Bax and Wang (1996) JACS 118 2492)

$\phi$
Wang-Bax Equation Compared to Ubiquitin Data

\[ \text{HN} H \quad \alpha \quad \phi \quad - \quad 60 \quad \text{NC} \alpha \quad \phi \quad \text{measured as} \quad C' - N - C_\alpha - C'' \]
Populations of Rotomeric States from Couplings
An Application of the Karplus Equation

- Occurs in pyranosides, furanosides, and nucleosides
- Assume only minimum energy states populated
- Assume rapid equilibration – averaging of coupling
- $J_{56} = 1.8 F_1 + 1.8 F_2 + 9.2 F_3$
- $J_{56}' = 1.8 F_1 + 9.2 F_2 + 1.8 F_3$
- $F_1 + F_2 + F_3 = 1$
Application of Karplus Equations (cont)

Measure $J_{65}$ and $J_{6'5}$ for β-Me-galactose

7.0 Hz, 3.0 Hz

Using averaging formula find:

0.15, 0.7, 0.15 for states 1, 2, and 3

Reference on scalar coupling in Levitt: 217-223
Scalar Couplings Can be Predicted Theoretically


Couplings And Hydrogen Bonds


$^{15}\text{N-H} \ldots \ldots^{15}\text{N \quad or \quad}^{15}\text{N-H} \ldots \ldots^{13}\text{O}$