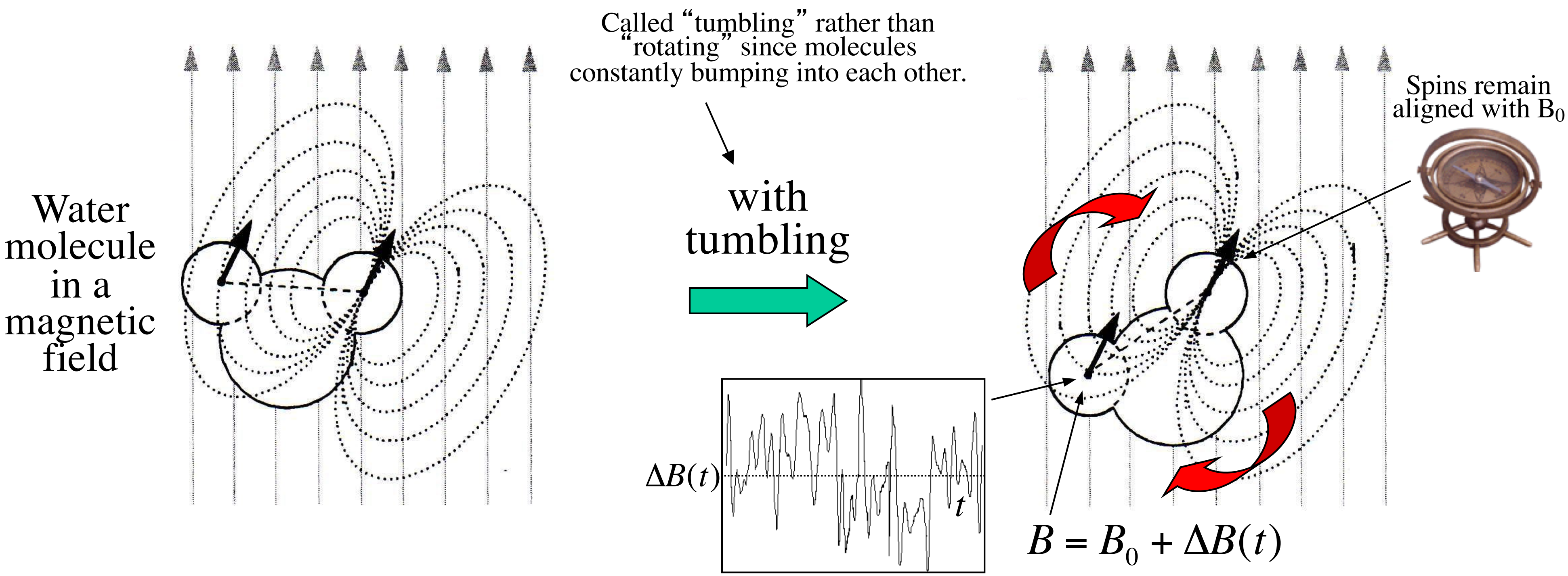
Lecture #4
Relaxation through Dipolar Coupling

- Topics
  - Solomon equations
  - Calculating transition rates
  - Nuclear Overhauser Effect
- Handouts and Reading assignments
  - Levitt, Chapters 19.1-3, 20.1-3,
  - Kowalewski, Chapter 3.
  - Solomon, I, "Relaxation process in a system of two spins", Physical Review, 99(2):559-565, 1955.

Dipolar Coupling

- The dominant source of random magnetic field variations is due to dipolar coupling and molecular tumbling.



- While $\langle \Delta B(t) \rangle = 0$, the instantaneous effect is *not* negligible.
- We need to take a close look at the properties of $\Delta B(t)$.

Random fields model

- Assume the magnetic field seen by a spin is given by

$$\underbrace{B_0\vec{z}}_{\text{large main field}} + \underbrace{B_x(t)\vec{x} + B_y(t)\vec{y} + B_z(t)\vec{z}}_{\text{small perturbation}} \quad \text{where} \quad \underbrace{\langle B_x^2 \rangle = \langle B_y^2 \rangle = \langle B_z^2 \rangle = \langle B^2 \rangle}_{\text{isotropic tumbling}}$$

the relaxation of M_z was given as: $\dfrac{1}{T_1} = \gamma^2 \langle B^2 \rangle J(\omega_0)$

- Given the field from a dipole falls off as $1/r^3$

$$\frac{1}{T_1} \propto \frac{\gamma^4}{r^6} J(\omega_0). \qquad \text{Similarly} \quad \frac{1}{T_2} \propto \frac{\gamma^4}{2r^6}\left(J(0) + J(\omega_0)\right).$$

Rapid decrease with distance $\Rightarrow$ Primarily *intra*molecular rotational rather than *inter*molecular translational motion.

- The seminal work of Bloembergen, Purcell, and Pound (BPP), Physical Review, 73(7) 1948, recognized the importance of dipolar coupling to NMR relaxation.

Bloembergen

Nobel Prize Physics 1981

Complete Dipolar Effect

- A more complete derivation taking into account the correlated perturbations among coupled spins was provided by Solomon Physical Review, 99(1) 1955.

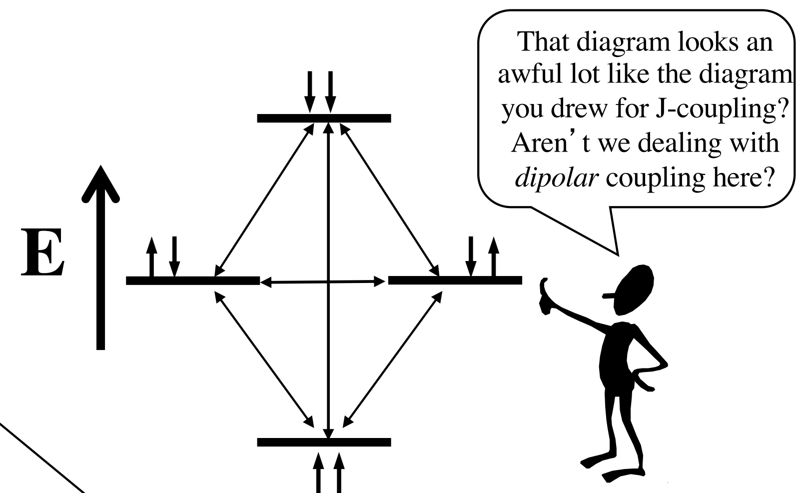
For identical spins, e.g. water,

$$\frac{1}{T_1} = \frac{3}{20}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(J(\omega_0) + 4J(2\omega_0)\right)$$

$$= \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right)$$

$$\frac{1}{T_2} = \frac{3}{40}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(3J(0) + 5J(\omega_0) + 2J(2\omega_0)\right)$$

$$= \frac{3}{20}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right)$$

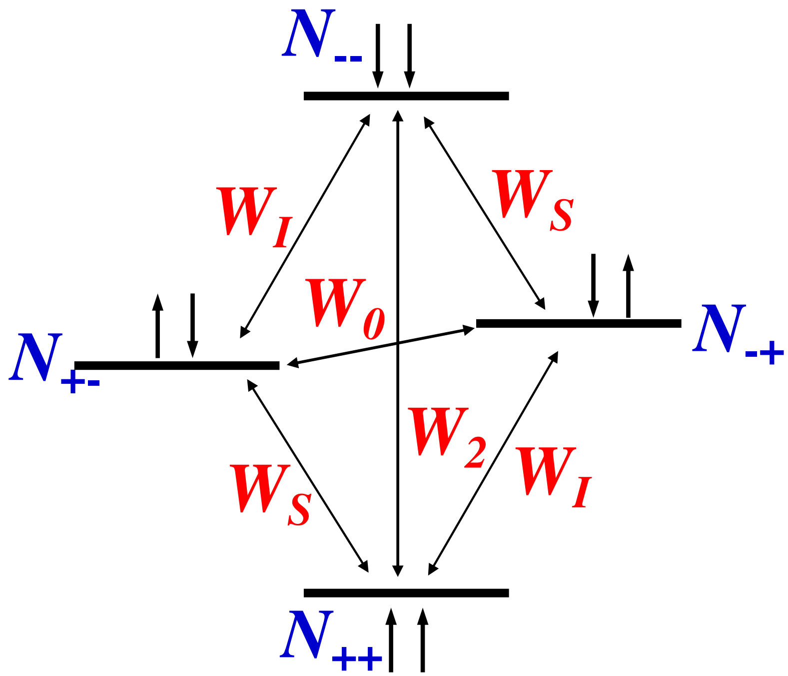


New term corresponds to both I and S spins flipping together, i.e. double quantum coherence.

