Lecture #7
Redfield theory of NMR relaxation

• Topics
  – The interaction frame of reference
  – Perturbation theory
  – The Master Equation

• Handouts and Reading assignments
  – van de Ven, Chapters 6.2.
  – Kowalewski, Chapter 4.
The Master Equation

• When the Hamiltonian can be written as the sum of a large static component plus a small time-varying perturbation...

\[ \hat{H} = \hat{H}_0 + \hat{H}_1(t) \]

...our goal is to find an equation of the form:

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

from which we can calculate any direct and cross relaxation terms of interest.

• In general, \( \hat{\Gamma} \) differs across different relaxation mechanisms.

• Reminder: Bloch’s equations are:

\[ \frac{d\vec{M}}{dt} = \gamma \vec{M} \times B_0 \hat{z} - \frac{M_x \hat{x} + M_y \hat{y}}{T_2} - \frac{(M_z - M_0) \hat{z}}{T_1} \]
Redfield Theory

- Redfield theory, also known as Wangsness, Bloch, and Redfield (WBR) theory, is more general than that derived by Solomon.

- Both Solomon and Redfield theory rely on 2nd-order perturbation theory (can be a limitation, but usually not for liquids)

- Like Solomon’s approach, Redfield theory is semi-classical, using the same Boltzmann correction for thermal equilibrium values.

- However, rather than directly dealing with energy level populations, the theory is derived in terms of the density operator.

- This allows for a more general description of relaxation and allows the derivation of relaxation rates from multiple mechanisms, e.g. dipolar coupling, CSA, scalar relaxation of the 1st and 2nd kind, etc.
Liouville-von Neumann equation

• We’ve seen where we can express the spin Hamiltonian as the sum of a large static component plus a small time-dependent spin lattice interaction term.

\[ \hat{H}(t) = \hat{H}_0 + \hat{H}_1(t) \]

• Starting with the Liouville-von Neumann equation for the density operator

\[ \frac{d\hat{\sigma}}{dt} = -i\hat{H}\hat{\sigma} \]

• It is helpful to switch to a rotating frame of reference where the spin-lattice interaction term is isolated from the static part of $\hat{H}_0$. 
The Interaction Frame

- Let \( \hat{\sigma}'(t) = e^{i\hat{H}_0 t} \hat{\sigma}(t) \)
  Rotation about the \( \hat{H}_0 \) axis in Liouville space

\[ \hat{H}'(t) = e^{i\hat{H}_0 t} \hat{H}(t) \]

\[ \hat{H}_1'(t) = e^{i\hat{H}_0 t} \hat{H}_1(t), \]

then \( \frac{d}{dt} \hat{\sigma}' = \frac{d}{dt} e^{i\hat{H}_0 t} \hat{\sigma}(t) = i\hat{H}_0 e^{i\hat{H}_0 t} \hat{\sigma}(t) + e^{i\hat{H}_0 t} \frac{d}{dt} \hat{\sigma}(t), \)

which simplifies to: \( \frac{d}{dt} \hat{\sigma}' = -i\hat{H}_1' \hat{\sigma}' \) (see homework)

- Hence in this frame of reference, known as the “interaction frame”, where the time dependence of the density operator depends only on \( \hat{H}_1' \).
Redfield theory

• Step 1. Let’s start by formally integrating \( \frac{d}{dt} \hat{\sigma}' = -i\hat{H}_1'\hat{\sigma}' \).

\[
\hat{\sigma}'(t) = \hat{\sigma}'(0) - i \int_0^t \hat{H}_1'(t')\hat{\sigma}'(t')dt'
\]

\[
= \hat{\sigma}'(0) - i \int_0^t \hat{H}_1'(t')\hat{\sigma}'(0)dt' - \int_0^t \int_0^{t'} \hat{H}_1'(t')\hat{H}_1'(t'')\hat{\sigma}'(t'')dt''dt'
\]

\[
= \hat{\sigma}'(0) - i \int_0^t \hat{H}_1'(t')\hat{\sigma}'(0)dt' - \int_0^t \int_0^{t'} \hat{H}_1'(t')\hat{H}_1'(t'')\hat{\sigma}'(0)dt''dt' + i \int_0^t \int_0^{t'} \int_0^{t''} \ldots
\]

• This is starting to get ugly, so we’ll just keep the first 3 terms (to be justified later).
Redfield theory (cont.)

