

Module III, Lecture 01: Perturbative Relaxation Theories

Time-dependent perturbation theory

The Schrödinger differential equation with a time-dependent Hamiltonian may be integrated formally to yield an equivalent integral equation:

$$\frac{\partial |\psi(t)\rangle}{\partial t} = -i\hat{H}(t)|\psi(t)\rangle \quad \Rightarrow \quad |\psi(t)\rangle = |\psi(0)\rangle - i \int_0^t \hat{H}(t_1)|\psi(t_1)\rangle dt_1 \quad (1)$$

The resulting expression for $|\psi(t)\rangle$ may be substituted back into Schrödinger equation to yield:

$$\frac{\partial}{\partial t} |\psi(t)\rangle = -i\hat{H}(t)|\psi(0)\rangle - \hat{H}(t) \int_0^t \hat{H}(t_1)|\psi(t_1)\rangle dt_1 \quad (2)$$

Another formal integration would then produce:

$$|\psi(t)\rangle = |\psi(0)\rangle - i \int_0^t \hat{H}(t_1)|\psi(0)\rangle dt_1 - \int_0^t \hat{H}(t_1) \int_0^{t_1} \hat{H}(t_2)|\psi(t_2)\rangle dt_2 dt_1 \quad (3)$$

After applying this procedure multiple times, we get *Dyson series* for the wavefunction:

$$|\psi(t)\rangle = \left[1 + (-i) \int_0^t dt_1 \hat{H}(t_1) + (-i)^2 \int_0^t dt_1 \int_0^{t_1} dt_2 \hat{H}(t_1) \hat{H}(t_2) + \dots \right] |\psi(0)\rangle = \left[\sum_{n=0}^{\infty} \hat{U}_n(t) \right] |\psi(0)\rangle \quad (4)$$

$$\hat{U}_n(t) = (-i)^n \int_0^t dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \hat{H}(t_1) \hat{H}(t_2) \dots \hat{H}(t_n)$$

in which the individual terms have order $O(t^n)$ with respect to the evolution time. If the time t is small compared to the scale of the system dynamics (strictly speaking, $t \ll \|\hat{H}\|^{-1}$), the series may be truncated – this is the substance of *time-dependent perturbation theory*. In an iterative formulation

$$|\psi_0(t)\rangle = |\psi(0)\rangle \quad |\psi_{k+1}(t)\rangle = |\psi_k(t)\rangle - i \int_0^t \hat{H}(t_1)|\psi_k(t_1)\rangle dt_1 \quad (5)$$

Equation (4) may be used to generate better and better approximations to the exact $|\psi(t)\rangle$ as a function of the iteration number k . In particular, the truncation of this process at the second order

$$|\psi_2(t)\rangle = |\psi(0)\rangle - i \int_0^t \hat{H}(t_1)|\psi(0)\rangle dt_1 - \int_0^t \hat{H}(t_1) \int_0^{t_1} \hat{H}(t_2)|\psi(0)\rangle dt_2 dt_1 + O(\|\hat{H}t\|^3) \quad (6)$$

will be useful below. Equation (4) in general and Equation (6) in particular are not required to start at time zero and may be applied sequentially, for example:

$$|\psi_2(t + \Delta t)\rangle = |\psi(t)\rangle - i \int_t^{t+\Delta t} \hat{H}(t_1)|\psi(t)\rangle dt_1 - \int_t^{t+\Delta t} \hat{H}(t_1) \int_t^{t_1} \hat{H}(t_2)|\psi(t)\rangle dt_2 dt_1 + O(\|\hat{H}\Delta t\|^3) \quad (7)$$

in which case the system is propagated forward in time with the accuracy that depends on the choice of the time step Δt and the norm of the Hamiltonian. Perturbation theory method in general is not specific to quantum mechanics and can be used with many linear and non-linear PDEs provided that they can be integrated with respect to time in a straightforward way. Interaction representations with respect to strong static interactions are advantageous, because they reduce the Hamiltonian norm and therefore improve the accuracy of the iterative procedure.