- Let's look at this derivation more closely…

Spin Population Dynamics*

- Consider a general dipolar coupled two-spin system.



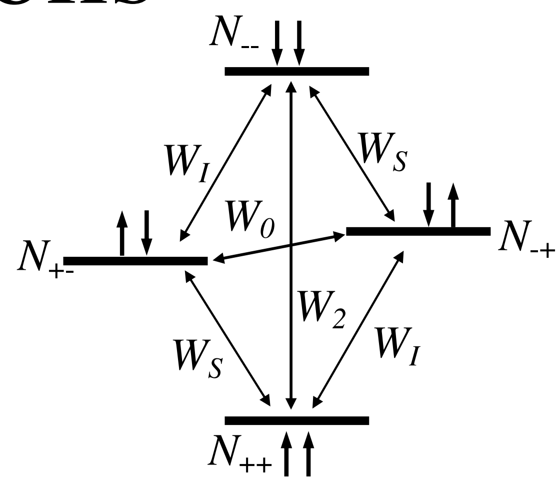
Note: J=0, but nuclei I and S are close enough in space that dipolar coupling is significant.

- At a given point in time, the energy levels are occupied by a certain number of spins, given by N_{++}, N_{+-}, N_{-+}, and N_{--}.
- Transition rates:
  - W_I and W_S = probability/time spin *I* or *S* change energy levels.
  - W_0 and W_2 = probability/time of zero of double quantum transition.

*see Solomon for details.

The Solomon Equations

- Given the transition rates and the populations, let's compute the dynamics. Namely…



$$\frac{dN_{++}}{dt} = -(W_S + W_I + W_2)N_{++} + W_S N_{+-} + W_I N_{-+} + W_2 N_{--}$$

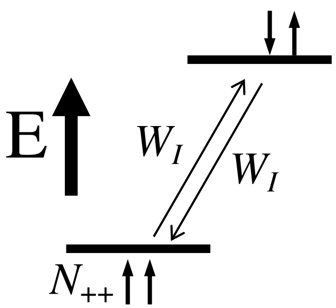
$$\frac{dN_{+-}}{dt} = -(W_0 + W_S + W_I)N_{+-} + W_0 N_{-+} + W_I N_{--} + W_S N_{++}$$

$$\frac{dN_{-+}}{dt} = -(W_0 + W_S + W_I)N_{-+} + W_0 N_{+-} + W_I N_{++} + W_S N_{--}$$

$$\frac{dN_{--}}{dt} = -(W_S + W_I + W_2)N_{--} + W_S N_{-+} + W_I N_{+-} + W_2 N_{++}$$

Correction for finite temperatures

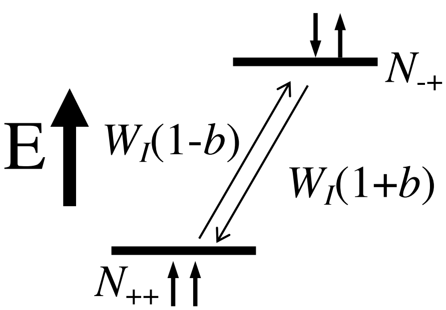
- Before proceeding further, we need to make a small addition, known as the finite temperature correction.
- The differential equations on the previous slide assumed equality of the transition probabilities, e.g. just looking at the *I* spin…



$$N_{-+} \rightarrow N_{++} = N_{++} \rightarrow N_{-+} = W_I$$

Under this assumption, the system will evolve until the energy states are equally populated, which, using the Boltzmann distribution, corresponds to an infinite temperature!

- To achieve a finite temperature, we can make an ad hoc correction reflecting the slightly increased probability of a transition that decreases the energy of the system.

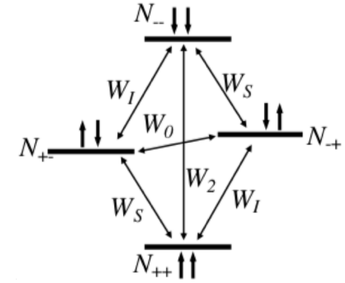


where $b = \dfrac{\gamma\hbar B_0}{kT}$

Boltzmann factor

This Boltzmann factor can be derived explicitly if we treat both the spin system and the lattice as quantum mechanical systems. See Abragam p. 267.

Solomon Equations: M_z



- Let's first look at T_1 relaxation.

$$\overline{\langle \hat{I}_z \rangle} \propto (N_{++} - N_{-+}) + (N_{+-} - N_{--}) \qquad \overline{\langle \hat{S}_z \rangle} \propto (N_{++} - N_{+-}) + (N_{-+} - N_{--})$$

- Substituting yields a set of coupled differential equations indicating longitudinal magnetization recovers via a combination of two exponential terms…

$$\frac{d\overline{\langle \hat{I}_z \rangle}}{dt} = \underbrace{-(W_0 + 2W_I + W_2)\left(\overline{\langle \hat{I}_z \rangle} - I_z^{eq}\right)}^{\text{direct relaxation}} \overbrace{-(W_2 - W_0)\left(\overline{\langle \hat{S}_z \rangle} - S_z^{eq}\right)}^{\text{cross relaxation}}$$

$$\frac{d\overline{\langle \hat{S}_z \rangle}}{dt} = -(W_0 + 2W_S + W_2)\left(\overline{\langle \hat{S}_z \rangle} - S_z^{eq}\right) - (W_2 - W_0)\left(\overline{\langle \hat{I}_z \rangle} - I_z^{eq}\right)$$

General Solution

- The solution can also be written

$$\frac{d}{dt}\begin{bmatrix} \overline{\langle \hat{I}_z \rangle} \\ \overline{\langle \hat{S}_z \rangle} \end{bmatrix} = -\begin{bmatrix} \rho_I & \sigma_{IS} \\ \sigma_{IS} & \rho_S \end{bmatrix}\begin{bmatrix} \overline{\langle \hat{I}_z \rangle} - I_z^{eq} \\ \overline{\langle \hat{S}_z \rangle} - S_z^{eq} \end{bmatrix} \quad \text{with} \quad I_z^{eq} = \frac{\gamma_I B_0}{2kT} \quad S_z^{eq} = \frac{\gamma_S B_0}{2kT}$$

$$\frac{d}{dt}\vec{V} = -\underline{R}\left(\vec{V} - \vec{V}^{eq}\right)$$

where R is called the *relaxation matrix* with elements given by:

$$\rho_I = W_0 + 2W_I + W_2$$
$$\rho_S = W_0 + 2W_S + W_2$$
$$\sigma_{IS} = W_2 - W_0$$

- The general solution is of the form

$$\overline{\langle \hat{I}_z \rangle} = \alpha_{11}e^{-\lambda_1 t} + \alpha_{12}e^{-\lambda_2 t}$$
$$\overline{\langle \hat{S}_z \rangle} = \alpha_{21}e^{-\lambda_1 t} + \alpha_{22}e^{-\lambda_2 t}$$

(not a single exponential)

Identical Spins

- For the case of S and I identical (i.e. $\omega_I = \omega_S$ and $W_I = W_S = W_1$)

$$\frac{d\left(\overline{\langle \hat{I}_z \rangle} + \overline{\langle \hat{S}_z \rangle}\right)}{dt} = -2(W_1 + W_2)\left(\overline{\langle \hat{I}_z \rangle} + \overline{\langle \hat{S}_z \rangle} - I_z^{eq} - S_z^{eq}\right) \quad \text{(pure exponential)}$$

$$\Rightarrow \quad \frac{1}{T_1} = 2(W_1 + W_2)$$

- We now need explicit expressions for the transition probabilities W_1, and W_2.

