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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

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## 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](http://www-keeler.ch.cam.ac.uk)

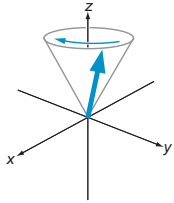
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## Outline

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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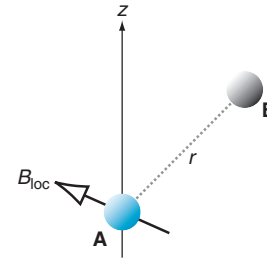
## Behaviour of individual magnetic moments



- ▶ 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

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## Local fields

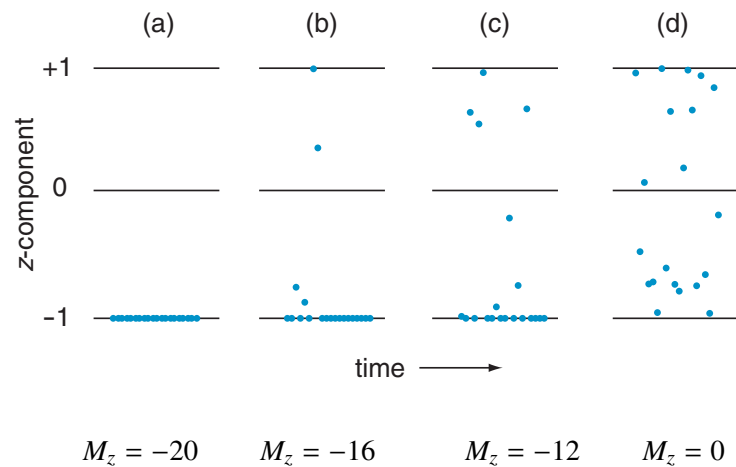


- ▶ e.g. spin **B** generates magnetic field at **A**
- ▶ a local field only significant over a short distance
- ▶ local field varies in size and direction according to length and orientation of **A–B** vector
- ▶ local field is random

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## How random fields drive the system to equilibrium

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



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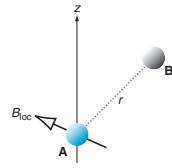
## Coming to equilibrium with the lattice

- ▶ 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

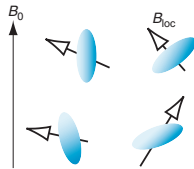
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## Relaxation mechanisms

- ▶ 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)

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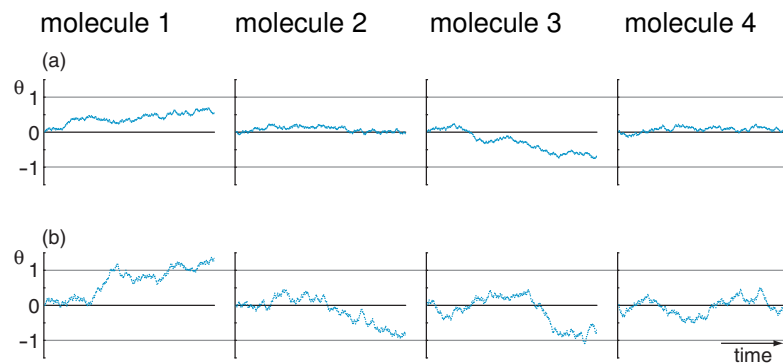
## Describing random motion – the correlation time

- ▶ 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*,  $\tau_c$ , is *average* time it takes a molecule to move through 1 radian
- ▶ *correlation time* describes the timescale of the random motion

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## Rotational diffusion

representative molecules undergoing rotational diffusion



(a) has longer correlation time than (b)