Bloch-Redfield-Wangsness relaxation theory

Also known as *Redfield theory*, this is perhaps the most successful spin relaxation theory, widely used in all areas of magnetic resonance. It is necessary because molecular motion that is driving spin relaxation happens on a very short timescale (femtoseconds to picoseconds). This makes brute-force calculations of multi-second NMR dynamics impractical. We are therefore looking for a theory that would incorporate molecular dynamics in terms of the energy spectrum and statistical properties of the molecular motion rather than its explicit time dependence.

Very roughly speaking, Redfield theory views molecular motion as the source of stochastic noise in the spin Hamiltonian. This noise has a frequency spectrum; some of the frequencies can coincide with transition frequencies of the spin system and thereby cause relaxation. The biggest challenge, which Redfield theory successfully addresses, is to find the equation of motion that depends on statistical properties of the noise, rather than its explicit time-dependent form. This is the objective of this lecture.

We shall start with the Liouville - von Neumann equation for the density matrix $\hat{\rho}(t)$ in Liouville space, in which the Hamiltonian will be separated into two parts:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i \left[\hat{H}_0 + \hat{H}_1(t) \right] \hat{\rho}(t), \quad \hat{O} \hat{\rho} = \hat{O} \hat{\rho} - \hat{\rho} \hat{O} \quad (8)$$

where \hat{H}_0 is the time-independent part of the Hamiltonian (for example, chemical shifts and J-couplings) and $\hat{H}_1(t)$ is the time-dependent part that is modulated by random molecular motion (for example, dipolar interactions and chemical shift anisotropy). We will assume $\hat{H}_1(t)$ to have a zero ensemble average (denoted by angular brackets):

$$\left\langle \hat{H}_1(t) \right\rangle = 0 \quad (9)$$

If the ensemble average of $\hat{H}_1(t)$ is non-zero, it can always be subtracted and put into \hat{H}_0 .

We will now move into the interaction representation with respect to \hat{H}_0 and perform a second-order TDPT treatment. The interaction representation transformation was covered in the previous lectures:

$$\hat{\sigma}(t) = e^{i\hat{H}_0 t} \hat{\rho}(t) \quad \hat{H}_1^R(t) = e^{i\hat{H}_0 t} \hat{H}_1(t) e^{-i\hat{H}_0 t} \quad (10)$$

After a bit of mathematics (differentiate the definition of $\hat{\sigma}(t)$ above and simplify the resulting expression), we can show that the Liouville - von Neumann equation for $\hat{\sigma}(t)$ is:

$$\frac{\partial \hat{\sigma}(t)}{\partial t} = -i \hat{H}_1^R(t) \hat{\sigma}(t) \quad (11)$$

Formal integration and re-substitution, as per the general recipe given in Equation (6), yields:

$$\frac{\partial \hat{\sigma}(t)}{\partial t} = -i \hat{H}_1^R(t) \hat{\sigma}(0) - \int_0^t \hat{H}_1^R(t) \hat{H}_1^R(t_1) \hat{\sigma}(t_1) dt_1 \quad (12)$$

If we now perform ensemble averaging, the first term on the right hand side would vanish because the initial condition $\hat{\sigma}(0)$ and the static Hamiltonian \hat{H}_0 are the same for each member of the ensemble, and we have assumed in Equation (9) that the ensemble average of $\hat{H}_1(t)$ is zero:

$$\begin{aligned} \left\langle \hat{H}_1^R(t) \hat{\sigma}(0) \right\rangle &= e^{i\hat{H}_0 t} \left\langle \hat{H}_1(t) \right\rangle e^{-i\hat{H}_0 t} \hat{\sigma}(0) = 0 \\ &\Downarrow \\ \frac{\partial}{\partial t} \langle \hat{\sigma}(t) \rangle &= - \int_0^t \left\langle \hat{H}_1^R(t) \hat{H}_1^R(t_1) \hat{\sigma}(t_1) \right\rangle dt_1 \end{aligned} \quad (13)$$