Time-dependent Perturbation Theory

- To compute the transition probabilities, we need to use a branch of QM known as time-dependent perturbation theory. Consider the case where:

$$\hat{H}(t) = \hat{H}_0 + \underbrace{\hat{H}_1(t)}_{\text{perturbation}} \quad \text{with} \quad \left|\hat{H}_1\right| << \left|\hat{H}_0\right|.$$

- Let $\left|m_j\right\rangle,\ j = 1 \ldots N$ be the eigenkets of the unperturbed Hamiltonian with energies E_j.

$$\hat{H}_0\left|m_j\right\rangle = \tfrac{1}{\hbar} E_j \left|m_j\right\rangle \quad \text{with} \quad j = 1, \ldots N$$

- Assuming the system starts in state $\left|m_j\right\rangle$, then, to 1st order, the probability of being in state $\left|m_k\right\rangle$ at time t is given by

$$\mathcal{P}_{kj} = \frac{1}{\hbar^2}\left|\int_o^t \left\langle m_k\right|\hat{H}_1(t')\left|m_j\right\rangle e^{-i\omega_{kj}t'}\,dt'\right|^2$$

(see homework for proof)

where $\omega_{kj} = (E_k - E_j)/\hbar$

Fermi's Golden Rule

- Consider a sinusoidal perturbation

$$\hat{H}_1(t) = \hat{V}_1 \cos\omega t = \frac{\hat{V}_1}{2}\left(e^{i\omega t} + e^{-i\omega t}\right)$$

This is actually quite general as we can always analyze the Fourier decomposition of any perturbation.

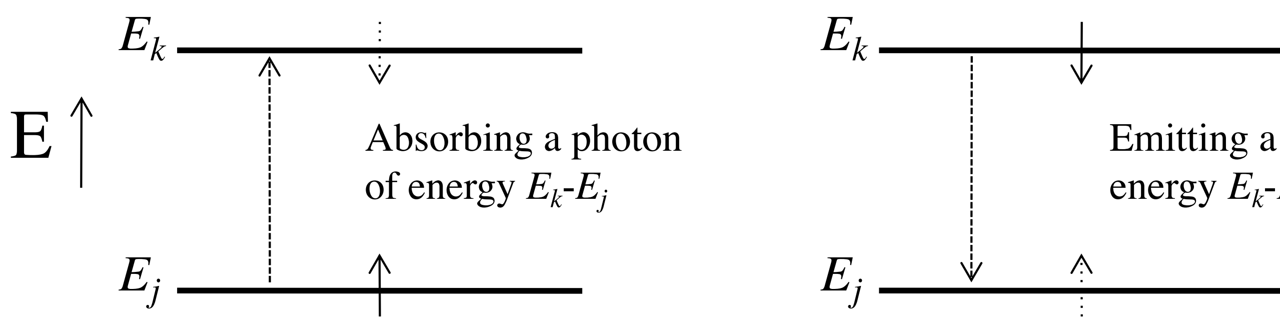
- The *transition rate* is then given by

$$W_{kj} = \lim_{t\to\infty} \frac{\mathcal{P}_{kj}}{t} = \lim_{t\to\infty} \frac{1}{t}\left|\int_o^t \langle m_k|\hat{H}_1(t')|m_j\rangle e^{-i\omega_{kj}t'}\, dt'\right|^2$$

Note, we can take the limit of $t \to \infty$ if our measurements are much longer than $1/\omega_{kj}$.

$$\boxed{W_{kj} = \underbrace{\frac{\left|\langle m_k|\hat{V}_1|m_j\rangle\right|^2}{4}}_{\text{Interaction term}} \underbrace{\left(\delta_{E_k-E_j,-\hbar\omega} + \delta_{E_k-E_j,+\hbar\omega}\right)}_{\text{Conservation of energy}}}$$

This is a famous result known as *Fermi's Golden Rule*.



Example: Rf Excitation

- For a two spin system (rotating frame, on resonance) …

$$\hat{H} = \underbrace{\Omega_I \hat{I}_z + \Omega_S \hat{S}_z + 2\pi J(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y + \hat{I}_z \hat{S}_z)}_{\hat{H}_0} + \underbrace{\omega_1^I \hat{I}_x + \omega_1^S \hat{S}_x}_{\hat{H}_1}$$

- The interaction term (matrix form with eigenkets of $\hat{H}_0$ as the basis) is given by …

$$\underline{H_1} \propto \begin{array}{c c} & \begin{array}{cccc} |++\rangle & |+-\rangle & |-+\rangle & |--\rangle \end{array} \\ \begin{array}{c} |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{array} & \begin{pmatrix} 0 & 1-i & 1-i & 0 \\ 1+i & 0 & 0 & 1-i \\ 1+i & 0 & 0 & 1-i \\ 0 & 1+i & 1+i & 0 \end{pmatrix} \end{array}$$

(Simple case of $\gamma_I = \gamma_S$)

– No excitation if Rf is "off resonance" (conservation of energy)

– No excitation of double or zero quantum coherences (zero interaction)

Dipolar Coupling

- The complete dipolar coupling Hamiltonian is given by

$$\hat{H}_{dipole} = -\frac{\gamma_I \gamma_S \hbar}{r^3}\frac{\mu_0}{4\pi}\left(\hat{\vec{I}}\cdot\hat{\vec{S}} - \frac{3}{r^2}(\hat{\vec{I}}\cdot\vec{r})(\hat{\vec{S}}\cdot\vec{r})\right)$$

where $\vec{r}$ is the vector from spin I to spin S

- Using the raising and lowering operators: $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$ and $\hat{I}_- = \hat{I}_x - i\hat{I}_y$ the the Hamiltonian can be written in polar coordinates as:

$$H_d = -\frac{\mu_0}{4\pi}\frac{\gamma_I \gamma_S \hbar}{r^3}\left(A + B + C + D + E + F\right)$$ where

$$A = \hat{I}_z \hat{S}_z F_0$$

$$B = -\tfrac{1}{4}\left(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+\right)F_0$$

zero quantum term

$$C = \left(\hat{I}_+\hat{S}_z + \hat{I}_z\hat{S}_+\right)F_1$$

$$D = \left(\hat{I}_-\hat{S}_z + \hat{I}_z\hat{S}_-\right)F_1^*$$

single quantum terms

$$E = \hat{I}_+\hat{S}_+F_2$$

$$F = \hat{I}_-\hat{S}_-F_2^*$$

double quantum terms

$$F_0(t) = 1 - 3\cos^2\theta$$

$$F_1(t) = \tfrac{3}{2}\sin\theta\cos\theta e^{-i\phi}$$

$$F_2(t) = \tfrac{3}{4}\sin^2\theta e^{-2i\phi}$$

Note, with molecular tumbling, both θ and ϕ are functions of time.

Example: Calculating W_1

- Assumption: $\left\langle F(t)F^*(t+\tau)\right\rangle = \left\langle \left|F(0)\right|^2\right\rangle e^{-|\tau|/\tau_c}$

  time average

- For a given pair of like spins:

$$W_1 = \lim_{t'\to\infty}\frac{1}{t}\left|\int_0^t \tfrac{1}{2}\frac{\gamma^2\hbar}{r^3}F_1(t')e^{-i\omega_0 t'}\,dt'\right|^2 = \left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma^4\hbar^2}{4r^6}\int_0^\infty \left\langle \left|F_1(0)\right|^2\right\rangle e^{-|\tau|/\tau_c}e^{-i\omega_0\tau}\,d\tau$$

- For an ensemble of spins:

$$W_1 = \left(\frac{\mu_0}{4\pi}\right)^2\frac{\gamma^4\hbar^2}{4r^6}\overline{\left\langle \left|F_1(0)\right|^2\right\rangle}\frac{\tau_c}{1+\omega_0^2\tau_c^2}$$

$$\overline{\left\langle \left|F_1(0)\right|^2\right\rangle} = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi}\tfrac{9}{4}\sin^2\theta\cos^2\theta\sin\theta\, d\theta\, d\phi$$

$$W_1 = \left(\frac{\mu_0}{4\pi}\right)^2\frac{3\gamma^4\hbar^2}{40r^6}J(\omega_0)$$

Transition Probabilities

- Using similar equations, the full set of transition rates are:

$$W_I = \tfrac{3}{2} q J(\omega_I)$$

$$W_S = \tfrac{3}{2} q J(\omega_S)$$

$$W_2 = 6 q J(\omega_I + \omega_S)$$

sum of chemical shifts

$$W_0 = q J(\omega_I - \omega_S)$$

difference of chemical shifts

where

$$J(\omega) = \frac{2\tau_c}{1 + \omega^2 \tau_c^2}$$

$$q = \frac{1}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r_{IS}^6}$$

rapid fall off with distance

Identical Spins

- For the case of S and I identical (i.e. $\omega_I = \omega_S$ and $W_I = W_S = W_1$)

$$\frac{1}{T_1} = 2(W_I + W_2) = \frac{3}{20}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(J(\omega_0) + 4J(2\omega_0)\right)$$

$$= \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right) \xrightarrow[\text{narrowing}]{\text{Extreme}} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3\gamma^4\hbar^2\tau_c}{2r^6}$$

- If we crunch through the numbers…

$$\frac{1}{T_2} = \frac{3}{40}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(3J(0) + 5J(\omega_0) + 2J(2\omega_0)\right)$$

$$= \frac{3}{20}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma^4\hbar^2}{r^6}\left(3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right) \xrightarrow[\text{narrowing}]{\text{Extreme}} \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3\gamma^4\hbar^2\tau_c}{2r^6}$$

- Later in the course, we'll develop Redfield theory and not have to "crunch the numbers" every time.