Describing random motion – the correlation time 11

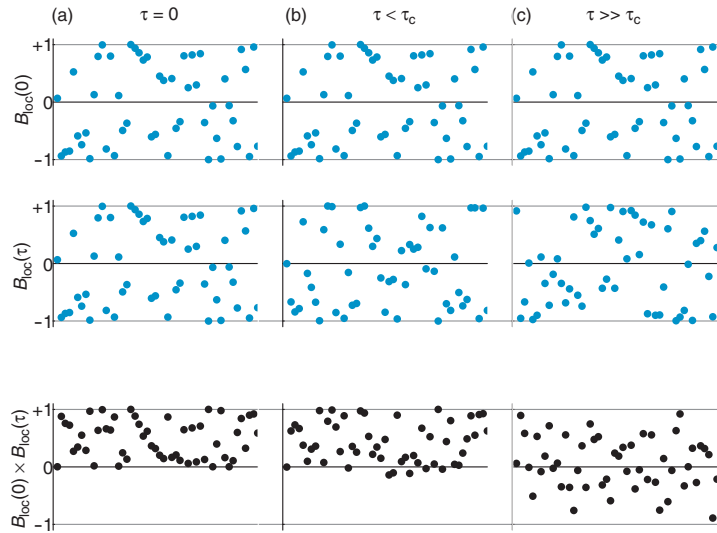
## The correlation function

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

- ▶ average of product of local field at time  $t$  with that at time  $(t + \tau)$
- ▶ usually only depends on  $\tau$ : *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  $\tau = 0$

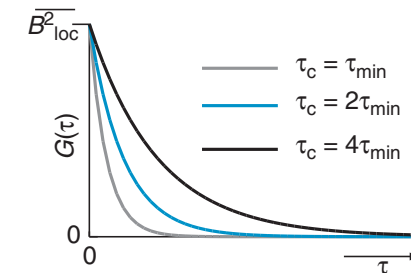
$$G(0) = \overline{B_{\text{loc}}(t)B_{\text{loc}}(t)}$$

$$= \overline{B_{\text{loc}}^2}$$

- ▶ 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

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## 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  $\omega$

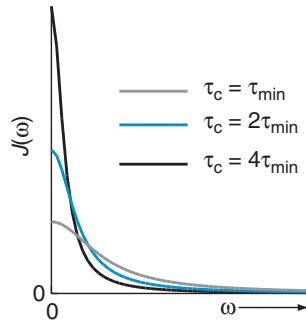
▶

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

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

Describing random motion – the correlation time 16

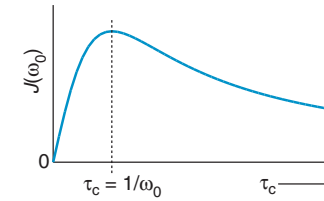
## Spectral density: interpretation



- ▶ area under curve is independent of  $\tau_c$
- ▶ the shorter  $\tau_c$ , 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  $\tau_c$

- ▶ 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  $\tau_c$
- ▶ 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  $\tau_c$

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

Motional regimes 20

## Populations

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

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

$n_\alpha$  population of  $\alpha$  state;  $n_\beta$  population of  $\beta$  state

- ▶ Boltzmann distribution gives equilibrium magnetization

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

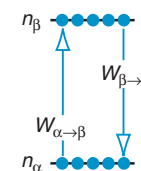
- ▶ omit constants

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

<sup>0</sup> indicates equilibrium values

Relaxation in terms of populations 21

## Rate equations



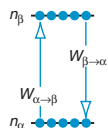
... just like chemical kinetics

$W$  are rate constants

- ▶ rate from  $\alpha$  to  $\beta = W_{\alpha \rightarrow \beta} n_\alpha$
- ▶ rate from  $\beta$  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

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

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

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

- ▶ rate depends on *deviation* from equilibrium population

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## 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  $n_\beta$
- ▶ 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  $M_z = 2W_{\alpha\beta}(n_\beta - n_\beta^0) - 2W_{\alpha\beta}(n_\alpha - n_\alpha^0)$   
 $= -2W_{\alpha\beta}[(n_\alpha - n_\beta) - (n_\alpha^0 - n_\beta^0)]$   
 $= -2W_{\alpha\beta}(M_z - M_z^0)$

## Writing the magnetization in terms of the populations

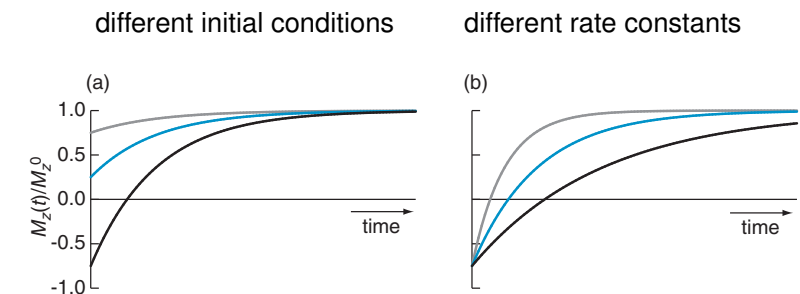
- ▶ we have  
rate of change of  $M_z = -2W_{\alpha\beta}(M_z - M_z^0)$
- ▶ usually written  
$$\frac{dM_z(t)}{dt} = -R_z [M_z(t) - M_z^0]$$
with  $R_z = 2W_{\alpha\beta}$ , longitudinal relaxation rate constant
- ▶ or  
$$\frac{dM_z(t)}{dt} = -\frac{1}{T_1} [M_z(t) - M_z^0]$$
with  $T_1 = 1/R_z$ , time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

