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Introduction to Relaxation Theory

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What is relaxation? Why might it be interesting?

- ▶ relaxation is the process which drives the spins to equilibrium (equilibrium z -magnetization, no xy -magnetization)
- ▶ a natural phenomenon, driven by molecular motion
- ▶ unusually slow in NMR
- ▶ useful probe of molecular motion
- ▶ the Nuclear Overhauser Effect (NOE) arises because of relaxation; estimation of distance

Introduction and outline 2

Further reading

- ▶ for more detail: James Keeler, *Understanding NMR Spectroscopy*, 2nd edit., Wiley 2010 (Chapter 9)
- ▶ a PDF of this presentation is available to download at www-keeler.ch.cam.ac.uk

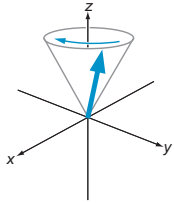
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Outline

1. How relaxation arises
2. Describing random motion – the correlation time
3. Motional regimes
4. Relaxation in terms of populations
5. Relaxation of a spin pair
6. Solomon equations and relaxation rate constants
7. Nuclear overhauser effect (NOE)
8. Transverse relaxation

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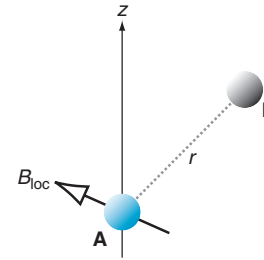
Behaviour of individual magnetic moments



- ▶ bulk magnetization result of sum of magnetic moments of each spin
- ▶ each moment behaves as the overall magnetization i.e. precesses about z, rotated away from z by transverse fields oscillating at Larmor frequency
- ▶ pulse affects all the same way, but relaxation caused by local fields which are *different* for each spin

How relaxation arises 5

Local fields

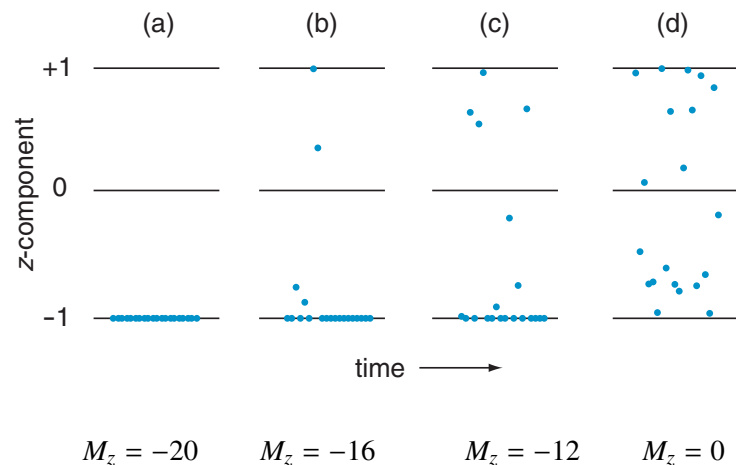


- ▶ e.g. spin **B** generates magnetic field at **A**
- ▶ a local field only significant over a short distance
- ▶ local field varies in size and direction according to length and orientation of **A–B** vector
- ▶ local field is random

How relaxation arises 6

How random fields drive the system to equilibrium

random fields fluctuating at close to the Larmor frequency should drive spins to equilibrium



How relaxation arises 7

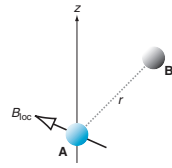
Coming to equilibrium with the lattice

- ▶ random fields would appear to drive the z-magnetization to zero
- ▶ incorrect: equilibrium z-magnetization is finite
- ▶ since 'surroundings' are large and at equilibrium, greater chance of losing energy to surroundings than gaining energy
- ▶ result is finite z-magnetization at equilibrium
- ▶ process is called *longitudinal* or *spin–lattice* relaxation

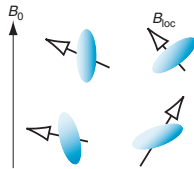
How relaxation arises 8

Relaxation mechanisms

- ▶ dipolar: local field goes as $\gamma_1\gamma_2/r^3$



- ▶ chemical shift anisotropy (CSA): local field goes as B_0 and typically depends on shift range



- ▶ paramagnetic species (e.g. dissolved oxygen)

How relaxation arises 9

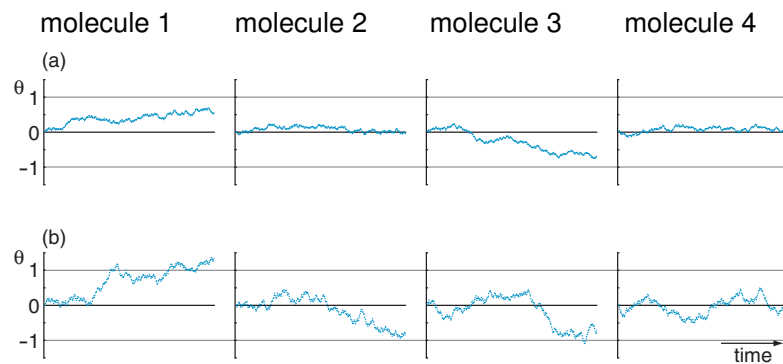
Describing random motion – the correlation time

- ▶ in solution, molecular collisions change orientation on about right timescale for relaxation
- ▶ each collision only alters orientation by a small amount – *rotational diffusion*
- ▶ *correlation time*, τ_c , is *average* time it takes a molecule to move through 1 radian
- ▶ *correlation time* describes the timescale of the random motion