T_1 and T_2 of water

- Some numbers for pure water….

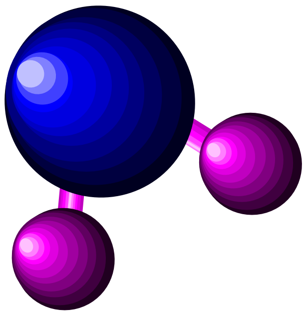
$$\tau_c = 5.0 \times 10^{-12}$$

$$K = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{3}{10} \frac{\gamma^4 \hbar^2}{r^6} = 1.02 \times 10^{10}$$

$$\frac{1}{T_1} = K\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right]$$

$$\frac{1}{T_2} = \frac{K}{2}\left[3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right]$$

water



$$T_1 \approx T_2 \approx 3.92 \text{ s}$$

(extreme narrowing condition)

Cross Relaxation

- Let's try to gain some more physical insight/intuition into the phenomenon of cross relaxation.

The Solomon Equations

$$\frac{d}{dt}\begin{bmatrix} \overline{\langle \hat{I}_z \rangle} \\ \overline{\langle \hat{S}_z \rangle} \end{bmatrix} = -\begin{bmatrix} \rho_I & \sigma_{IS} \\ \sigma_{IS} & \rho_S \end{bmatrix}\begin{bmatrix} \overline{\langle \hat{I}_z \rangle} - I_z^{eq} \\ \overline{\langle \hat{S}_z \rangle} - S_z^{eq} \end{bmatrix}$$

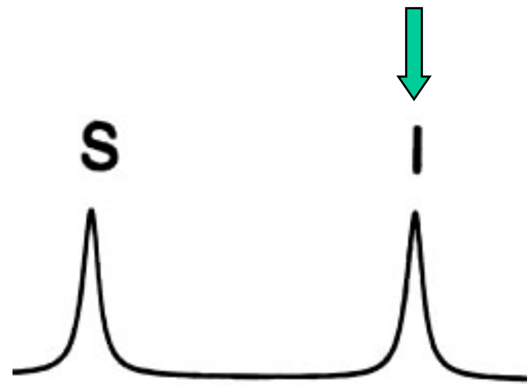
- We'll start by examining the results of a series of *saturation recovery* experiments in which the z magnetization from the I or S spins (or both) are saturated, and we then watch the recovery of the longitudinal magnetization over time.

Saturation Recovery

- Case (a)

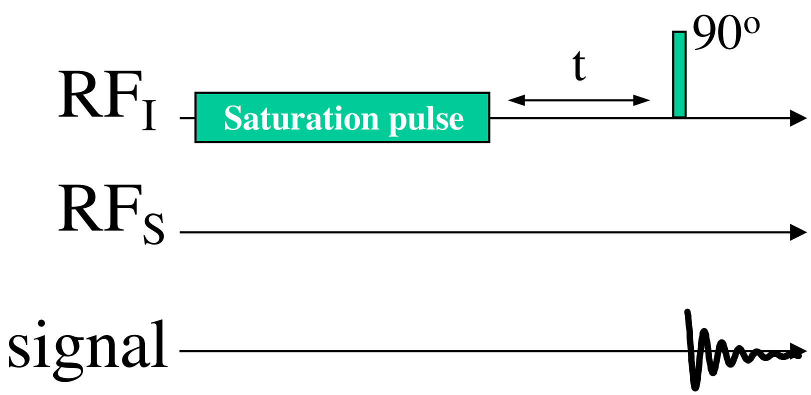
Initial conditions

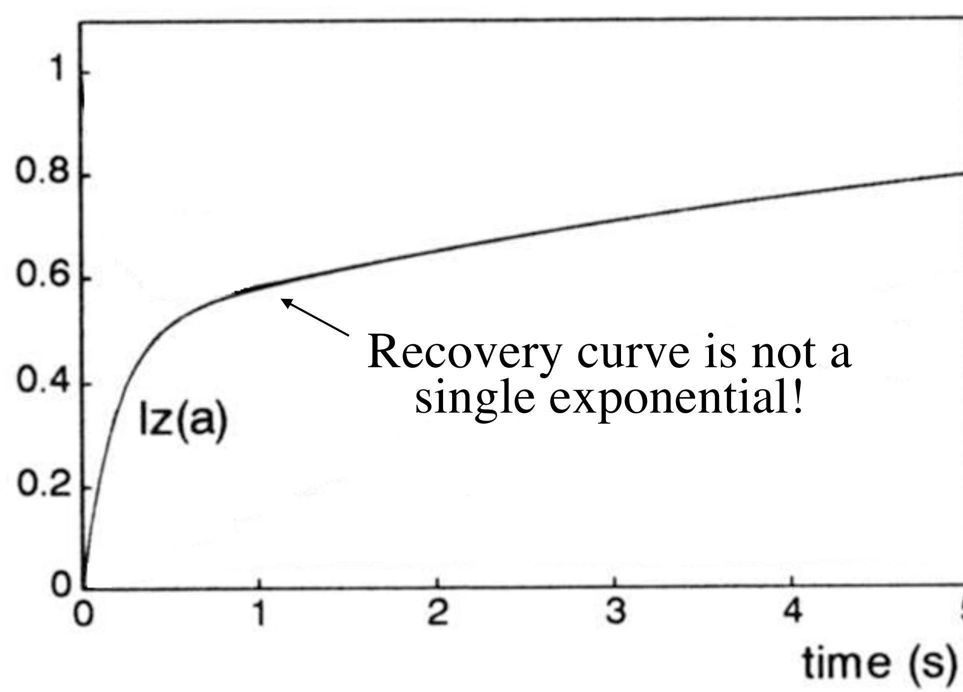
Saturate M_z for *I* spins
Leave *S* spins untouched



Experiment

Observe recovery of M_z for *I* spins





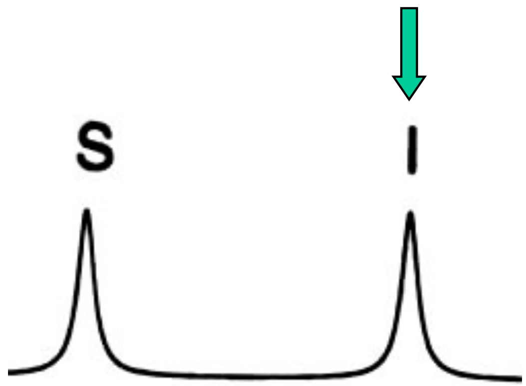
Saturation Recovery

- Case (a*)

