Spin-Spin Coupling

Importance:
- Transfer of magnetization in COSY, TOCSY, HSQC, etc..
- Also structurally useful

Measurement:
- Splitting in 1D, 2D spectra.
- J resolved spectroscopy.
- New intensity based techniques
  - will come back to this.
Spin-spin coupling

Familiar View:

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

\[ 2^2 \times 3 = 12 \]

Problem: dipolar interactions average to zero in isotropic solution

Reasons to understand:
- magnetization transfers (COSY, HSQC, etc.)
- structural information
Origin of Scalar Coupling:

Hamiltonian: \( \mathcal{H}_J = \sum_{i \neq j} T_{ij} \hat{I}_i \cdot \hat{I}_j \)

or: \( \mathcal{H}_J = \sum_{i \neq j} T_{ij} \hat{I}_i \hat{I}_j \)

but where does \( J \) come from?

Fermi Contact Mechanism is a through-bond mechanism.

\[ \begin{array}{c}
\text{low energy state} & \text{\('H' - anti parallel) } \\
\text{high energy: } & \text{\('H' for. like } \uparrow \downarrow \text{ \& like } \uparrow \downarrow\end{array} \]
Rationalization of Fermi Contact.

easiest physical picture is through-space dipole interaction (origin of NOEs).

\[ B'_2 \propto \frac{1}{r^3} (1 - 3\cos^2 \theta) \]

but: \( (1 - 3\cos^2 \theta) \) averages to zero in isotropic distribution when doesn't it.?

- when e\(^-\) at nucleus.

\[ H'_f = \frac{8\pi^3 g_\beta y_N \mathbf{h}}{3} \sum \delta(r_N) \mathbf{l} \cdot \mathbf{s} \]

\(<\text{only finite when } r_N = 0>\)
Interested in Energy due to $\psi_i$.  

$E' = \langle \psi_0 | \psi' | \psi_0 \rangle$ - but $\alpha + \beta$ e- equally represented in $\psi_0$.

... need second order...

$\psi' = \psi_0 + \sum \zeta_i \psi_i$.  $\zeta_i = \frac{\langle \psi_0 | \psi' | \psi_i \rangle}{E_i - E_0}$

expect.  $E' \propto |\psi'|^2$.

$E' \approx -\left(\frac{\beta g}{3}\right)^2 \sum \frac{\langle \psi_0 | \delta(r_{BA}) \delta(r_{jB}) \rangle}{\Delta E} \hat{S}_{jz} \hat{S}_{kz} |\psi_0\rangle \langle \hat{\tau}_A \hat{\tau}_B \rangle$

... ave. energy approx. removes $\leq$ over excited states.
Observations from Fermi Contact Exp.  

1. $I_{2A}I_{2B}$ dep. as expected for $N_f$
2. $\gamma^2$ or $\gamma_A\gamma_B$ dep. as expected: for $N_f$.
3. depends on electron density at pair of nuclei $(s)_+^t$ electron density on these must be correlated – hence bonded!

$$S_jS_k = 0$$ if spins of electrons on $A + B$ are uncorrelated
i.e. equally $\sigma\sigma + \beta\beta$ pairs.

4. depends on "s" character of bonds
Predictions about Couplings

$^2\text{H}-^2\text{H}$ can be calculated from high level. 4. — even at crude VB level

- 200 Hz.
- measured. (via $^1\text{H}-^2\text{H}$) 44 Hz.

$$J_{^1\text{H},^1\text{H}} = 0.44 \times 44 = 265 \text{ Hz}.$$  

Directly bonded pairs should have much larger couplings. (better correlation)

$$\{2.5 \text{ vs. 265} \}$$

1-2 orders of magnitude less.
2 bond is actually negative J in this case --.

\( \overset{\text{H}}{\text{H}} \overset{\text{C}}{\text{C}} \overset{\text{H}}{\text{H}} \)

\( \overset{\text{H}}{\text{H}} \overset{\text{H}}{\text{H}} \) is shared on central C.

\( \overset{\text{H}}{\text{H}} \overset{\text{H}}{\text{H}} \) - parallel is low energy.

- actually this works against.

\( \overset{\text{H}}{\text{H}} \overset{\text{H}}{\text{H}} \) mechanism - this is why J is small.

- then goes up for 3 bond -
Correlation with "s" Character

<table>
<thead>
<tr>
<th></th>
<th>( J_{CC} )</th>
<th>s.s.</th>
<th>( J_{CH} )</th>
<th>s.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3-\text{CH}_3 )</td>
<td>125</td>
<td>( \frac{1}{4}.1 )</td>
<td>35</td>
<td>( \frac{1}{4}.1 )</td>
</tr>
<tr>
<td>( \text{CH}_2=\text{CH}_2 )</td>
<td>156</td>
<td>( \frac{1}{2}.1 )</td>
<td>67</td>
<td>( \frac{1}{2}.\frac{1}{2} )</td>
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<tr>
<td>( \text{C}_6\text{H}_6 )</td>
<td>158</td>
<td>( \frac{1}{2}.1 )</td>
<td>57</td>
<td>( \frac{1}{2}.\frac{1}{2} )</td>
</tr>
<tr>
<td>( \text{HC}≡\text{C}-\text{H} )</td>
<td>249</td>
<td>( \frac{1}{2}.1 )</td>
<td>171</td>
<td>( \frac{1}{2}.\frac{1}{2} )</td>
</tr>
</tbody>
</table>
Vicinal Coupling (\(^3J_{HH}\))

- M. Karplus JCP 30 11 (1959)
- frequently used structural tool

\[ J_{AB} = 8.5 \cos^2 \phi - 1.28 \quad 0 \leq \phi \leq 90 \]
\[ = 9.5 \cos^2 \phi - 1.28 \quad 90 \leq \phi \leq 180 \]

more recent:
Wang + Bax JACS 118 2492 (1996)
\[ J = 6.98 \cos^2(\phi - 60) - 1.38 \cos(\phi - 60) + 1.72 \]
Scalar Couplings Can be Predicted Theoretically


Couplings Across Hydrogen Bonds


$^{15}\text{N-H} \ldots \ldots \text{or } \text{or } \text{or }^{15}\text{N-H} \ldots \ldots \text{O}=^{13}\text{C}$
Application of Karplus Eqn.

- averaging of $H_5-H_6 + H_5-H_6'$ in nucleosides or pyranosides - assume
- we measure $J$ properly -
- assume only minimum energy rotamers are populated

\[
\begin{align*}
J_{65} &= 1.8 f_1 + 1.8 f_2 + 9.2 f_3 \\
J_{65}' &= 1.8 f_1 + 9.2 f_2 + 1.8 f_3.
\end{align*}
\]

\[f_1 + f_2 + f_3 = 1\]
Application of Karplus Equations (contd.)

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

7.0 Hz, 3.0 Hz

Using averaging formula, find 0.15, 0.7, and 0.15 for fractional populations of states 1, 2, and 3