

Lecture #9

Redfield theory of NMR relaxation

- Topics
 - Redfield theory recap
 - Relaxation supermatrix
 - Dipolar coupling revisited
 - Scalar relaxation of the 1st kind
- Handouts and Reading assignments
 - van de Ven, Chapters 6.2.
 - Kowalewski, Chapter 4.
 - Abragam Chapter VIII.C, pp 289-305, 1955.

Redfield theory

- We ended the last lecture with the following master equation

$$\frac{d\hat{\sigma}}{dt} = -i\hat{H}_0\hat{\sigma} - \hat{\Gamma}(\hat{\sigma} - \hat{\sigma}_B)$$



...and we were
happy!

relaxation superoperator

Redfield theory

- The relaxation superoperator was defined as: $\hat{\Gamma} = \sum_q J_q(e_q) \hat{A}_{-q} \hat{A}_q$
 - spectral density functions: $J_q(e_q) = \int_0^\infty G_q(\tau) e^{-ie_q\tau} d\tau.$ \hat{H}_0 eigenoperators
 - correlation functions: $G_q(\tau) = \overline{F_{-q}(t') F_q(t' - \tau)}$

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 Random functions of time

- Recipe:

1. Given $\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t).$

2. Express $\hat{H}_1(t)$ as a linear combination of eigenoperators of $\hat{H}_0,$

$$\hat{H}_1(t) = \sum_q F_q(t) \hat{A}_q.$$

3. Plug and chug.

But how do we
compute T_1 or T_2 ?



The Relaxation Supermatrix

- Rather than directly solving the master equation, we often just want to calculate the time dependence of particular coherences, e.g.

$$\overline{\langle \hat{I}_x \rangle}, \overline{\langle \hat{I}_y \rangle}, \text{ or } \overline{\langle \hat{I}_z \rangle}.$$

- Express the density operator in the product operator basis...

$$\hat{\sigma} = \sum_j \overline{\langle \hat{C}_j \rangle} \hat{C}_j \quad \longleftrightarrow \quad \vec{\sigma} = \begin{pmatrix} 1 \\ \overline{\langle I_x \rangle} \\ \overline{\langle S_x \rangle} \\ \vdots \\ \overline{\langle 2I_z S_z \rangle} \end{pmatrix}$$

Two-spin case
 $\hat{C}_j \in \{ \frac{1}{2} \hat{E}, \hat{I}_x, \hat{S}_x, \hat{I}_y, \hat{S}_y, \dots, 2\hat{I}_z \hat{S}_z \}$

← “vector” in a 16-D coherence (Liouville) space

$$\overline{\langle \hat{C} \rangle} = \text{Tr}(\hat{\sigma} \hat{C})$$

- Rewrite the master equation as a vector/matrix equation:

The Relaxation Supermatrix

- Rewrite the master equation as a matrix equation:

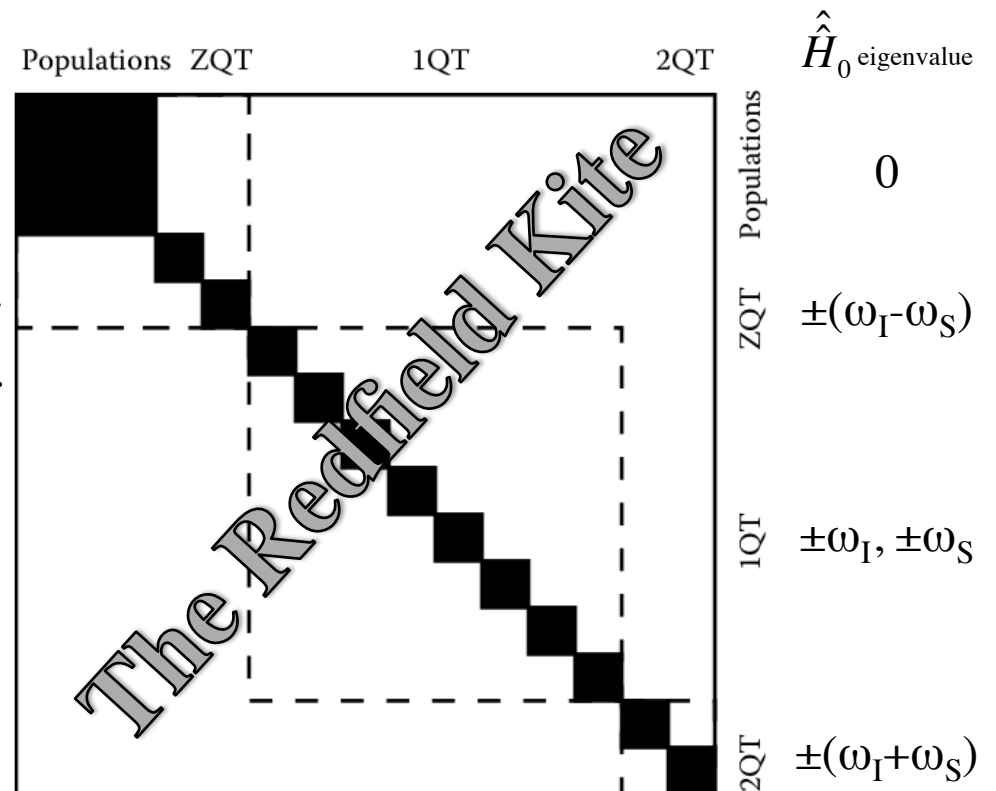
$$\hat{\Gamma} \longleftrightarrow \underline{R} \quad \text{“Supermatrix” with elements } R_{j k} = \text{Tr} \left(\hat{C}_j \hat{\Gamma} \hat{C}_k \right) = \left\langle \hat{C}_j \left| \hat{\Gamma} \right| \hat{C}_k \right\rangle$$