<u>Initial conditions</u>

Saturate M_z for *I* spins

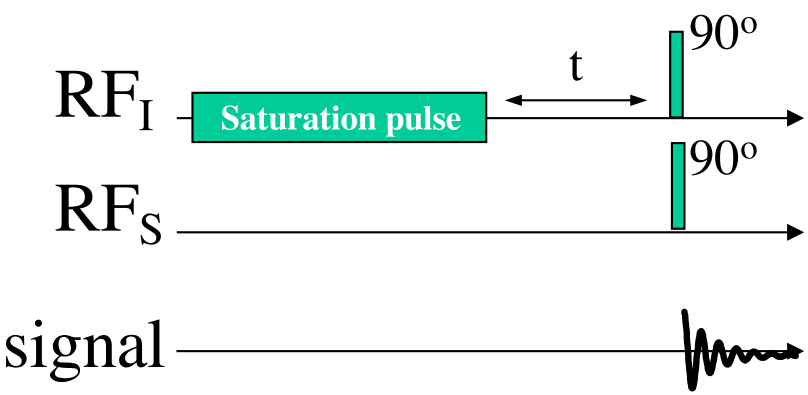
Leave *S* spins untouched

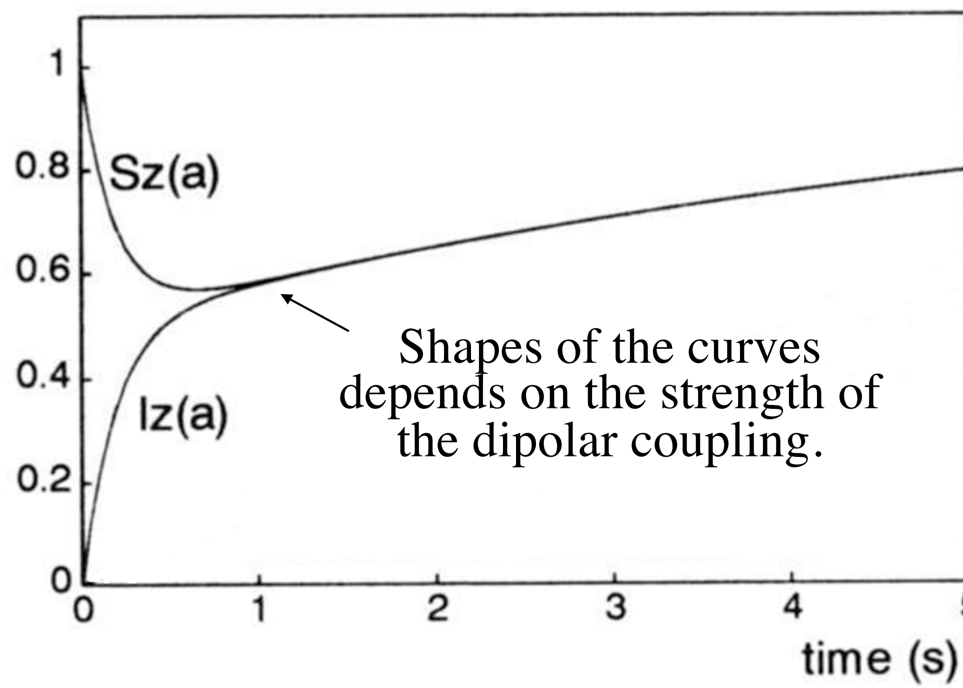


<u>Experiment</u>

Observe recovery of M_z for *I* spins

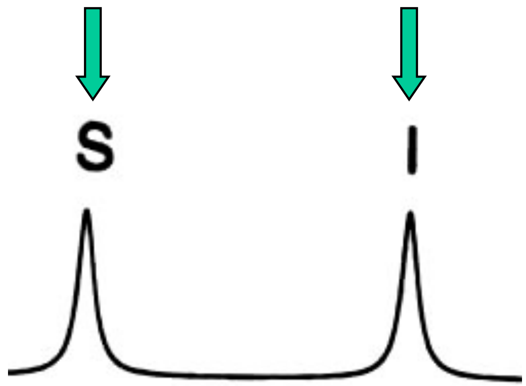
Observe recovery of M_z for *S* spins





Saturation Recovery

- Case (b)

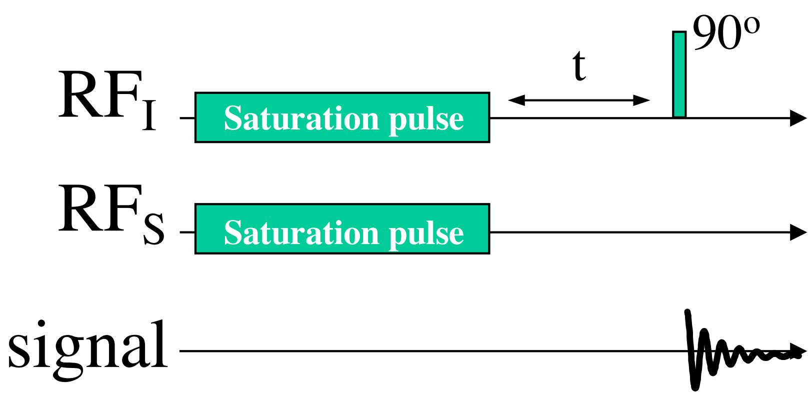


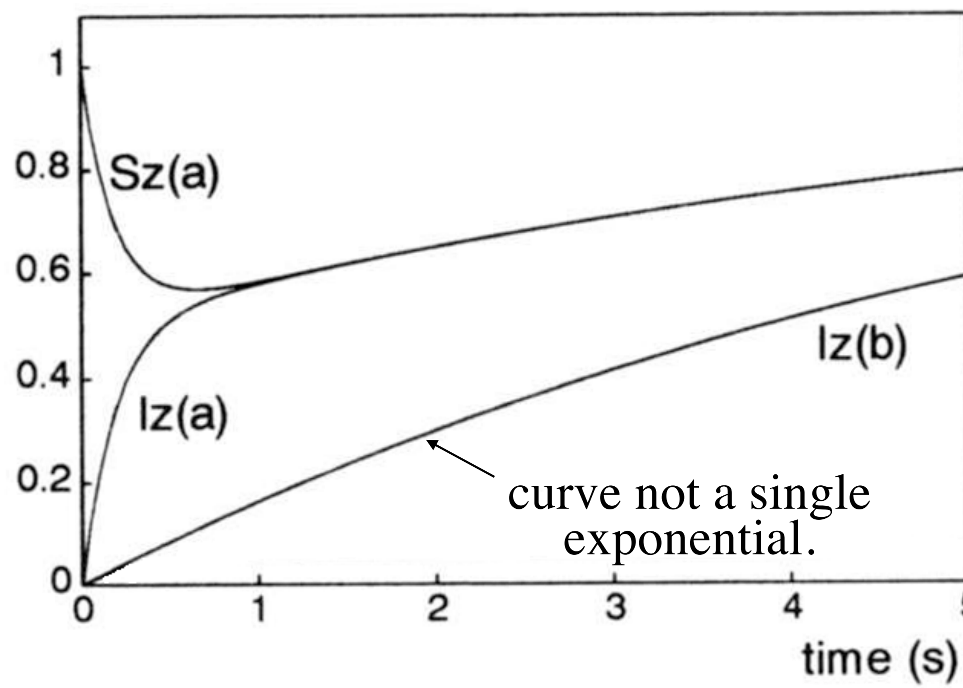
Initial conditions

Saturate M_z for *I* spins
Saturate M_z for *S* spins

Experiment

Observe recovery of M_z for *I* spins



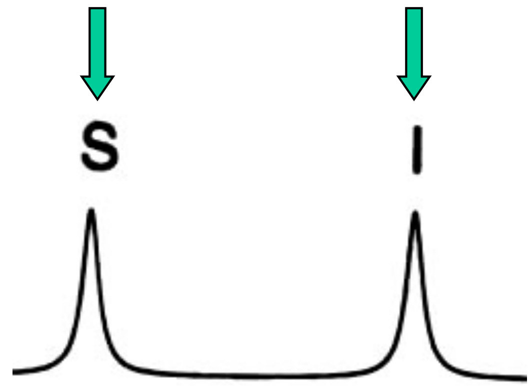


Saturation Recovery

- Case (c)