Describing random motion – the correlation time 10

Rotational diffusion

representative molecules undergoing rotational diffusion



(a) has longer correlation time than (b)

Describing random motion – the correlation time 11

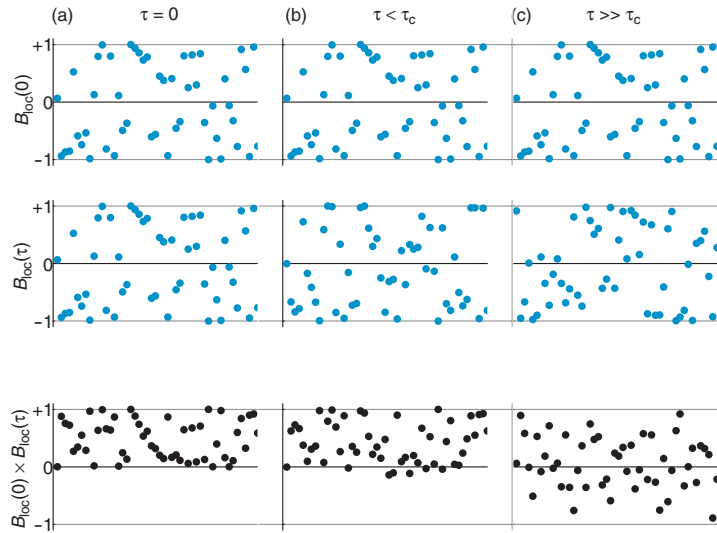
The correlation function

$$\begin{aligned}
 G(t, \tau) &= \frac{1}{N} [B_{\text{loc},1}(t)B_{\text{loc},1}(t + \tau) + B_{\text{loc},2}(t)B_{\text{loc},2}(t + \tau) + \dots] \\
 &= \frac{1}{N} \sum_{i=1}^N B_{\text{loc},i}(t)B_{\text{loc},i}(t + \tau) \\
 &= \overline{B_{\text{loc}}(t)B_{\text{loc}}(t + \tau)}
 \end{aligned}$$

- ▶ average of product of local field at time t with that at time $(t + \tau)$
- ▶ usually only depends on τ : *stationary* random function

Describing random motion – the correlation time 12

The correlation function



Describing random motion – the correlation time 13

Typical correlation function

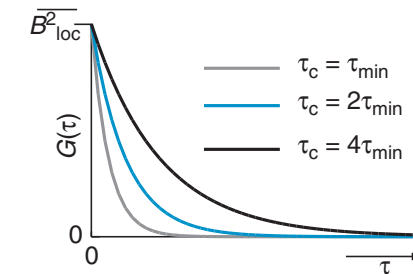
- ▶ maximum at $\tau = 0$

$$\begin{aligned} G(0) &= \overline{B_{\text{loc}}(t)B_{\text{loc}}(t)} \\ &= \overline{B_{\text{loc}}^2} \end{aligned}$$

- ▶ simplest form is an exponential

$$G(\tau) = \overline{B_{\text{loc}}^2} \exp(-|\tau|/\tau_c)$$

- ▶ typical behaviour



Describing random motion – the correlation time 14

Reduced correlation function

- ▶ time dependent part (max value 1)

$$g(\tau) = \exp(-|\tau|/\tau_c)$$

- ▶ hence

$$G(\tau) = \overline{B_{\text{loc}}^2} g(\tau)$$

- ▶ recall that we need motion at the Larmor frequency to cause relaxation; $g(\tau)$ describes time dependence

Describing random motion – the correlation time 15

The spectral density

- ▶ need to know amount of motion at Larmor frequency
- ▶ Fourier transform of function of time, $G(\tau)$, gives function of frequency, $J(\omega)$

$$G(\tau) \xrightarrow{\text{Fourier transform}} J(\omega)$$

- ▶ $J(\omega)$ gives amount of motion at frequency ω

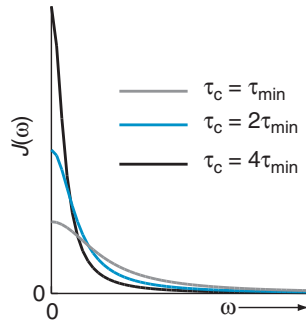
▶

$$\overline{B_{\text{loc}}^2} \exp(-|\tau|/\tau_c) \xrightarrow{\text{FT}} \overline{B_{\text{loc}}^2} \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

$$J(\omega) = \overline{B_{\text{loc}}^2} \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

Describing random motion – the correlation time 16

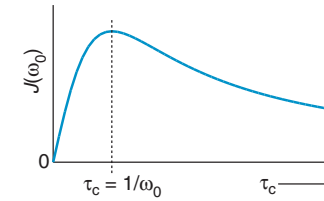
Spectral density: interpretation



- ▶ area under curve is independent of τ_c
- ▶ the shorter τ_c , the higher the frequency present in motion
- ▶ always has maximum value at zero frequency

Describing random motion – the correlation time 17

Spectral density at Larmor frequency



$J(\omega_0)$ plotted against τ_c

- ▶ maximum when $\tau_c = 1/\omega_0$; fastest relaxation with this value
- ▶ reduced spectral density, $j(\omega)$

$$g(\tau) \xrightarrow{\text{FT}} j(\omega)$$

$$\exp(-|\tau|/\tau_c) \xrightarrow{\text{FT}} \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

