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.
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: \( J_q(e_q) = \int_{0}^{\infty} G_q(\tau)e^{-i e_q \tau} d\tau \).

  - correlation functions: \( G_q(\tau) = F_{-q}(t')F_q(t' - \tau) \)

- 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. \( \langle \hat{I}_x \rangle, \langle \hat{I}_y \rangle, \) or \( \langle \hat{I}_z \rangle \).

• Express the density operator in the product operator basis…

\[
\hat{\sigma} = \sum_j \langle \hat{C}_j \rangle \hat{C}_j \quad \leftrightarrow \quad \vec{\sigma} = \left( \begin{array}{c}
1 \\
\langle \hat{I}_x \rangle \\
\langle \hat{S}_x \rangle \\
\vdots \\
\langle 2\hat{I}_z \hat{S}_z \rangle
\end{array} \right)
\]

Two-spin case

\( \hat{C}_j \in \{ \frac{1}{2} \hat{E}, \hat{I}_x, \hat{S}_x, \hat{I}_y, \hat{S}_y, \ldots, 2\hat{I}_z \hat{S}_z \} \)

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

• Rewrite the master equation as a vector/matrix equation:
The Relaxation Supermatrix

- Rewrite the master equation as a matrix equation:

\[ \hat{\Gamma} \leftrightarrow R \] “Supermatrix” with elements

\[ R_{jk} = \text{Tr} \left( \hat{C}_j \hat{\Gamma} \hat{C}_k \right) = \left\langle \hat{C}_j \right| \hat{\Gamma} \left| \hat{C}_k \right\rangle \]

- If we reorder \( \vec{\sigma} \) to first list populations, then single-quantum terms, then double-quantum terms, ...
  - Relaxation supermatrix, \( R \), 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:

\[
\frac{d}{dt} \langle \hat{C}_j \rangle = \sum_k \left( -i \langle \hat{C}_j | \hat{H}_0 | \hat{C}_k \rangle \langle \hat{C}_k \rangle - \left( \langle \hat{C}_k \rangle - \langle \hat{C}_k \rangle_B \right) \langle \hat{C}_j | \hat{\Gamma} | \hat{C}_k \rangle \right)
\]

\[\text{Rotations} \quad \text{Relaxation}\]

- Examples

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

\[
\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \langle \hat{I}_y | \hat{\Gamma} | \hat{I}_y \rangle \quad \text{...we just need to compute some (a bunch) of commutators.}
\]
Relaxation due to a random field
(or hints for Problem Set #5)

• Consider a Hamiltonian of the form

\[ \hat{H} = \hat{H}_0 + \hat{H}_1(t) = -\gamma B_0 \hat{I}_z - \gamma \Delta B(t) \hat{I}_z \]

with \( \langle \Delta B(t) \rangle = 0 \)

\( \langle \Delta B(t) \Delta B(t - \tau) \rangle = B^2 e^{-|\tau|/\tau_c} \)

• Noting that \( \hat{H}_0 \hat{I}_z = 0 \cdot \hat{I}_z \)

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

Assumed to be normalized

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

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

Hence:

\[ \frac{1}{T_2} = \gamma^2 B^2 \tau_c \quad \frac{1}{T_1} = ? \]
Dipolar Coupling Revisited

- The complete dipolar coupling Hamiltonian is given by

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

where the vector from spin \( I \) to spin \( S \) is \( \vec{r} \), and \( \gamma \) is the gyromagnetic ratio.

- This can be written as:

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

where

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

\[
F_0(t) = \sqrt{\frac{3}{2}} \left( 3\cos^2 \theta - 1 \right)
\]

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

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

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

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

Hey! These look like rank 2 spherical harmonics.

With tumbling, both \( \theta \) and \( \phi \) are functions of time.
Dipolar Coupling Revisited

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

<table>
<thead>
<tr>
<th>Eigenoperator</th>
<th>Eigenvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\hat{I}_z\hat{S}_z$</td>
<td>0</td>
</tr>
<tr>
<td>$\hat{I}<em>+\hat{S}</em>+$</td>
<td>$-(\omega_I + \omega_S)$</td>
</tr>
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</tr>
<tr>
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<td>$\omega_I - \omega_S$</td>
</tr>
<tr>
<td>$\hat{I}_+\hat{S}_z$</td>
<td>$-\omega_I$</td>
</tr>
<tr>
<td>$\hat{I}_-\hat{S}_z$</td>
<td>$\omega_I$</td>
</tr>
<tr>
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<td>$-\omega_S$</td>
</tr>
<tr>
<td>$\hat{I}<em>z\hat{S}</em>-$</td>
<td>$\omega_S$</td>
</tr>
</tbody>
</table>

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...

\[ \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}_z \hat{S}_x \hat{I}_z \hat{S}_x + \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( \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}_x \hat{I}_x \hat{S}_y - \hat{I}_x \hat{S}_x \hat{I}_y \hat{S}_x - \hat{I}_y \hat{S}_x \hat{I}_x \hat{S}_y \right) \left. \right\} \\

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 $\hat{C}_q \hat{C}_q$, and this can make things easier…

\[
\hat{C}_q \hat{C}_q \hat{C}_p = \begin{cases} 
0 & \text{if } \hat{C}_q \hat{C}_p = 0 \\
\hat{C}_p & \text{if } \hat{C}_q \hat{C}_p \neq 0
\end{cases}
\]

Remember all product operators cyclically commute.

• Terms of the form $\hat{C}_q \hat{C}_r$ 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 $q = \frac{\mu_0^2 \gamma_I^2 \gamma_S^2 \hbar^2}{16\pi^2 10r^6}$

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

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

• Let’s calculate $T_1$.

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

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

• And the cross relaxation term is:

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

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

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

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

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

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 \( e_1, e_2, \text{etc.} \) 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 1\(^{st}\) and 2\(^{nd}\) 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 \( \tau_{ex} \), the coupling constant between the \( I \) spin and a spin \( S_i \) becomes a random function of time. Rewriting the perturbing Hamiltonian:
  \[
  \hat{H}_1(t) = A_i(t) \hat{I} \cdot \hat{S}
  \]

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} \]

\[
\langle A_i(t) A_i(t + \tau) \rangle = A^2 e^{-\tau/\tau_{ex}} = \text{probability the } I \text{ and } S_i \text{ spins are on the same molecule at time } t + \tau, \text{ given that they are at time } t.
\]
Example: Scalar relaxation of the 1\textsuperscript{st} 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 \( \hat{H}_0 \)

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<td>( \omega_I - \omega_S )</td>
</tr>
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</table>

- 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 \( J_{\text{ex}}(\omega) \).

Let \( P_i \) be the probability spins \( I \) and \( S \) are on the same molecule, then

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

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

\[
\Longrightarrow J_{\text{ex}}(\omega) = A^2 \frac{\tau_{\text{ex}}}{1 + \omega^2 \tau_{\text{ex}}^2}
\]
Example: Scalar relaxation of the 1

• Hence:

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

• 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.

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

• For those who complete the homework, we note that these equations have the same form as scalar relaxation of the 2
nd kind with the correlation time given by \(\tau_{ex}\) instead of \(T_{1,S}\) and \(T_{2,S}\).
Next Lecture: Redfield theory- Examples