## 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

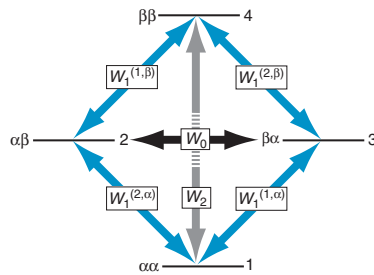
$$M_z(t) = [M_z(0) - M_z^0] \exp(-R_z t) + M_z^0$$

## Longitudinal relaxation



note  $M_z$  always tends to equilibrium value

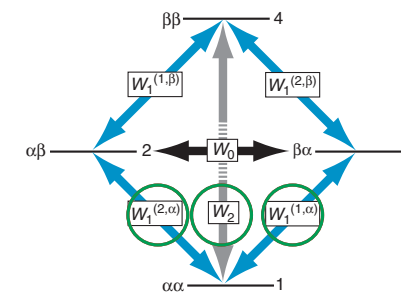
## Two spins: energy levels and transition rates



- ▶ two spins, four energy levels
- ▶ dipolar interaction causes relaxation-induced transitions between *any* two levels
- ▶ rate constants  $W_{\Delta M}$ ,  $\Delta M$  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

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

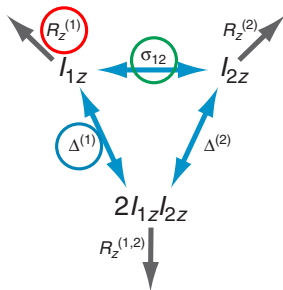
- ▶ rate constants in terms of the  $W$

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

Relaxation of a spin pair 32



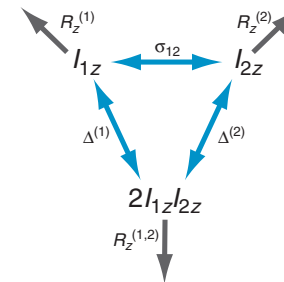
## Rate equations for the populations and z-magn.



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

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
- ▶  $\sigma_{12}$  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,  $\gamma$
- ▶  $j(\omega_{ij})$  reduced spectral density at  $\omega_{ij}$ , 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  $j(\omega) = 2\tau_c$

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

- ▶  $\sigma_{12}$  positive in this limit

## Cross relaxation in the two motional regimes

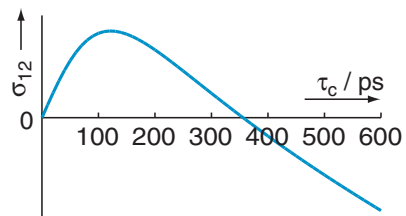
$$\sigma_{12} = \underbrace{b^2 \frac{3}{10} j(2\omega_0)}_{W_2} - \underbrace{b^2 \frac{1}{20} j(0)}_{W_0}$$

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

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

- ▶  $\sigma_{12}$  negative in this limit

## Cross relaxation as a function of $\tau_c$



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

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

- ▶ 360 ps in this case

Solomon equations and relaxation rate constants 41

## The nuclear overhauser effect (NOE)

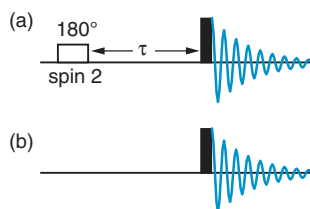
- ▶ Solomon equation

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

- ▶ 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

Nuclear overhauser effect (NOE) 42

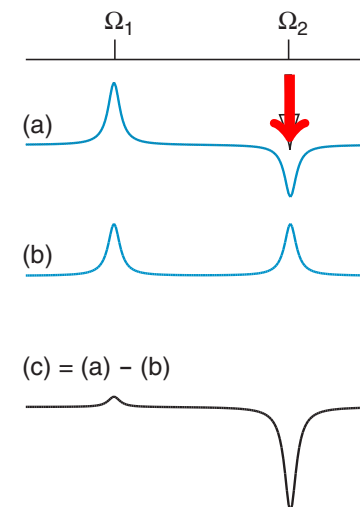
## The transient NOE experiment



- ▶ (a) perturb spin 2 with a *selective* inversion pulse
- ▶ wait time  $\tau$  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

