

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.
 - Abragam Chapter VIII.C, pp 272-284, 1955.

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:

$$\frac{\partial}{\partial t} \hat{\sigma} = \underbrace{-i\hat{H}_0 \hat{\sigma}}_{\text{Rotations}} - \underbrace{\hat{\Gamma}}_{\text{Relaxation}} (\hat{\sigma} - \hat{\sigma}_B)$$

Relaxation superoperator

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:

$$\frac{d\vec{M}}{dt} = \underbrace{\gamma \vec{M} \times B_0 \hat{z}}_{\text{Rotations}} - \underbrace{\frac{M_x \hat{x} + M_y \hat{y}}{T_2}}_{\text{Relaxation terms}} - \frac{(M_z - M_0) \hat{z}}{T_1}$$

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.

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

↙ perturbation

- 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

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

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

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

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

- 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 $\frac{d}{dt} \hat{\sigma}' = -i\hat{H}'_1 \hat{\sigma}'$.

$$\begin{aligned}\hat{\sigma}'(t) &= \hat{\sigma}'(0) - i \int_0^t \hat{H}'_1(t') \hat{\sigma}'(t') dt' \\ &= \hat{\sigma}'(0) - i \int_0^t \hat{H}'_1(t') \hat{\sigma}'(0) dt' - \int_0^t \int_0^{t'} \hat{H}'_1(t') \hat{H}'_1(t'') \hat{\sigma}'(t'') dt'' dt' \\ &= \hat{\sigma}'(0) - i \int_0^t \hat{H}'_1(t') \hat{\sigma}'(0) dt' - \int_0^t \int_0^{t'} \hat{H}'_1(t') \hat{H}'_1(t'') \hat{\sigma}'(0) dt'' dt' + i \int_0^t \int_0^{t'} \int_0^{t''} \dots\end{aligned}$$

- 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..

$$\int_0^t \overline{\hat{H}'_1(t') \hat{\sigma}'(0)} dt' = 0 \quad \text{because} \quad \overline{\hat{H}'_1(t)} = 0$$

If $\overline{\hat{H}'_1(t)} \neq 0$, we can always incorporate the non-zero part into \hat{H}_0 .

and we've assumed $\hat{H}'_1(t)$ and $\hat{\sigma}'(0)$ are uncorrelated.

This leads to....

$$\hat{\sigma}'(t) - \hat{\sigma}'(0) = - \int_0^t \int_0^{t'} \overline{\hat{H}'_1(t') \hat{H}'_1(t'') \hat{\sigma}'(0)} dt'' dt'$$

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 $\hat{H}'_1(t)$.

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

- Step 4. Define a new variable, $\tau = t' - t''$

$$\Delta\hat{\sigma}' = \hat{\sigma}'(\Delta t) - \hat{\sigma}'(0) = -\int_0^{\Delta t} \int_0^{t'} \hat{H}'_1(t') \hat{H}'_1(t' - \tau) \hat{\sigma}'(0) d\tau dt'$$

Redfield theory (cont.)

- Step 5. Introduce a correlation superoperator:

$$\hat{G}(\tau) = \overline{\hat{H}'_1(t')\hat{H}'_1(t' - \tau)} \quad \longrightarrow \quad \frac{\Delta\hat{\sigma}'}{\Delta t} = -\int_0^{\Delta t} \hat{G}(\tau)\hat{\sigma}' d\tau$$

- Step 6. Make some more assumptions.

Assume Δt sufficiently small that $\frac{\Delta\hat{\sigma}'}{\Delta t} \approx \frac{d\hat{\sigma}'}{dt}$,

but that Δt is sufficiently large that we can extend the integration to ∞ .

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

Can we actually find such a Δt ???

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 correlation 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 eigenoperator of \hat{H}_0 : $\hat{H}_0 \hat{A}_q = e_q \hat{A}_q$ eigenvalue

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

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

$$\hat{I}_+ \hat{S}_+ \Rightarrow \hat{H}_0 \hat{I}_+ \hat{S}_+ = -(\omega_I + \omega_S) \hat{I}_+ \hat{S}_+ \quad (\text{See Problem Set 1 for more examples})$$

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

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

- 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 $\hat{G}(\tau) = \sum_q \overline{F_{-q}(t') F_q(t' - \tau)} \hat{A}_{-q} \hat{A}_q e^{-ie_q \tau}$
- Defining a set of correlation functions: $G_q(\tau) = \overline{F_{-q}(t') F_q(t' - \tau)}$

yields
$$\frac{d\hat{\sigma}'}{dt} = - \int_0^\infty \sum_q G_q(\tau) e^{-ie_q \tau} \hat{A}_{-q} \hat{A}_q \hat{\sigma}' d\tau.$$

- Step 9. Define a set of spectral density functions:

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

Correlation time characteristic
of the perturbation.

Redfield theory (cont.)

- The spectral density functions are:

Correlation time characteristic of the perturbation.

$$J_q(\omega_q) = \int_0^{\infty} G_q(\tau) e^{-i\omega_q \tau} d\tau, \quad \text{with} \quad G_q(\tau) = G_q(0) e^{-\tau/\tau_c}$$

- As defined, J_q s, 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:

$$\hat{\Gamma} = \sum_q J_q(e_q) \hat{A}_{-q} \hat{A}_q \quad \text{with} \quad J_q(e_q) = \int_0^{\infty} \overline{F_{-q}(t') F_q(t' - \tau)} e^{-ie_q \tau} d\tau$$

- 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