**Basic Theory: Nuclear Overhauser Effect**

Albert Overhauser (1953)

**Single Quantum Transition**
- Larmor precession $10^8$ to $10^9$ Hz.
- Double quantum transition probability - very fast
- Twice Larmor Frequencies
- Difference in Larmor Frequencies
- Very slow field fluctuation.

**References:**
- David Neuhaus and Michael Williamson "The Nuclear Overhauser Effect".
- Timothy Claridge "High-Resolution NMR Techniques" Chapter 8.

**Steady State Solomon Equation**

Two spins system

$$f_i(S) = \frac{Y_i}{Y} \cdot \left\{ \frac{W_{11} - W_{10}}{W_{11} + W_{10} + W_{00}} \right\}$$

Function of
- Gyromagnetic ratio, $1/R^2$
- Molecular motion, Larmor Frequencies

$$W_{11} = \gamma_i^2 \gamma_s^2 / [s + (\alpha_i - \alpha_s) \epsilon_c^2]$$

$$W_{10} = \gamma_i^2 \gamma_s^2 / [s + (\alpha_i + \alpha_s) \epsilon_c^2]$$

$$W_{00} = \gamma_i^2 \gamma_s^2 / \epsilon_c^2$$

$$W_{01} = \gamma_i^2 \gamma_s^2 / [s + (\alpha_i + \alpha_s) \epsilon_c^2]$$

Figures sourced from Guillermo Moyna, U of the Sciences.
NOE and molecular motion

Most small molecules ~ rapid tumbling motion
Positive NOE

Positive NOE after a selective Spin S Population is excited!
W2 and W0 will take place

Zero NOE

Most large molecules ~ slow tumbling motion
Negative NOE

NOE application

Cross relaxation
Perturbation from one spin
Inducing changes in the intensity of other spins

- Transient NOE
- Using Shaped pulse
e.g. 1D Selective NOE, 2-D NOESY

Steady state NOE
e.g. C-13 with all H-1 decoupled
C-13 Application --- Steady state NOE

\[ f(S) = \frac{\gamma_{H1}}{\gamma_{C13}} = -2 \text{ to } 4 \]

**CPO**: Composite Pulse Decoupling

A repeated series of strong pulses

to obtain the effect of random broad band decoupling

---

1D proton Transient NOE

- Selective excitation H-1 (essential variable: mixing time)

- To estimate the distance between nuclei. (\(< 5 \sim 6 \text{ A}\))
  The sign of NOE can be positive, zero, or negative!

- To detect existence of Conformer s (Slow conformation change)
  The sign of the NOE is negative
  (negative NOE, also known as Chemical exchange NOE).
Any other NOE? ROE

- Depends on Mixing time and spin-lattice relaxation;
  - Large molecules such as protein D8 ~ 100 to 50 ms
  - Small molecules D8: range 0.2 s to 0.9 s.

- Can show either Positive NOE, negative NOE, and/or zero!

- ROESY: to distinguish positive and negative NOE.

END of Basic NOE review