Lecture #8
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

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

relaxation superoperator

...and we were happy!
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: \( G_q(\tau) = \frac{F_{-q}(\tau')}{} F_q(\tau' - \tau) \).

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

• Express the density operator in the product operator basis…

\[
\hat{\sigma} = \sum_j \langle \hat{C}_j \rangle \hat{C}_j \quad \leftrightarrow \quad \vec{\sigma} = \begin{pmatrix}
1 \\
\langle \hat{I}_x \rangle \\
\langle \hat{S}_x \rangle \\
\vdots \\
\langle 2\hat{I}_z \hat{S}_z \rangle
\end{pmatrix}
\]

Two-spin case

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

“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:

\[ \hat{\Gamma} \rightarrow R \]  "Supermatrix" with elements \( R_{jk} = \text{Tr}\left( \hat{C}_j \hat{\Gamma} \hat{C}_k \right) = \langle \hat{C}_j | \hat{\Gamma} | \hat{C}_k \rangle \)

• If we reorder \( \tilde{\sigma} \) 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:

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

Rotations \hspace{2cm} Relaxation

- Examples

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

\[
\frac{1}{T_{2,I}} = \langle \hat{I}_x | \hat{\Gamma} | \hat{I}_x \rangle = \langle \hat{I}_y | \hat{\Gamma} | \hat{I}_y \rangle \hspace{1cm} \text{...we just need to compute some (a bunch) of commutators.}
\]
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 \( \langle \Delta B(t) \rangle = 0 \) and \( \langle \Delta B(t) \Delta B(t - \tau) \rangle = B^2 e^{-|\tau|/\tau_c} \)

- 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 \( J_0(\omega) = \gamma^2 B^2 \frac{\tau_c}{1 + \omega^2 \tau_c^2} \)

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

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

  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

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

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

- 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

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

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

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

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

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

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

Hey! These look like rank 2 spherical harmonics.
Dipolar Coupling Revisited

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

<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>
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</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>
<td>$\hat{I}<em>z \hat{S}</em>+$</td>
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</tr>
<tr>
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<td>$\omega_S$</td>
</tr>
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</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. + \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}_y \hat{S}_x + \hat{I}_y \hat{S}_x \hat{I}_y \hat{S}_x \right) \right. 

\left. + \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) \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\} \]

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 $q = \frac{\mu_0^2 \gamma_i^2 \gamma_s^2 \hbar^2}{16 \pi^2 10 r^6}$

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

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

• Let’s calculate $T_1$.

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

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

• 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 \( \hat{I}_\pm \hat{S}_\mp \).

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

• But now there is also transverse cross relaxation between spins \( I \) and \( S \).

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

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

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 \( e_1, e_2, \) 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\textsuperscript{st} and 2\textsuperscript{nd} kind are readily calculated.
Example: Scalar relaxation of the 1\textsuperscript{st} 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 1st kind

Thus we have:  \( \hat{H}_0 = -\omega_I \hat{I}_z - \omega_S \hat{S}_z \) and  \( \hat{H}_1(t) = A_i(t)\left( \hat{I}_z \hat{S}_z + \hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y \right) \).

Noting the eigenoperators and corresponding eigenvalues of  \( \hat{H}_0 \)

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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.  \( \sum_i P_i = 1 \)

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

- Hence:

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

- From which it follows

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

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.

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

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