- ▶ hence $J(\omega) = \overline{B_{\text{loc}}^2} j(\omega)$

Describing random motion – the correlation time 18

Motional regimes

$$j(\omega_0) = \frac{2\tau_c}{1 + \omega_0^2\tau_c^2}$$

- ▶ fast motion $\omega_0\tau_c \ll 1$

$$\text{fast motion: } j(\omega_0) = 2\tau_c$$

$j(\omega_0)$ independent of frequency

- ▶ slow motion $\omega_0\tau_c \gg 1$

$$\text{slow motion: } j(\omega_0) = \frac{2}{\omega_0^2\tau_c} \quad \text{or} \quad j(\omega_0) = \frac{j(0)}{\omega_0^2\tau_c^2}$$

- ▶ small molecules: $\tau_c \approx 10$ ps – fast motion
- ▶ small protein: $\tau_c \approx 10$ ns – slow motion

Motional regimes 19

Summary

- ▶ rotational diffusion gives motion suitable for NMR relaxation
- ▶ rotational diffusion characterised by the correlation time τ_c
- ▶ spectral density gives the frequency distribution of the motion e.g.

$$J(\omega) = \overline{B_{\text{loc}}^2} \frac{2\tau_c}{1 + \omega^2\tau_c^2}$$

$J(\omega)$ depends on τ_c

- ▶ rate of longitudinal relaxation depends on spectral density at ω_0 ; max. when $\omega_0\tau_c = 1$

Motional regimes 20

Populations

- ▶ useful to think in terms of 'populations' of the spin states (energy levels) α ('spin up') and β ('spin down')
- ▶ z-magnetization due to a population *difference* between these two states

$$M_z = \frac{1}{2} \hbar \gamma (n_\alpha - n_\beta)$$

n_α population of α state; n_β population of β state

- ▶ Boltzmann distribution gives equilibrium magnetization

$$M_z^0 = \frac{\gamma^2 \hbar^2 N B_0}{4 k_B T}$$

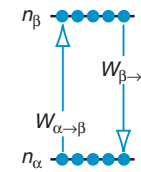
- ▶ omit constants

$$M_z = n_\alpha - n_\beta \quad \text{and} \quad M_z^0 = n_\alpha^0 - n_\beta^0$$

⁰ indicates equilibrium values

Relaxation in terms of populations 21

Rate equations



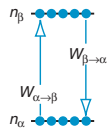
... just like chemical kinetics

W are rate constants

- ▶ rate from α to $\beta = W_{\alpha \rightarrow \beta} n_\alpha$
- ▶ rate from β to $\alpha = W_{\beta \rightarrow \alpha} n_\beta$
- ▶ rate of change of $n_\alpha = \underbrace{+W_{\beta \rightarrow \alpha} n_\beta}_{\text{increase in } n_\alpha} - \underbrace{W_{\alpha \rightarrow \beta} n_\alpha}_{\text{decrease in } n_\alpha}$
- ▶ rate of change of $n_\beta = \underbrace{+W_{\alpha \rightarrow \beta} n_\alpha}_{\text{increase in } n_\beta} - \underbrace{W_{\beta \rightarrow \alpha} n_\beta}_{\text{decrease in } n_\beta}$

Relaxation in terms of populations 22

Problem with the rate equations



- ▶ at equilibrium, no change in population with time

$$0 = W_{\beta \rightarrow \alpha} n_\beta^0 - W_{\alpha \rightarrow \beta} n_\alpha^0 \quad 0 = +W_{\alpha \rightarrow \beta} n_\alpha^0 - W_{\beta \rightarrow \alpha} n_\beta^0$$

- ▶ hence

$$\frac{n_\alpha^0}{n_\beta^0} = \frac{W_{\beta \rightarrow \alpha}}{W_{\alpha \rightarrow \beta}}$$

- ▶ simple theory predicts $W_{\beta \rightarrow \alpha} = W_{\alpha \rightarrow \beta}$, hence $n_\alpha^0 = n_\beta^0$, which is **wrong**
- ▶ need more advanced theory, or ...

Relaxation in terms of populations 23

Modifying the rate equations

- ▶ instead of

$$\text{rate of change of } n_\alpha = +W_{\beta \rightarrow \alpha} n_\beta - W_{\alpha \rightarrow \beta} n_\alpha$$

$$\text{rate of change of } n_\beta = +W_{\alpha \rightarrow \beta} n_\alpha - W_{\beta \rightarrow \alpha} n_\beta$$

- ▶ set $W_{\beta \rightarrow \alpha}$ and $W_{\alpha \rightarrow \beta}$ equal to $W_{\alpha\beta}$ and write

$$\text{rate of change of } n_\alpha = W_{\alpha\beta} (n_\beta - n_\beta^0) - W_{\alpha\beta} (n_\alpha - n_\alpha^0)$$

$$\text{rate of change of } n_\beta = -W_{\alpha\beta} (n_\beta - n_\beta^0) + W_{\alpha\beta} (n_\alpha - n_\alpha^0)$$