trace
Notation used in van de Ven. Don't confuse with expected value.

- If we reorder $\vec{\sigma}$ to first list populations, then single-quantum terms, then double-quantum terms, ...

- Relaxation supermatrix, \underline{R} , is block diagonal (secular approx).
- Cross relaxation only occurs for coherences with degenerate eigenvalues of \hat{H}_0 .

From Problem Set 1, these eigenvalues are the transition frequencies, i.e. sums and differences of the system energy levels



Calculating Relaxation Times

- Rewrite the master equation in terms of the operator coefficients:

$$\frac{d}{dt} \overline{\langle \hat{C}_j \rangle} = \sum_k \left(\underbrace{-i \langle \hat{C}_j | \hat{H}_0 | \hat{C}_k \rangle \overline{\langle \hat{C}_k \rangle}}_{\text{Rotations}} - \underbrace{\left(\overline{\langle \hat{C}_k \rangle} - \langle \hat{C}_k \rangle_B \right) \langle \hat{C}_j | \hat{\Gamma} | \hat{C}_k \rangle}_{\text{Relaxation}} \right)$$

- Examples

$$\frac{1}{T_{1,I}} = \langle \hat{I}_z | \hat{\Gamma} | \hat{I}_z \rangle \quad \frac{1}{T_{1,S}} = \langle \hat{S}_z | \hat{\Gamma} | \hat{S}_z \rangle \quad \frac{1}{T_{1,cross}} = \langle \hat{I}_z | \hat{\Gamma} | \hat{S}_z \rangle$$

$$\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \langle \hat{I}_y | \hat{\Gamma} | \hat{I}_y \rangle$$

...we just need to compute some (a bunch) of commutators.

Relaxation due to a random field

(or hints for Problem Set #5)

- Consider a Hamiltonian of the form

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t) = -\gamma B_0 \hat{I}_z - \gamma \Delta B(t) \hat{I}_z \quad \text{with} \quad \begin{aligned} \langle \Delta B(t) \rangle &= 0 \\ \langle \Delta B(t) \Delta B(t-\tau) \rangle &= B^2 e^{-|\tau|/\tau_c} \end{aligned}$$

- Noting that $\hat{H}_0 \hat{I}_z = 0 \cdot \hat{I}_z$
Eigenvalue Eigenoperator

then $\hat{A}_0 = \hat{I}_z$, $F_0(t) = -\gamma \Delta B(t)$, and $J_0(\omega) = \gamma^2 B^2 \frac{\tau_c}{1 + \omega^2 \tau_c^2}$

$\rightarrow \hat{\Gamma} = \sum_q J_q(e_q) \hat{A}_{-q} \hat{A}_q = J_0(0) B^2 \hat{I}_z \hat{I}_z$

Assumed to be normalized

$$\frac{1}{T_2} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \gamma^2 B^2 \tau_c \text{Tr} \left(\hat{I}_x \hat{I}_z \hat{I}_z \hat{I}_x \right) = \gamma^2 B^2 \tau_c \text{Tr} \left(-i \hat{I}_x \hat{I}_z \hat{I}_y \right) = \gamma^2 B^2 \tau_c \text{Tr} \left(\hat{I}_x \hat{I}_x \right)$$