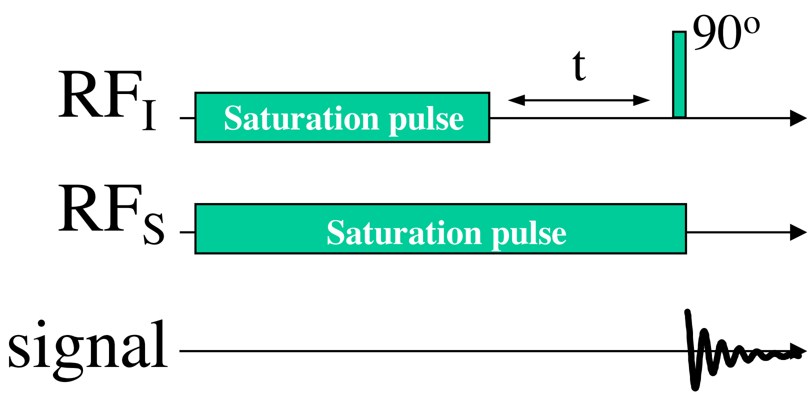
<u>Initial conditions</u>

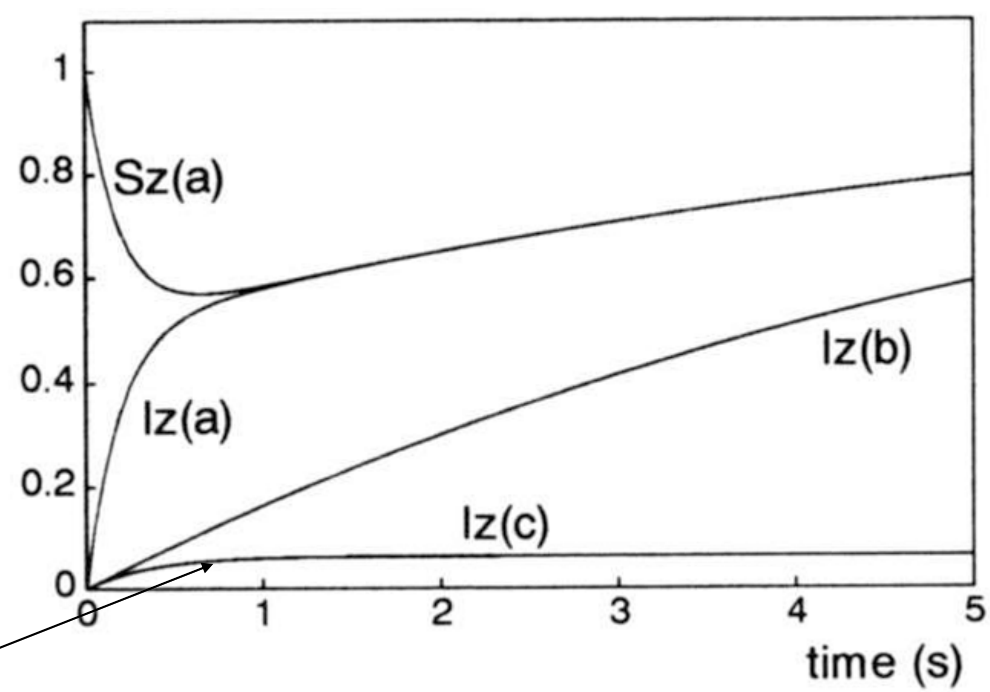
Saturate M_z for *I* spins
Saturate M_z for *S* spins



<u>Experiment</u>

Continue keeping M_z for *S* spins saturated
Observe recovery of M_z for *I* spins





This curve *does* recover exponential with the true T_1 of spin *I*. However it does *not* recover to I_z^{eq}!

Nuclear Overhauser Effect (NOE)

- The NOE is the change in the equilibrium magnetization of one nuclei with the RF irradiation of a nearby nuclei (nearby defined in terms of dipole coupling)
- The change in magnetization can be positive (generally with small rapidly tumbling molecules) or negative (as with slower tumbling molecules)
- The effect was first proposed by Albert Overhauser in 1953.
- We will describe NOE…
  - mathematically
  - graphically (via energy diagrams)
  - with in vivo examples

Albert Overhauser

Calculating the NOE

- Start: $\dfrac{d\overline{\langle \hat{I}_z \rangle}}{dt} = -(W_0 + 2W_I + W_2)\left(\overline{\langle \hat{I}_z \rangle} - I_z^{eq}\right) + (W_2 - W_0)\left(\overline{\langle \hat{S}_z \rangle} - S_0\right)$
- Saturate S_z $\Rightarrow$ $\overline{\langle \hat{S}_z \rangle} = 0$
- At steady state… $\dfrac{d\overline{\langle \hat{I}_z \rangle}}{dt} = 0$ $\Rightarrow$ $\dfrac{\overline{\langle \hat{I}_z \rangle}}{I_z^{eq}} = 1 + \dfrac{S_0}{I_z^{eq}}\left(\dfrac{W_2 - W_0}{W_0 + 2W_I + W_2}\right)$
- Rewriting in a more convenient form and letting I_e be the steady state magnetization…

$$I_e = (1+\eta)I_z^{eq} \quad \text{where} \quad \eta = \frac{\gamma_S}{\gamma_I}\left(\frac{W_2 - W_0}{W_0 + 2W_I + W_2}\right)$$

This is often just expressed as:

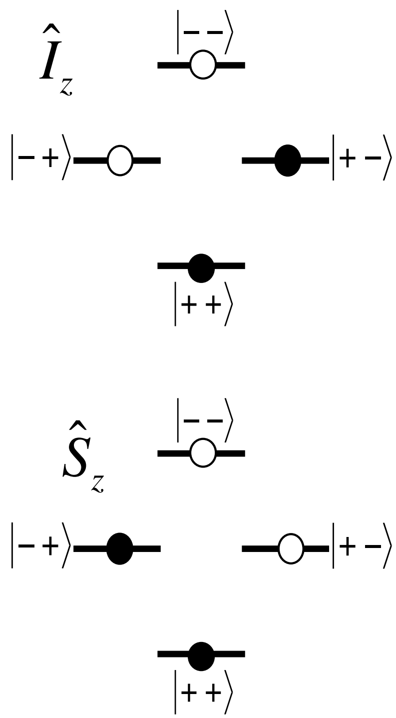
$$\text{NOE} = 1 + \frac{\gamma_S}{\gamma_I}\left(\frac{W_2 - W_0}{W_0 + 2W_I + W_2}\right) = 1 + \eta$$

enhancement factor (can be positive or negative)