- ▶ rate depends on *deviation* from equilibrium population

Relaxation in terms of populations 24

Relaxation in terms of populations

- ▶ recall $M_z = n_\alpha - n_\beta$, so
rate of change of $M_z =$ rate of change of $n_\alpha -$ rate of change of n_β
- ▶ using
rate of change of $n_\alpha = W_{\alpha\beta}(n_\beta - n_\beta^0) - W_{\alpha\beta}(n_\alpha - n_\alpha^0)$
rate of change of $n_\beta = -W_{\alpha\beta}(n_\beta - n_\beta^0) + W_{\alpha\beta}(n_\alpha - n_\alpha^0)$
- ▶ gives
rate of change of $M_z = 2W_{\alpha\beta}(n_\beta - n_\beta^0) - 2W_{\alpha\beta}(n_\alpha - n_\alpha^0)$
 $= -2W_{\alpha\beta}[(n_\alpha - n_\beta) - (n_\alpha^0 - n_\beta^0)]$
 $= -2W_{\alpha\beta}(M_z - M_z^0)$

Relaxation in terms of populations 25

Writing the magnetization in terms of the populations

- ▶ we have
rate of change of $M_z = -2W_{\alpha\beta}(M_z - M_z^0)$
- ▶ usually written
$$\frac{dM_z(t)}{dt} = -R_z [M_z(t) - M_z^0]$$
with $R_z = 2W_{\alpha\beta}$, longitudinal relaxation rate constant
- ▶ or
$$\frac{dM_z(t)}{dt} = -\frac{1}{T_1} [M_z(t) - M_z^0]$$
with $T_1 = 1/R_z$, time constant for longitudinal relaxation

Relaxation in terms of populations 26

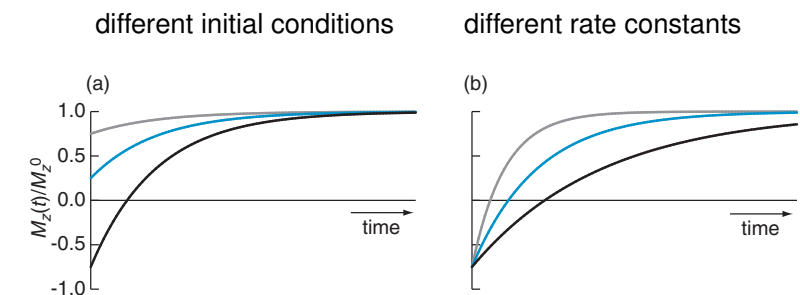
Longitudinal relaxation

- ▶ we have
$$\frac{dM_z(t)}{dt} = -R_z [M_z(t) - M_z^0]$$
- ▶ implies that the rate of change of M_z is proportional to the deviation of M_z from the equilibrium value M_z^0
- ▶ implies that M_z tends to M_z^0
- ▶ can integrate using $M_z = M_z(0)$ at time $t = 0$ to give

$$M_z(t) = [M_z(0) - M_z^0] \exp(-R_z t) + M_z^0$$

Relaxation in terms of populations 27

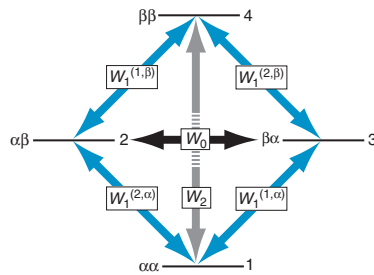
Longitudinal relaxation



note M_z always tends to equilibrium value

Relaxation in terms of populations 28

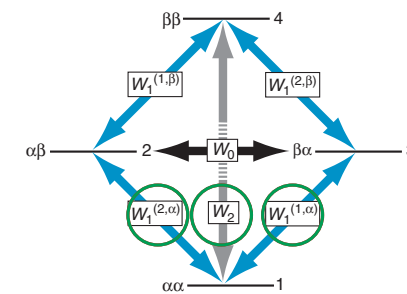
Two spins: energy levels and transition rates



- ▶ two spins, four energy levels
- ▶ dipolar interaction causes relaxation-induced transitions between *any* two levels
- ▶ rate constants $W_{\Delta M}$, ΔM gives change in M
- ▶ note $W_1^{(1,\alpha)}$ and $W_1^{(1,\beta)}$

Relaxation of a spin pair 29

Rate equations for the populations and z-magn.



- ▶ as before, look at gain and loss processes for level 1

$$\frac{dn_1}{dt} = \underbrace{-W_1^{(2,\alpha)}(n_1 - n_1^0) - W_1^{(1,\alpha)}(n_1 - n_1^0) - W_2(n_1 - n_1^0)}_{\text{loss from level 1}} + \underbrace{W_1^{(2,\alpha)}(n_2 - n_2^0)}_{\text{gain from level 2}} + \underbrace{W_1^{(1,\alpha)}(n_3 - n_3^0)}_{\text{gain from level 3}} + \underbrace{W_2(n_4 - n_4^0)}_{\text{gain from level 4}}$$

Relaxation of a spin pair 30

Rate equations for the populations and z-magn.

- ▶ define z-magn. for spin 1 as population difference across the spin-1 transitions 1–3 and 2–4

$$I_{1z} = (n_1 - n_3) + (n_2 - n_4)$$

- ▶ similarly for spin 2

$$I_{2z} = (n_1 - n_2) + (n_3 - n_4)$$

- ▶ also need the difference in the population difference across the spin 1 levels

$$2I_{1z}I_{2z} = (n_1 - n_3) - (n_2 - n_4) \quad \text{or} \quad 2I_{1z}I_{2z} = (n_1 - n_2) - (n_3 - n_4)$$

- ▶ and equilibrium values ($2I_{1z}I_{2z} = 0$ at equil.)

$$I_{1z}^0 = n_1^0 - n_3^0 + n_2^0 - n_4^0 \quad I_{2z}^0 = n_1^0 - n_2^0 + n_3^0 - n_4^0$$

Relaxation of a spin pair 31

Rate equations for the populations and z-magn.