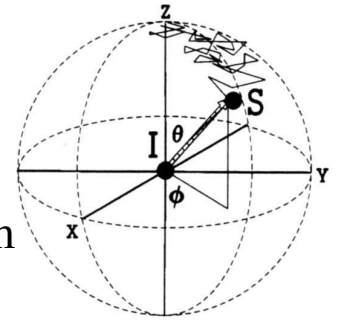
Hence: $\frac{1}{T_2} = \gamma^2 B^2 \tau_c$ $\frac{1}{T_1} = ?$

Dipolar Coupling Revisited

- The complete dipolar coupling Hamiltonian is given by

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

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



With tumbling, both θ and ϕ are functions of time.

- This can be written as:

$$\hat{H}_D(t) = -\frac{\gamma_I \gamma_S \hbar}{r^3} \frac{\mu_0}{4\pi} \sum_q F_q(t) \hat{A}_q \quad \text{where}$$

$$\hat{A}_0 = \sqrt{\frac{1}{6}} \left(2\hat{I}_z \hat{S}_z - \frac{1}{2}\hat{I}_+ \hat{S}_- - \frac{1}{2}\hat{I}_- \hat{S}_+ \right)$$

$$F_0(t) = \sqrt{\frac{3}{2}} (3\cos^2 \theta - 1)$$

$$\hat{A}_{\pm 1} = \pm \frac{1}{2} \left(\hat{I}_{\pm} \hat{S}_z + \hat{I}_z \hat{S}_{\pm} \right)$$

and

$$F_{\pm 1}(t) = \pm 3 \sin \theta \cos \theta e^{\mp i\phi}$$

$$\hat{A}_{\pm 2} = \frac{1}{2} \hat{I}_{\pm} \hat{S}_{\pm}$$

$$F_{\pm 2}(t) = \frac{3}{2} \sin^2 \theta e^{\mp 2i\phi}$$

Hey! These look like rank 2 spherical harmonics.



Dipolar Coupling Revisited

- Noting the following are eigenoperators of \hat{H}_0 (see Problem Set #1)

Eigenoperator	Eigenvalue
$\hat{I}_z \hat{S}_z$	0
$\hat{I}_+ \hat{S}_+$	$-(\omega_I + \omega_S)$
$\hat{I}_- \hat{S}_-$	$\omega_I + \omega_S$
$\hat{I}_+ \hat{S}_-$	$-(\omega_I - \omega_S)$
$\hat{I}_- \hat{S}_+$	$\omega_I - \omega_S$
$\hat{I}_+ \hat{S}_z$	$-\omega_I$
$\hat{I}_- \hat{S}_z$	ω_I
$\hat{I}_z \hat{S}_+$	$-\omega_S$
$\hat{I}_z \hat{S}_-$	ω_S

Together with $\overline{F_q^* F_q} = \frac{6}{5}$

- We can now compute $\hat{\Gamma}$.

Dipolar coupling superoperator

- Case 1: unlike spins, after much algebra...

$$\begin{aligned}
 \hat{\Gamma} = & 4 \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{10r^6} \left\{ 2J(0) \left(\hat{I}_z \hat{S}_z \hat{I}_z \hat{S}_z \right) \right. \\
 & + \left(\frac{1}{4} J(\omega_I - \omega_S) + \frac{3}{2} J(\omega_I + \omega_S) \right) \left(\hat{I}_x \hat{S}_x \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y \hat{I}_y \hat{S}_y + \hat{I}_x \hat{S}_y \hat{I}_x \hat{S}_y + \hat{I}_y \hat{S}_x \hat{I}_y \hat{S}_x \right) \\
 & + \frac{3}{2} J(\omega_I) \left(\hat{I}_x \hat{S}_z \hat{I}_x \hat{S}_z + \hat{I}_y \hat{S}_z \hat{I}_y \hat{S}_z \right) + \frac{3}{2} J(\omega_S) \left(\hat{I}_z \hat{S}_x \hat{I}_z \hat{S}_x + \hat{I}_z \hat{S}_y \hat{I}_z \hat{S}_y \right) \\
 & \left. - \left(\frac{1}{4} J(\omega_I - \omega_S) - \frac{3}{2} J(\omega_I + \omega_S) \right) \left(\hat{I}_x \hat{S}_x \hat{I}_y \hat{S}_y + \hat{I}_y \hat{S}_y \hat{I}_x \hat{S}_x - \hat{I}_x \hat{S}_y \hat{I}_y \hat{S}_x - \hat{I}_y \hat{S}_x \hat{I}_x \hat{S}_y \right) \right\}
 \end{aligned}$$