Energy Diagram Formulation

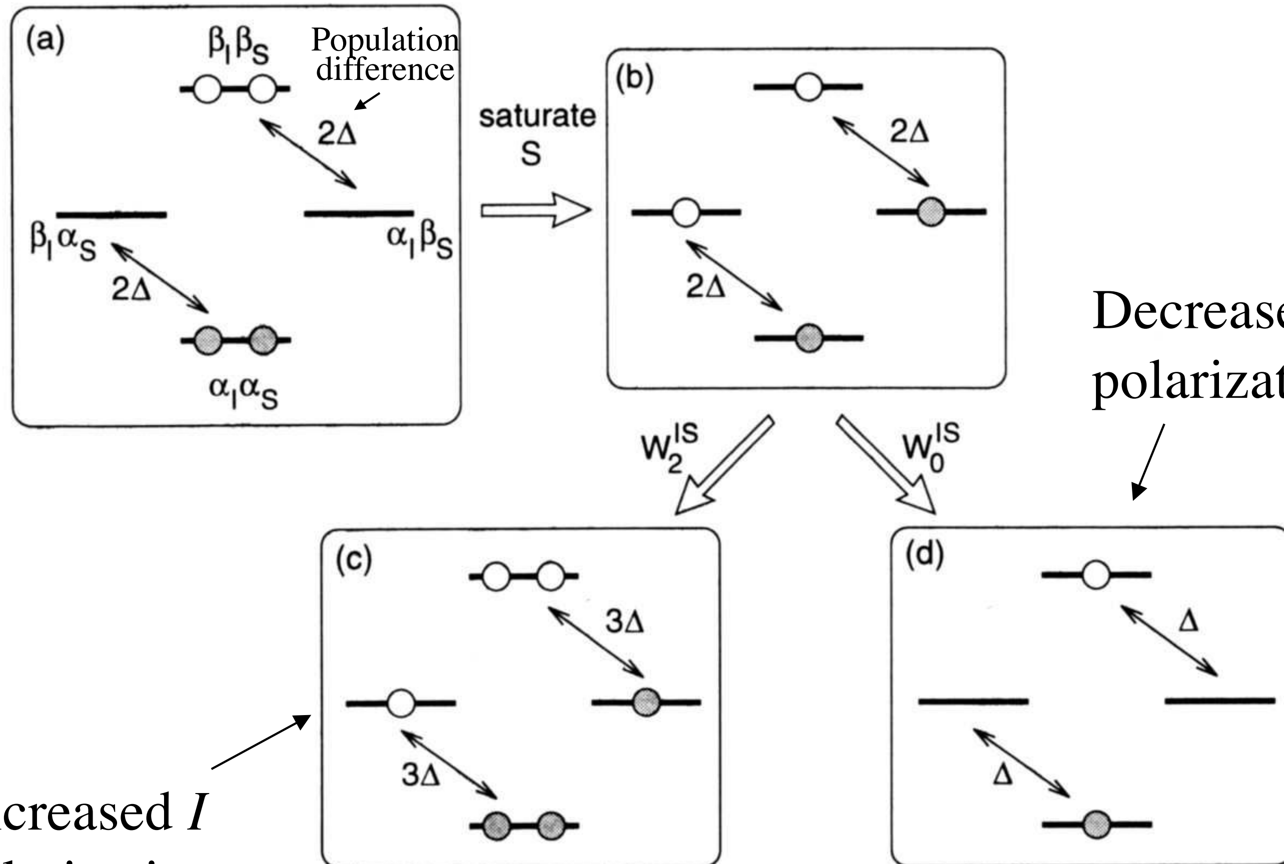
- Using an energy diagram notation…

Starting conditions



● Population excess
○ Population deficit

$\hat{I}_z + \hat{S}_z$



Decreased I polarization

Increased I polarization

(ignores W_I and W_S relaxation pathways)

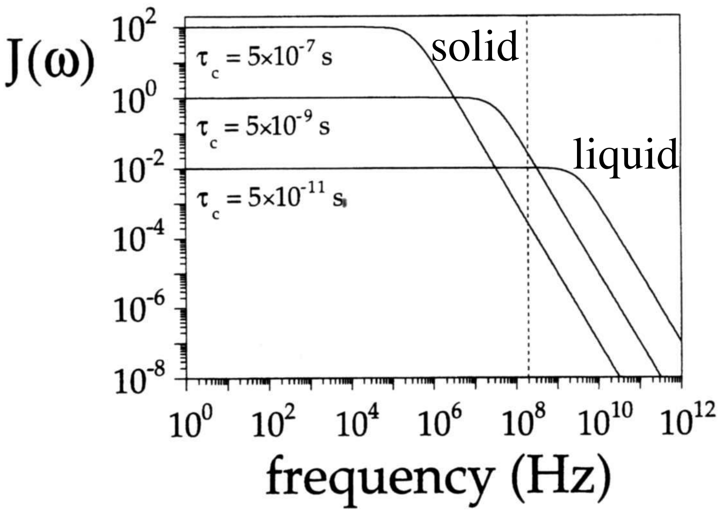
P. J. Hore, NMR, Oxford University Press, p 62.

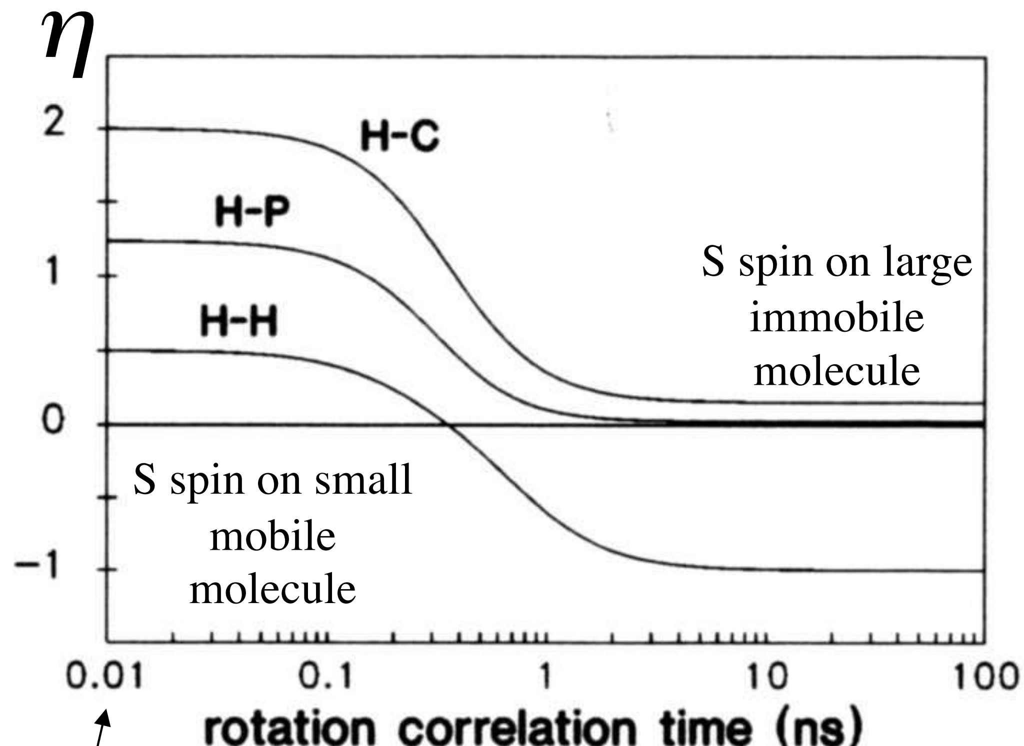
NOE versus τ_c

$$\mathrm{NOE} = 1 + \frac{\gamma_S}{\gamma_I}\left(\frac{W_2 - W_0}{W_0 + 2W_I + W_2}\right)$$