- ▶ after much algebra

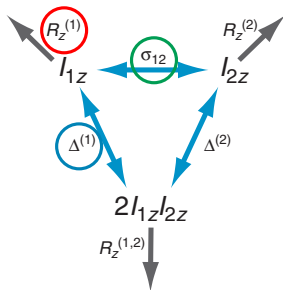
$$\begin{aligned} \frac{dI_{1z}}{dt} &= -R_z^{(1)}(I_{1z} - I_{1z}^0) - \sigma_{12}(I_{2z} - I_{2z}^0) - \Delta^{(1)} 2I_{1z}I_{2z} \\ \frac{dI_{2z}}{dt} &= -\sigma_{12}(I_{1z} - I_{1z}^0) - R_z^{(2)}(I_{2z} - I_{2z}^0) - \Delta^{(2)} 2I_{1z}I_{2z} \\ \frac{d 2I_{1z}I_{2z}}{dt} &= -\Delta^{(1)}(I_{1z} - I_{1z}^0) - \Delta^{(2)}(I_{2z} - I_{2z}^0) - R_z^{(1,2)} 2I_{1z}I_{2z} \end{aligned}$$

- ▶ rate constants in terms of the W

$$\begin{aligned} R_z^{(1)} &= W_1^{(1,\alpha)} + W_1^{(1,\beta)} + W_2 + W_0 \\ R_z^{(2)} &= W_1^{(2,\alpha)} + W_1^{(2,\beta)} + W_2 + W_0 \\ \sigma_{12} &= W_2 - W_0 \\ \Delta^{(1)} &= W_1^{(1,\alpha)} - W_1^{(1,\beta)} \\ \Delta^{(2)} &= W_1^{(2,\alpha)} - W_1^{(2,\beta)} \\ R_z^{(1,2)} &= W_1^{(1,\alpha)} + W_1^{(1,\beta)} + W_1^{(2,\alpha)} + W_1^{(2,\beta)} \end{aligned}$$

Relaxation of a spin pair 32

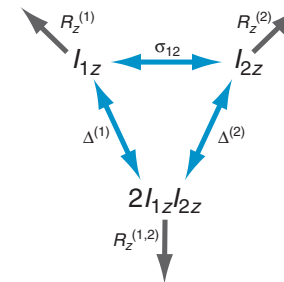
Rate equations for the populations and z-magn.



$$\begin{aligned}\frac{dI_{1z}}{dt} &= -R_z^{(1)}(I_{1z} - I_{1z}^0) - \sigma_{12}(I_{2z} - I_{2z}^0) - \Delta^{(1)} 2I_{1z}I_{2z} \\ \frac{dI_{2z}}{dt} &= -\sigma_{12}(I_{1z} - I_{1z}^0) - R_z^{(2)}(I_{2z} - I_{2z}^0) - \Delta^{(2)} 2I_{1z}I_{2z} \\ \frac{d2I_{1z}I_{2z}}{dt} &= -\Delta^{(1)}(I_{1z} - I_{1z}^0) - \Delta^{(2)}(I_{2z} - I_{2z}^0) - R_z^{(1,2)} 2I_{1z}I_{2z}\end{aligned}$$

Relaxation of a spin pair 33

Rate equations for the populations and z-magn.



- ▶ pure dipolar relaxation: $W_1^{(1,\alpha)} = W_1^{(1,\beta)}$, $W_1^{(2,\alpha)} = W_1^{(2,\beta)}$
- ▶ hence $\Delta^{(1)} = 0$ and $\Delta^{(2)} = 0$
- ▶ $2I_{1z}I_{2z}$ not connected to I_{1z} or I_{2z}

Relaxation of a spin pair 34

Solomon equations

$$\begin{aligned}\frac{dI_{1z}}{dt} &= -R_z^{(1)}(I_{1z} - I_{1z}^0) - \sigma_{12}(I_{2z} - I_{2z}^0) \\ \frac{dI_{2z}}{dt} &= -\sigma_{12}(I_{1z} - I_{1z}^0) - R_z^{(2)}(I_{2z} - I_{2z}^0) \\ \frac{d2I_{1z}I_{2z}}{dt} &= -R_z^{(1,2)} 2I_{1z}I_{2z}\end{aligned}$$

with

$$\begin{aligned}R_z^{(1)} &= 2W_1^{(1)} + W_2 + W_0 \\ R_z^{(2)} &= 2W_1^{(2)} + W_2 + W_0 \\ \sigma_{12} &= W_2 - W_0 \\ R_z^{(1,2)} &= 2W_1^{(1)} + 2W_1^{(2)}\end{aligned}$$

Solomon equations and relaxation rate constants 35

Solomon equations

$$\begin{aligned}\frac{dI_{1z}}{dt} &= -R_z^{(1)}(I_{1z} - I_{1z}^0) - \sigma_{12}(I_{2z} - I_{2z}^0) \\ \frac{dI_{2z}}{dt} &= -\sigma_{12}(I_{1z} - I_{1z}^0) - R_z^{(2)}(I_{2z} - I_{2z}^0) \\ \frac{d2I_{1z}I_{2z}}{dt} &= -R_z^{(1,2)} 2I_{1z}I_{2z}\end{aligned}$$