Note: $\hat{I}_z \hat{S}_z \neq \hat{I}_z \hat{S}_z$

Dipolar coupling superoperator

- Before calculating a bunch of commutators, we should note that there are multiple terms of the form $\hat{\hat{C}}_q \hat{\hat{C}}_q$, and this can make things easier...

$$\hat{\hat{C}}_q \hat{\hat{C}}_q \hat{\hat{C}}_p = \begin{cases} 0 & \text{if } \hat{\hat{C}}_q \hat{\hat{C}}_p = 0 \\ \hat{\hat{C}}_p & \text{if } \hat{\hat{C}}_q \hat{\hat{C}}_p \neq 0 \end{cases} \quad \text{Remember all product operators cyclically commute.}$$

- Terms of the form $\hat{\hat{C}}_q \hat{\hat{C}}_r$ give rise to cross relaxation

Example: $\hat{I}_x \hat{S}_y \hat{I}_y \hat{S}_x \hat{I}_z = \frac{1}{4} \hat{S}_z$

Dipolar coupling – unlike Spins

- Calculating T_2 . Let $q = \frac{\mu_0^2}{16\pi^2} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{10r^6}$

$$\hat{\Gamma} \hat{I}_x = q \left(2J(0) + \frac{1}{2} J(\omega_I - \omega_S) + 3J(\omega_I + \omega_S) + \frac{3}{2} J(\omega_I) + 3J(\omega_S) \right) \hat{I}_x$$

$$\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \frac{q}{2} \left(4J(0) + J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S) + 3J(\omega_I) + 6J(\omega_S) \right)$$

- Let's calculate T_1 .

$$\hat{\Gamma} \hat{I}_z = q \left[\left(J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S) + 3J(\omega_I) \right) \hat{I}_z + \left(J(\omega_I - \omega_S) - 6J(\omega_I + \omega_S) \right) \hat{S}_z \right]$$

$$\frac{1}{T_{1,I}} = \langle \hat{I}_z | \hat{\Gamma} | \hat{I}_z \rangle = q \left(J(\omega_I - \omega_S) + 6J(\omega_I + \omega_S) + 3J(\omega_I) \right)$$

- And the cross relaxation term is:

$$\frac{1}{T_{1,IS}} = \langle \hat{S}_z | \hat{\Gamma} | \hat{I}_z \rangle = q \left(6J(\omega_I + \omega_S) - J(\omega_I - \omega_S) \right)$$

Dipolar coupling – like spins

- Case 2: The equation for spins with the same (or nearly the same) chemical shift, $\sim\omega_0$, is even longer due to cross terms between $\hat{I}_z\hat{S}_z$ and $\hat{I}_\pm\hat{S}_\mp$.

$$\hat{\Gamma} = \text{see van de Ven p. 355} \quad \rightarrow \quad \frac{1}{T_1} = q(3J(\omega_0) + 12J(2\omega_0))$$

- But now there is also transverse cross relaxation between spins I and S .

$$\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \frac{q}{2}(5J(0) + 9J(\omega_0) + 6J(2\omega_0))$$

$$\frac{1}{T_{2,IS}} = \langle \hat{S}_x | \hat{\Gamma} | \hat{I}_x \rangle = q(2J(0) + 3J(\omega_0))$$

This effect is exploited in some spin lock experiments.

Summary of Redfield theory

$$\frac{d\hat{\sigma}}{dt} = -i\hat{H}_0\hat{\sigma} - \hat{\Gamma}(\hat{\sigma} - \hat{\sigma}_B)$$

- Relaxation arises from perturbations having energy at the transition frequencies. That is, if the eigenvalues of \hat{H}_0 (= energies of the system/ \hbar) are e_1, e_2 , etc. Then, the spectral density function is probed as frequencies $\pm(e_i - e_j)$.
- Cross relaxation only occurs between coherences with the same transition frequencies.
- Although Redfield theory may seem much more complicated than the Solomon equations for dipolar relaxation, it is actually very useful.
- For example, T_1 and T_2 due to chemical shift anisotropy or scalar relaxation of the 1st and 2nd kind are readily calculated.