• Step 2 is to take the ensemble average (technically this is an ensemble of ensembles), and note..

\[ \int_0^t \hat{H}'(t') \hat{\sigma}'(0) dt' = 0 \text{ because } \hat{H}'(t) = 0 \]

If \( \hat{H}'(t) \neq 0 \), we can always incorporate the non-zero part into \( \hat{H}_0 \).

and we’ve assumed \( \hat{H}'(t) \) and \( \hat{\sigma}'(0) \) are uncorrelated.

This leads to….

\[ \hat{\sigma}'(t) - \hat{\sigma}'(0) = -\int_0^t \int_0^{t'} \hat{H}'(t') \hat{H}'(t'') \hat{\sigma}'(0) dt'' dt' \]

Technically, from here on we should be using \( \overline{\hat{\sigma}}' \) but we’re just going to go with the simpler notation of \( \hat{\sigma}' \).
Redfield theory (cont.)

• Step 3. Choose \( t = \Delta t \) very small, such that \( \hat{\sigma}'(t) \approx \hat{\sigma}'(0) \)

This assumption is the one that allows us to drop those higher order terms. In essence, \( \hat{\sigma}'(t) \) is assumed to vary slowly in time as compared to \( \hat{H}'_1(t) \).

\[
\Delta \hat{\sigma}' = \hat{\sigma}'(\Delta t) - \hat{\sigma}'(0) = -\int_0^\Delta \int_0^{t'} \hat{H}'_1(t') \hat{H}'_1(t'') \hat{\sigma}'(0) dt'' dt'
\]

• Step 4. Define a new variable, \( \tau = t' - t'' \)

\[
\Delta \hat{\sigma}' = \hat{\sigma}'(\Delta t) - \hat{\sigma}'(0) = -\int_0^\Delta \int_0^{t'} \hat{H}'_1(t') \hat{H}'_1(t' - \tau) \hat{\sigma}'(0) d\tau dt'
\]
Redfield theory (cont.)

• Step 5. Introduce a correlation superoperator:

\[ \hat{G}(\tau) = \hat{H}_1(t') \hat{H}_1(t' - \tau) \]

\[ \frac{\Delta \hat{\sigma}'}{\Delta t} = -\int_0^{\Delta t} \hat{G}(\tau) \hat{\sigma}' d\tau \]

• Step 6. Make some more assumptions.

Assume \( \Delta t \) sufficiently small that

\[ \frac{\Delta \hat{\sigma}'}{\Delta t} \approx \frac{d\hat{\sigma}'}{dt} \]

but that \( \Delta t \) is sufficiently large that we can extend the integration to \( \infty \).

\[ \frac{d\hat{\sigma}'}{dt} = -\int_0^{\infty} \hat{G}(\tau) \hat{\sigma}' d\tau \]

Can we actually find such a \( \Delta t \) ?!
Redfield theory assumptions

• Let’s look at some numbers…

Consider $\Delta t = 10^{-6}$ s.

Typically NMR relaxation times are on the order of milliseconds to seconds, hence \[
\frac{\Delta \hat{\sigma}'}{\Delta t} \approx \frac{d\hat{\sigma}'}{dt}.
\]

Tissue water correlation times due to molecular tumbling are on the order of $10^{-9}$ s. Hence $\hat{G}(\Delta t) \approx 0$ for $\Delta t \geq 10^{-6}$ s.

• In general, Redfield theory is valid for relaxation times several orders of magnitude longer than the correlations times driving the relaxation processes, e.g. liquids.
Redfield theory (cont.)

• Step 7. We need to find an explicit expression for $\hat{H}_1(t)$.

$$\hat{H}_1'(t) = e^{i\hat{H}_0 t} \hat{H}_1(t)$$

• The best choice is to express $\hat{H}_1(t)$ as a linear combination of eigenoperators of $\hat{H}_0$.

• Let $\hat{A}_q$ be an eigenoperators of $\hat{H}_0$: $\hat{H}_0 \hat{A}_q = e_q \hat{A}_q$

• Examples. Let $\hat{H}_0 = -\omega_I \hat{I}_z - \omega_S \hat{S}_z$ then...

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \Rightarrow \hat{H}_0 \hat{I}_+ = \hat{H}_0 \left( \hat{I}_x + i\hat{I}_y \right) = -\omega_I i\hat{I}_y - \omega_I \hat{I}_x = -\omega_I \hat{I}_+$$

$$\hat{I}_+ \hat{S}_+ \Rightarrow \hat{H}_0 \hat{I}_+ \hat{S}_+ = -\left(\omega_I + \omega_S\right) \hat{I}_+ \hat{S}_+$$

(See Problem Set 1 for more examples)
Redfield theory (cont.)