- ▶ $R_z^{(1)}$ is rate constant for *self relaxation* of spin 1
- ▶ likewise $R_z^{(2)}$ for spin 2
- ▶ σ_{12} is *cross-relaxation* rate constant between spins 1 and 2
- ▶ cross relaxation connects the z-magnetizations of the two spins

Solomon equations and relaxation rate constants 36

Relaxation rate constants

- ▶ detailed theory shows rate constants W_{ij} always given by expression of the form

$$W_{ij} = A_{ij} \times Y^2 \times j(\omega_{ij})$$

- ▶ A_{ij} is a quantum mechanical factor
- ▶ Y^2 relates to magnitude of local field (always squared) depends on e.g. distance between spins, γ
- ▶ $j(\omega_{ij})$ reduced spectral density at ω_{ij} , the transition frequency between the two levels

Relaxation rate constants: dipolar

- ▶ dipolar only

$$W_1^{(1)} = \frac{3}{40} b^2 j(\omega_{0,1}) \quad W_1^{(2)} = \frac{3}{40} b^2 j(\omega_{0,2})$$

$$W_2 = \frac{3}{10} b^2 j(\omega_{0,1} + \omega_{0,2}) \quad W_0 = \frac{1}{20} b^2 j(\omega_{0,1} - \omega_{0,2})$$

magnitude factor

$$b = \frac{\mu_0 \gamma_1 \gamma_2 \hbar}{4\pi r^3}$$

- ▶ hence

$$R_z^{(1)} = b^2 \left[\frac{3}{20} j(\omega_{0,1}) + \frac{3}{10} j(\omega_{0,1} + \omega_{0,2}) + \frac{1}{20} j(\omega_{0,1} - \omega_{0,2}) \right]$$

$$R_z^{(2)} = b^2 \left[\frac{3}{20} j(\omega_{0,2}) + \frac{3}{10} j(\omega_{0,1} + \omega_{0,2}) + \frac{1}{20} j(\omega_{0,1} - \omega_{0,2}) \right]$$

$$\sigma_{12} = b^2 \left[\frac{3}{10} j(\omega_{0,1} + \omega_{0,2}) - \frac{1}{20} j(\omega_{0,1} - \omega_{0,2}) \right]$$

$$R_z^{(1,2)} = b^2 \left[\frac{3}{20} j(\omega_{0,1}) + \frac{3}{20} j(\omega_{0,2}) \right]$$

Cross relaxation in the two motional regimes

homonuclear: $\omega_{0,1} = \omega_{0,2} \rightarrow \omega_0$

$$\sigma_{12} = \underbrace{b^2 \frac{3}{10} j(2\omega_0)}_{W_2} - \underbrace{b^2 \frac{1}{20} j(0)}_{W_0}$$

- ▶ fast motion $j(\omega) = 2\tau_c$

$$\begin{aligned} \text{fast motion: } \sigma_{12} &= \underbrace{b^2 \frac{3}{10} j(2\omega_0)}_{W_2} - \underbrace{b^2 \frac{1}{20} j(0)}_{W_0} \\ &= b^2 \frac{3}{10} 2\tau_c - b^2 \frac{1}{20} 2\tau_c \\ &= \frac{1}{2} b^2 \tau_c \end{aligned}$$

- ▶ σ_{12} positive in this limit

Cross relaxation in the two motional regimes

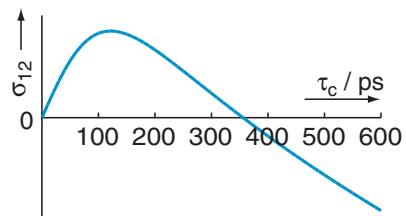
$$\sigma_{12} = \underbrace{b^2 \frac{3}{10} j(2\omega_0)}_{W_2} - \underbrace{b^2 \frac{1}{20} j(0)}_{W_0}$$

- ▶ slow motion $j(0) = 2\tau_c$, $j(2\omega_0)$ negligible in comparison

$$\begin{aligned} \text{slow motion: } \sigma_{12} &= \underbrace{b^2 \frac{3}{10} j(2\omega_0)}_{W_2} - \underbrace{b^2 \frac{1}{20} j(0)}_{W_0} \\ &= 0 - b^2 \frac{1}{20} 2\tau_c \\ &= -\frac{1}{10} b^2 \tau_c \end{aligned}$$

- ▶ σ_{12} negative in this limit

Cross relaxation as a function of τ_c



- ▶ computed for proton at 500 MHz
- ▶ cross over at

$$\omega_0 \tau_c = \sqrt{\frac{5}{4}}$$

- ▶ 360 ps in this case

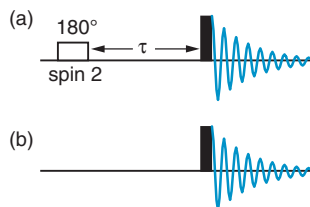
The nuclear overhauser effect (NOE)

- ▶ Solomon equation

$$\frac{dI_{1z}}{dt} = -R_z^{(1)}(I_{1z} - I_{1z}^0) - \sigma_{12}(I_{2z} - I_{2z}^0)$$