Example: Scalar relaxation of the 1st kind

- Consider a J-coupled spin pair with the following Hamiltonian:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 = -\omega_I \hat{I}_z - \omega_S \hat{S}_z + 2\pi J \left(\hat{I}_z \hat{S}_z + \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y \right)$$

- We would normally expect a doublet from the I spin, however chemical exchange by the S spin can become a relaxation mechanism.
- Under exchange, with an exchange time of τ_{ex} , the coupling constant between the I spin and a spin S_i becomes a random function of time. Rewriting the perturbing Hamiltonian:

$$\hat{H}_1(t) = A_i(t) \vec{I} \cdot \vec{S}$$

$$\text{where } \langle A_i^2 \rangle = \begin{cases} A^2 = 4\pi^2 J^2 & \text{if } I \text{ and } S_i \text{ are on the same molecule} \\ 0 & \text{otherwise} \end{cases}$$

$$\langle A_i(t) A_i(t + \tau) \rangle = A^2 e^{-\tau/\tau_{\text{ex}}} = \text{probability the } I \text{ and } S_i \text{ spins are on the same molecule at time } t + \tau, \text{ given that they are at time } t.$$

Example: Scalar relaxation of the 1st kind

- Thus we have: $\hat{H}_0 = -\omega_I \hat{I}_z - \omega_S \hat{S}_z$ and $\hat{H}_1(t) = A_i(t) (\hat{I}_z \hat{S}_z + \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y)$.
- Noting the eigenoperators and corresponding eigenvalues of \hat{H}_0

Eigenoperator	Eigenvalue
$\hat{I}_z \hat{S}_z$	0
$\hat{I}_+ \hat{S}_-$	$-(\omega_I - \omega_S)$
$\hat{I}_- \hat{S}_+$	$\omega_I - \omega_S$

- Written as a sum of eigenoperators of \hat{H}_0 , the perturbing Hamiltonian becomes

$$\hat{H}_1(t) = A_i(t) \hat{I}_z \hat{S}_z + \frac{1}{2} A_i(t) \hat{I}_+ \hat{S}_- + \frac{1}{2} A_i(t) \hat{I}_- \hat{S}_+$$

- All we need now is the spectral density function, which we'll denote $J_{ex}(\omega)$.

Let P_i be the probability spins I and S_i are on the same molecule, then

$$J_{ex}(\omega) = \sum_i P_i \int_0^\infty \langle A_i(t) A_i(t+\tau) \rangle \cos \omega \tau d\tau.$$

Assume the I spin is always coupled to some S spin, i.e. $\sum_i P_i = 1$

$$\Rightarrow J_{ex}(\omega) = A^2 \frac{\tau_{ex}}{1 + \omega^2 \tau_{ex}^2}$$

Example: Scalar relaxation of the 1st kind

- Hence:

$$\hat{\Gamma} = A^2 J_{ex}(0) \hat{I}_z \hat{S}_z \hat{I}_z \hat{S}_z + \frac{1}{4} A^2 J_{ex}(\omega_I - \omega_S) \hat{I}_+ \hat{S}_- \hat{I}_+ \hat{S}_- + \frac{1}{4} A^2 J_{ex}(\omega_I - \omega_S) \hat{I}_- \hat{S}_+ \hat{I}_- \hat{S}_+$$

- From which it follows

$$\frac{1}{T_{1,I}} = \langle \hat{I}_z | \hat{\Gamma} | \hat{I}_z \rangle = 2A^2 \frac{S(S+1)}{3} \frac{\tau_{ex}}{1 + (\omega_I - \omega_S)^2 \tau_{ex}^2} = \frac{8\pi^2 J^2 S(S+1)}{3} \frac{\tau_{ex}}{1 + (\omega_I - \omega_S)^2 \tau_{ex}^2}$$

Note: the $S(S+1)/3$ factor comes from $\text{Tr}(\hat{S}_p^2) = \frac{S(S+1)}{3}$, p = product operator
where S = spin of the unpaired electron system or nucleus.

$$\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \langle \hat{I}_y | \hat{\Gamma} | \hat{I}_y \rangle = \langle \hat{I}_+ | \hat{\Gamma} | \hat{I}_+ \rangle = \frac{4\pi^2 J^2 S(S+1)}{3} \left(\tau_{ex} + \frac{\tau_{ex}}{1 + (\omega_I - \omega_S)^2 \tau_{ex}^2} \right)$$

- For those who complete the homework, we note that these equations have the same form as scalar relaxation of the 2nd kind with the correlation time given by τ_{ex} instead of $T_{1,S}$ and $T_{2,S}$.

Next Lecture: Redfield theory- Examples