Nuclear overhauser effect (NOE) 43

## Difference spectroscopy reveals the NOE



difference reveals NOE

Nuclear overhauser effect (NOE) 44

## 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

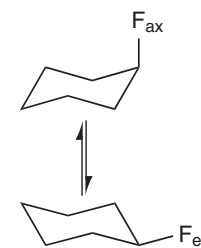
Transverse relaxation 46

## 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

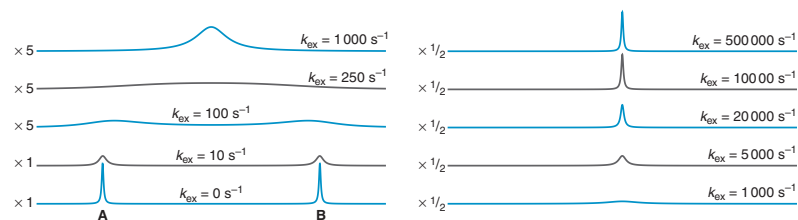
## Chemical exchange



- ▶  $F_{ax}$  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  $350 \text{ s}^{-1}$
- ▶ further increase in exchange rate constant results in a narrower line: *exchange narrowing*

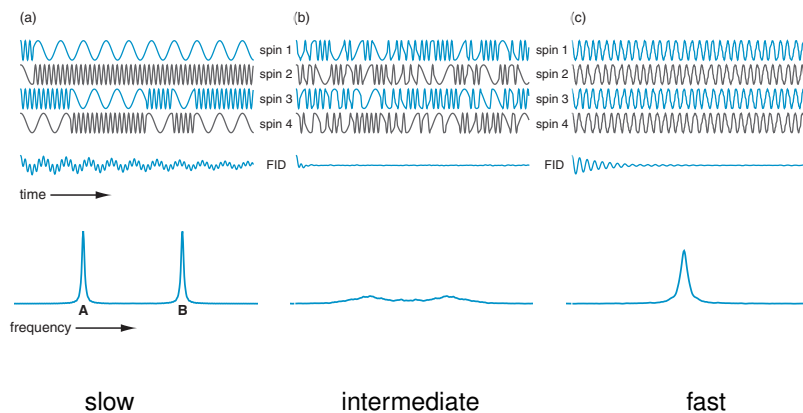
Transverse relaxation 49

## 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

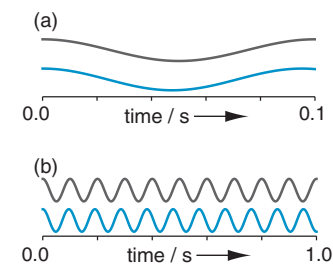
Transverse relaxation 50

## Simulation of two-site exchange



Transverse relaxation 51

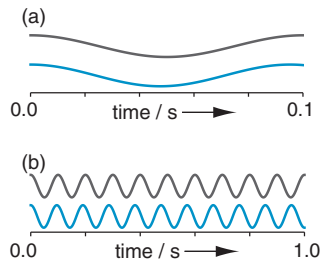
## Slow and fast exchange: interpretation



- ▶ 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  $\tau$  is  $2\pi\Delta \times \tau$ ; must be significant if frequencies are to be distinguished

Transverse relaxation 52

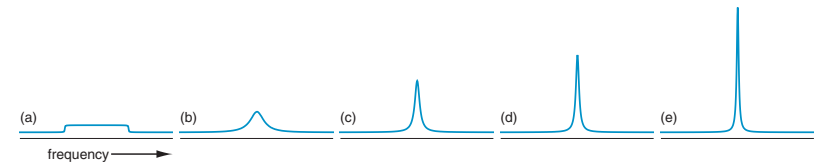
## Slow and fast exchange: interpretation



- ▶ phase difference over period  $\tau_{\text{ex}}$  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

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

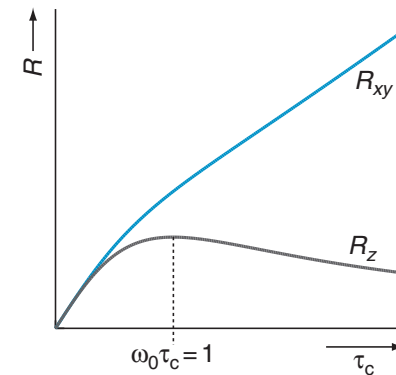
- ▶ comparing

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

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