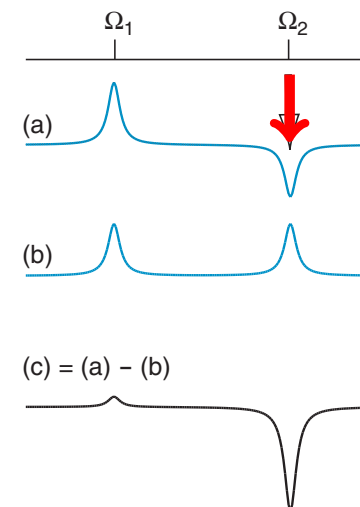
- ▶ implies that if spin 2 not at equilibrium, spin 1 will be affected
- ▶ but *only* if cross-relaxation rate constant $\sigma_{12} \neq 0$
- ▶ cross relaxation is a feature of dipolar relaxation, hence detection of cross relaxation implies dipolar relaxation i.e. nearby spins
- ▶ origin of Nuclear Overhauser Effect

The transient NOE experiment



- ▶ (a) perturb spin 2 with a *selective* inversion pulse
- ▶ wait time τ for cross relaxation to occur
- ▶ 90° pulse to give observable signal
- ▶ (b) repeat without inversion pulse (reference spectrum)
- ▶ compute difference spectrum (a) – (b) to reveal changes
- ▶ can analyze the experiment using the Solomon equations

Difference spectroscopy reveals the NOE



difference reveals NOE

Transverse relaxation: non-secular contribution

- ▶ transverse relaxation is decay of xy -components of magnetization; determines rate of decay of FID and hence linewidth
- ▶ *transverse* local fields, oscillating near to the Larmor frequency, cause *longitudinal* relaxation
- ▶ such fields can also affect the x - and y -components of individual magnetic moments, and therefore also cause *transverse* relaxation
- ▶ called the *non-secular* contribution to transverse relaxation

Transverse relaxation 45

Transverse relaxation: secular contribution

- ▶ the z -component of the local field will cause a change in the (local) Larmor frequency
- ▶ individual magnetic moments will precess at slightly different Larmor frequencies and so get out of step with one another
- ▶ result is a decay in the transverse magnetization
- ▶ called the *secular* contribution to transverse relaxation

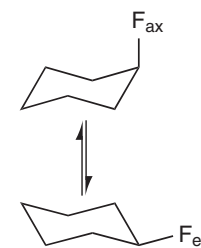
Transverse relaxation 46

Transverse relaxation

- ▶ *non-secular* contribution to transverse relaxation: description similar to longitudinal relaxation; rate depends on $j(\omega_0)$
- ▶ *secular* contribution to transverse relaxation: rate depends on spectral density at *zero frequency*, $j(0)$
- ▶ chemical exchange is a useful analogy for the secular contribution

Transverse relaxation 47

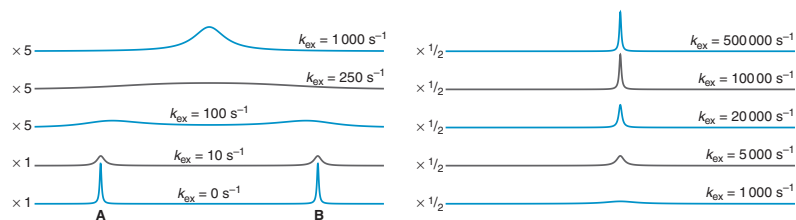
Chemical exchange



- ▶ F_{ax} and F_{eq} have different shifts: frequency difference between two resonances
- ▶ if rate constant for exchange is much less than the frequency difference \rightarrow two lines (*slow exchange*)
- ▶ if rate constant for exchange is much greater than the frequency difference \rightarrow one line (*fast exchange*)

Transverse relaxation 48

Two-site chemical exchange



- ▶ shift difference 160 Hz
- ▶ initial broadening and then coalescence when exchange rate constant is 350 s^{-1}
- ▶ further increase in exchange rate constant results in a narrower line: *exchange narrowing*

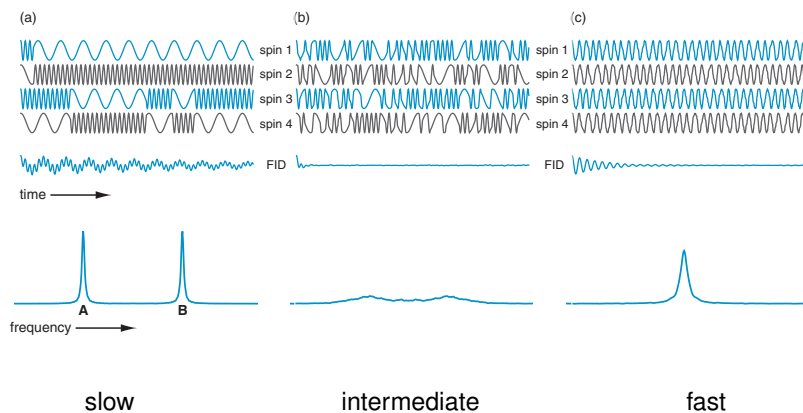
Transverse relaxation 49

Exchange processes from the point of view of single spins

- ▶ consider behaviour of individual spins
- ▶ either in environment A or B
- ▶ the spin jumps between them randomly
- ▶ the larger the exchange rate constant, the more frequent the jumps