$$W_2 = 6qJ(\omega_I + \omega_S)$$

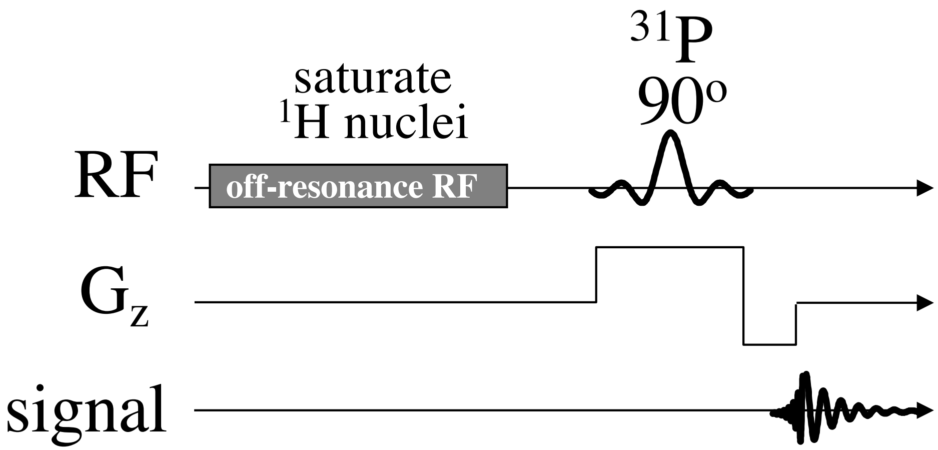
$$W_0 = qJ(\omega_I - \omega_S)$$

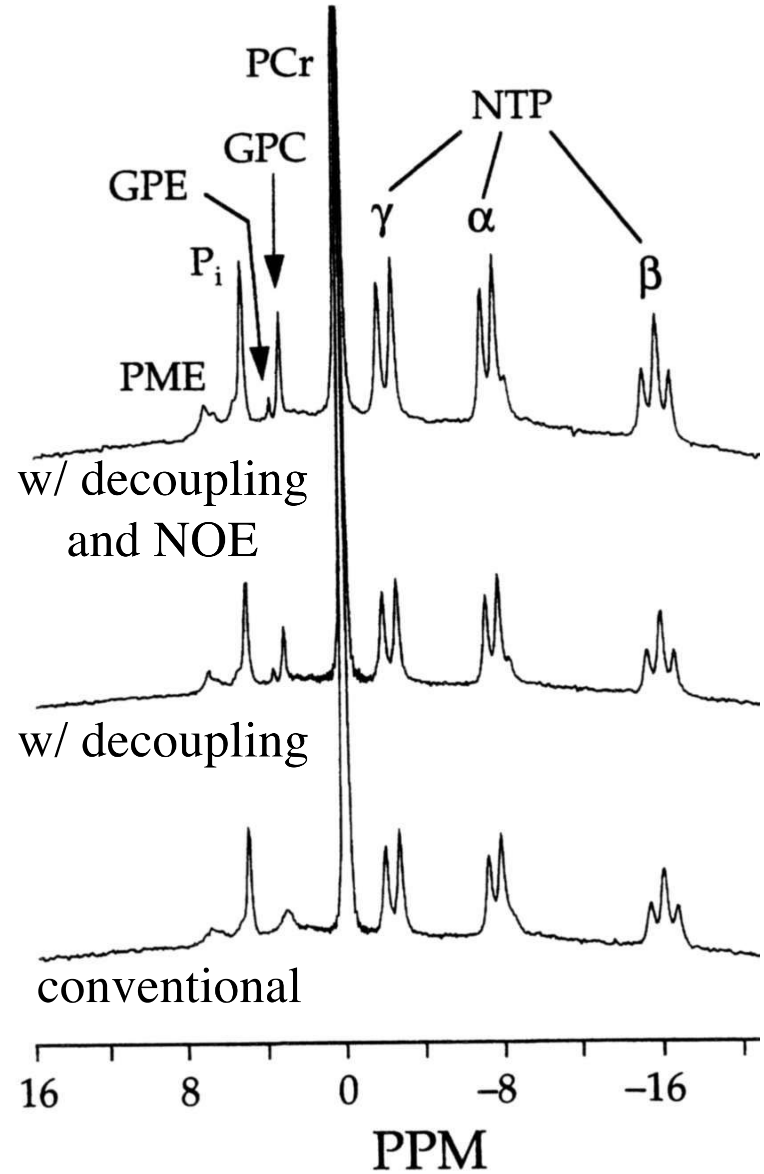




$$\omega^2\tau_c^2 << 1 \Rightarrow \mathrm{NOE} = 1 + \frac{\gamma_S}{2\gamma_I}$$

^{31}P Muscle NOE Example

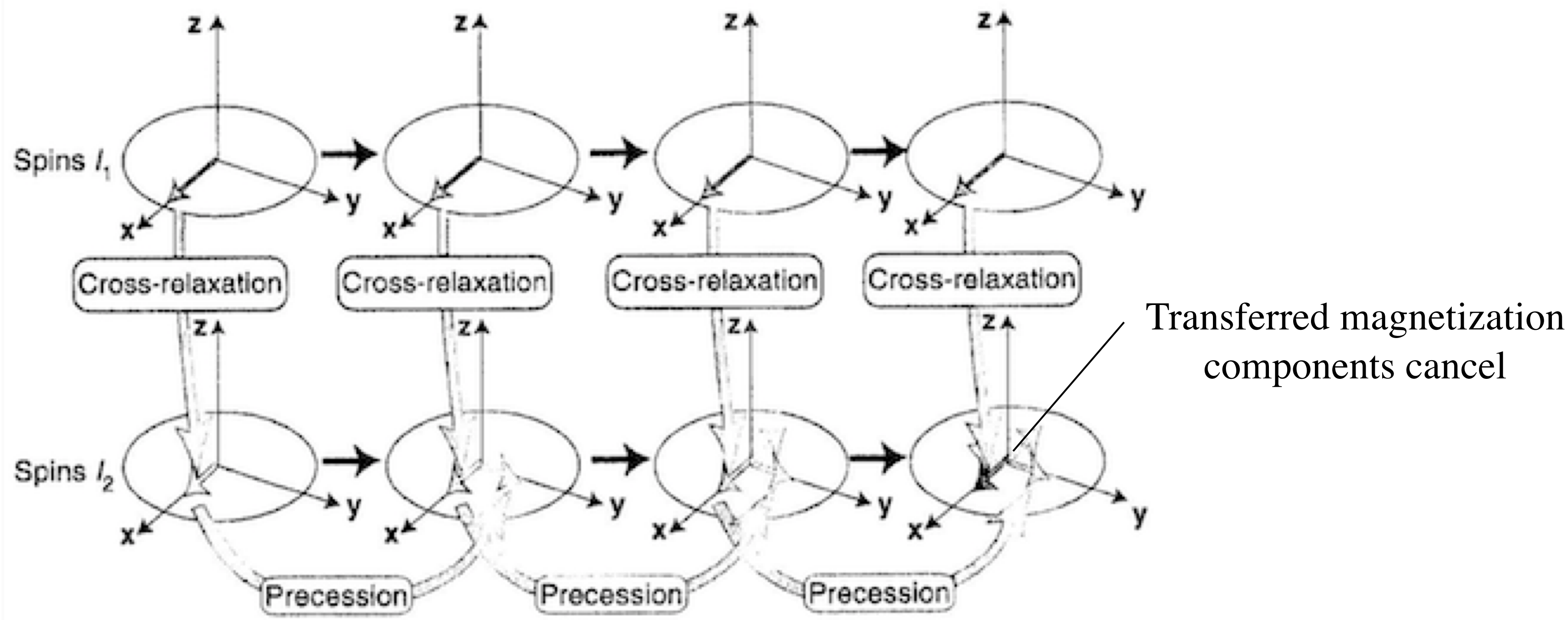




Typical *in vivo* NOE enhancement factors for ^{31}P-^{1}H and ^{13}C-^{1}H interactions are 1.4-1.8 and 1.3-2.9 respectively.

Transverse Cross Relaxation

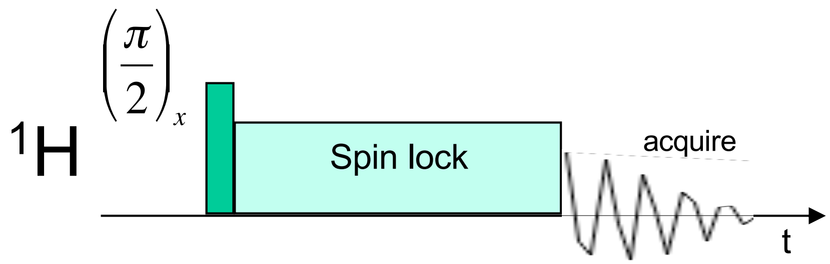
- NOE based on cross relaxation of longitudinal magnetization, but can cross relaxation of transverse magnetization be observed?
- Answer: usually no, but sometimes yes
- No effects for identical spins. But consider a dipolar-coupled system with the two spins having different chemical shifts.

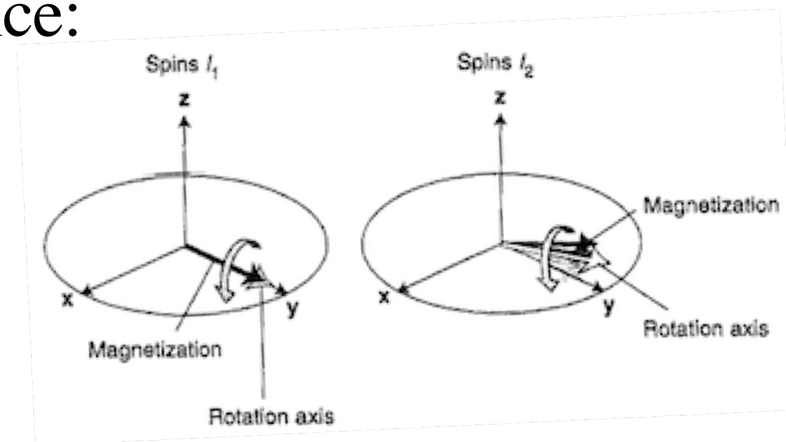


- Hence, cross relaxation of transverse magnetization is not observed between spins with different chemical shifts.

Spin Locking

- Consider the following pulse sequence:





The spin-lock Rf pulse inhibits chemical shift evolution.

- Cross relaxation of transverse magnetization can now occur

$$R^T_{auto} = \frac{K}{20}\left(5J(0) + 9J(\omega_0) + 6J(2\omega_0)\right) \qquad R^T_{cross} = -\frac{K}{10}\left(2J(0) + 3J(\omega_0)\right)$$

- Relaxation during a spin-lock pulse is characterized by a time constant $T_{1\rho}$, (more in upcoming lecture on cartilage).

Next Lecture: Chemical Exchange