- Hence, let...

\[ \hat{H}_1(t) = \sum_{q} F_q(t)\hat{A}_q \]

Eigenoperator

Random functions of time (typically dependent on molecular orientation)

- We first note, that for \( \hat{H}_1(t) \) to represent a physical process, \( \hat{H}_1(t) \) must be Hermitian.

- However, the \( F_q(t)\hat{A}_q \)s can be complex.

- Thus, for every \( F_q(t)\hat{A}_q \) the sum must also contain a term \( F_q^*(t)\hat{A}_q^* \), which, we will denote as \( \hat{F}_{-q}(t)\hat{A}_{-q} \).
Redfield theory (cont.)

- Noting $\hat{H}_0 \hat{A}_q = e_q \hat{A}_q \implies e^{i\hat{H}_0 t} \hat{A}_q = e^{ie_q t} \hat{A}_q$

- We have $\hat{H}'_1(t) = e^{i\hat{H}_0 t} \hat{H}_1(t) = \sum_q F_q(t) \hat{A}_q e^{ie_q t}$

- We can now write the full expression for the correlation superoperator as

$$\hat{G}(\tau) = \hat{H}'_1(t') \hat{H}'_1(t' - \tau) = \sum_p \sum_q F_p(t') F_q(t' - \tau) \hat{A}_p \hat{A}_q e^{ie_p t'} e^{ie_q (t' - \tau)}$$

- Using a secular approximation, one can show that only the terms for which $e_p = -e_q$ need to be kept. The other terms average out as they oscillate fast as compared to the relaxation rate of $\hat{\sigma}'$. 
Redfield theory (cont.)

• Thus \( \hat{G}(\tau) = \sum_q F_{-q}(t') F_q(t' - \tau) \hat{A}_q \hat{A}_q e^{-i e_q \tau} \)

• Defining a set of correlation functions:
\[
G_q(\tau) = \sum_q F_{-q}(t') F_q(t' - \tau)
\]
yields
\[
\frac{d\hat{\sigma}'}{dt} = -\int_0^\infty \sum_q G_q(\tau) e^{-i e_q \tau} \hat{A}_q \hat{A}_q \hat{\sigma}' d\tau.
\]

• Step 9. Define a set of spectral density functions:
\[
J_q(e_q) = \int_0^\infty G_q(\tau) e^{-i e_q \tau} d\tau, \quad \text{with} \quad G_q(\tau) = G_q(0) e^{-\tau/\tau_c}
\]

Correlation time characteristic of the perturbation.
Redfield theory (cont.)

• The spectral density functions are:

\[ J_q(e_q) = \int_0^\infty G_q(\tau) e^{-ie_q \tau} d\tau, \quad \text{with} \quad G_q(\tau) = G_q(0) e^{-\tau/\tau_c} \]

• As defined, \( J_q \), are complex, however, in practice the real part is much larger than the imaginary component*.

• A more formal treatment shows the imaginary components basically cancel due to the combination of the terms:

\[ \hat{A}_{-q} \hat{A}_{q} \quad \text{and} \quad \hat{A}_{q} \hat{A}_{-q} \]

• thus we’ll use..

\[ J_q(\omega) = \int_0^\infty G_q(\tau) e^{-i\omega \tau} d\tau \approx \int_0^\infty G_q(\tau) \cos \omega_q \tau = G_q(0) \frac{\tau_c}{1 + \omega^2 \tau_c^2} \]

*If you’re curious about these imaginary terms, look up “dynamic frequency shifts” in the NMR literature.
The Relaxation Superoperator

• Putting it all together, we can now define the relaxation superoperator as:

$$\hat{\Gamma} = \sum_q J_q(e_q) \hat{A}_q \hat{A}_q$$

with

$$J_q(e_q) = \int_0^\infty F_{-q}(t') F_q(t' - \tau) e^{-ie_q \tau} d\tau$$

• Substituting:$$\frac{d\hat{\sigma}'}{dt} = -\hat{\Gamma}\hat{\sigma}$$

• We can now add the Boltzmann correction and finally switch back to the laboratory frame* (see homework) to yield:

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

The Master Equation of NMR

*Note the relaxation superoperator is the same in both frames of reference, as befits relaxation times.
Next Lecture: Redfield theory II