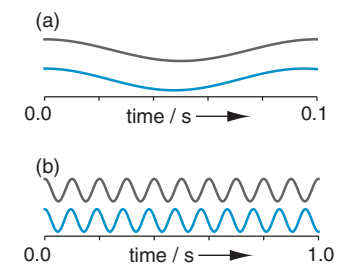
Transverse relaxation 50

Simulation of two-site exchange



Transverse relaxation 51

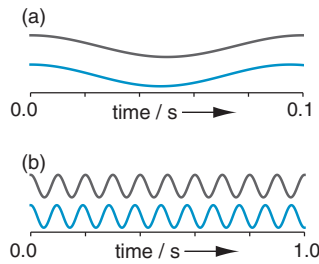
Slow and fast exchange: interpretation



- ▶ two cosine waves at 10.0 and 10.5 Hz; $\Delta = 0.5 \text{ Hz}$
- ▶ (a): observing for 0.1 s, can hardly see that the waves are at different frequencies
- ▶ (b): observing for 1 s, difference is clear
- ▶ phase difference over period τ is $2\pi\Delta \times \tau$; must be significant if frequencies are to be distinguished

Transverse relaxation 52

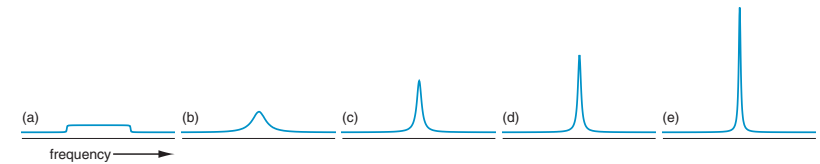
Slow and fast exchange: interpretation



- ▶ phase difference over period τ_{ex} is $2\pi\Delta \times \tau_{\text{ex}}$
- ▶ for significant phase difference $\tau_{\text{ex}} \gg (1/\Delta)$
- ▶ can only distinguish frequencies if $\tau_{\text{ex}} \gg (1/\Delta)$;
since $\tau_{\text{ex}} = 1/k_{\text{ex}}$ the condition for slow exchange is $k_{\text{ex}} \ll \Delta$
- ▶ frequencies indistinguishable if $\tau_{\text{ex}} \ll (1/\Delta)$;
the condition for fast exchange is $k_{\text{ex}} \gg \Delta$

Transverse relaxation 53

The secular contribution to transverse relaxation



- ▶ continuous range of Larmor frequencies due to spread of local fields
- ▶ square profile in absence of motion: (a)
- ▶ molecular motion is fast compared to range of Larmor frequencies, so line is exchange narrowed: (e)

Transverse relaxation 54

The secular contribution to transverse relaxation

- ▶ for $\mathbf{A} \rightleftharpoons \mathbf{B}$, in fast exchange limit

$$\text{linewidth} \approx \frac{\pi\Delta_{\text{AB}}^2}{2k_{\text{ex}}}$$

- ▶ molecular motion: $k_{\text{ex}} \rightarrow 1/\tau_c$; $\Delta_{\text{AB}} \rightarrow W$, width of distribution of Larmor frequencies

$$\text{width of narrowed line} \approx W^2 \times \tau_c$$

- ▶ $W = 100 \text{ kHz}$, $\tau_c = 100 \text{ ps}$ gives width of 1 Hz

- ▶ $j(0) = 2\tau_c$ hence

$$\text{width of narrowed line} \approx \frac{1}{2}W^2 \times j(0)$$

Transverse relaxation 55

Secular and non-secular contribution to relaxation

Summary

- ▶ **non-secular**: due to transverse local fields oscillating near to the Larmor frequency
- ▶ the same fluctuations cause longitudinal relaxation
- ▶ **secular**: due to a distribution of local fields along z giving a spread in Larmor frequencies
- ▶ molecular motion results in a linewidth *very much* less than the spread of Larmor frequencies
- ▶ non-secular depends on $j(\omega_0)$; secular depends on $j(0)$

Transverse relaxation 56

Relaxation by random fields

- ▶ assume a randomly varying field with mean square value $\overline{B_{\text{loc}}^2}$ in all three directions

- ▶ $R_z = \gamma^2 \overline{B_{\text{loc}}^2} j(\omega_0)$

- ▶ transverse relaxation

$$R_{xy} = \underbrace{\frac{1}{2} \gamma^2 \overline{B_{\text{loc}}^2} j(0)}_{\text{secular}} + \underbrace{\frac{1}{2} \gamma^2 \overline{B_{\text{loc}}^2} j(\omega_0)}_{\text{non-secular}}$$

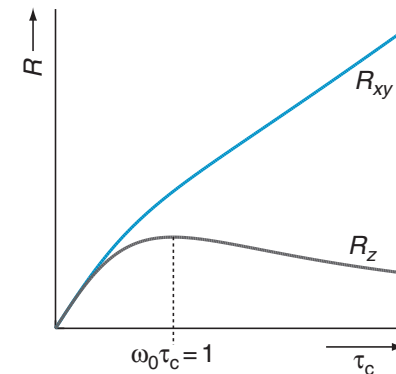
- ▶ comparing

$$R_{xy} = \underbrace{\frac{1}{2} \gamma^2 \overline{B_{\text{loc}}^2} j(0)}_{\text{secular}} + \underbrace{\frac{1}{2} R_z}_{\text{non-secular}}$$

i.e. non-secular part is precisely *half* of the overall longitudinal rate constant

Transverse relaxation 57

Relaxation by random fields



- ▶ Fast motion: $R_z = R_{xy}$
- ▶ Slow motion: R_{xy} continues to increase due to secular term: $J(0) \propto \tau_c$, but R_z decreases as spectral density at Larmor frequency decreases

Transverse relaxation 58

EUROMAR
Zürich, 2014

Introduction to Relaxation Theory

The End

Want more on the basic theory of NMR?
Search for "ANZMAG" on *YouTube*

The end 59