We will now take advantage of the fact that any time-dependent operator has an expansion in time-independent operators with time-dependent complex coefficients:

$$\hat{H}_1(t) = \sum_k q_k(t) \hat{Q}_k = \sum_m q_m^*(t) \hat{Q}_m^\dagger \quad (14)$$

where $q_k(t)$ are those coefficients and \hat{Q}_k are the time-independent basis operators, which do acquire a deterministic time dependence in the rotating frame:

$$\hat{Q}_k^R(t) = e^{i\hat{H}_0 t} \hat{Q}_k e^{-i\hat{H}_0 t} \quad \Rightarrow \quad \frac{\partial}{\partial t} \langle \hat{\sigma}(t) \rangle = - \sum_{km} \int_0^t \left\langle q_k(t) q_m^*(t_1) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t_1) \hat{\sigma}(t_1) \right\rangle dt_1 \quad (15)$$

To facilitate subsequent treatment, one copy of the Hermitian \hat{H}_1^R superoperator has been pasted in a conjugated form. In the case of rotationally modulated interactions $q_k(t)$ would be Wigner functions and \hat{Q}_k the associated spherical tensor operators – see the rotations theory lecture.

We need to introduce further assumptions at this point. Firstly, we shall assume that the amplitude (*i.e.* the norm) of the perturbation Hamiltonian $\hat{H}_1(t)$ is much smaller than the norm of \hat{H}_0

$$\left\| \hat{H}_1(t) \right\| \ll \left\| \hat{H}_0 \right\| \quad (16)$$

and therefore the spin system dynamics is not correlated with the stochastic noise in $\hat{H}_1(t)$. This would allow us to take ensemble averages separately for the Hamiltonians and the state vector:

$$\left\langle q_k(t) q_m^*(t_1) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t_1) \hat{\sigma}(t_1) \right\rangle = \left\langle q_k(t) q_m^*(t_1) \right\rangle \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t_1) \langle \hat{\sigma}(t_1) \rangle \quad (17)$$

The operators $\hat{Q}_k^R(t)$ were also taken out of the ensemble average bracket here because their time dependence is the same for every molecule and is not affected by the ensemble averaging. What we now have in the first angular brackets is the correlation function between $q_k(t)$ and $q_m(t)$:

$$\left\langle q_k(t) q_m^*(t_1) \right\rangle = g_{km}(t, t_1) \quad (18)$$

The second significant assumption is that the noise in the system is stationary. This means that the correlation functions only depend on the time separation between the two functions, and not the absolute time t . This means that we can change the definition of the correlation function:

$$\left\langle q_k(t) q_m^*(t_1) \right\rangle = g_{km}(t - t_1) \quad (19)$$

With Equations (17) and (19) in place, Equation (15) becomes:

$$\frac{\partial}{\partial t} \langle \hat{\sigma}(t) \rangle = - \sum_{km} \int_0^t g_{km}(t - t_1) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t_1) \langle \hat{\sigma}(t_1) \rangle dt_1 \quad (20)$$

The third assumption is that the correlation functions decay so fast on the time scale of the spin system evolution (typically nanoseconds to femtoseconds in non-viscous liquids), that the latter barely happens. We can therefore take the density matrix out of the integral:

$$\frac{\partial}{\partial t} \langle \hat{\sigma}(t) \rangle = - \sum_{km} \int_0^t g_{km}(t-t_1) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t_1) dt_1 \langle \hat{\sigma}(t) \rangle \quad (21)$$

Because the implicit coarse-graining schemes are known to be more stable than the explicit ones, we take $\hat{\sigma}(t)$ out of the integral rather than $\hat{\sigma}(0)$. In the remaining integral we will perform a variable substitution $\tau = t - t_1$ and then turn the integration limits around to get:

$$\frac{\partial}{\partial t} \langle \hat{\sigma}(t) \rangle = - \sum_{km} \int_0^t g_{km}(\tau) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t-\tau) d\tau \langle \hat{\sigma}(t) \rangle \quad (22)$$

The second consequence of our assumption about the very rapid decay of the correlation functions is that it is permissible to extend the upper integration limit to infinity without affecting the value of the integral. We shall also drop the angular brackets on the density matrix for convenience:

$$\frac{\partial}{\partial t} \hat{\sigma}(t) = \left[- \sum_{km} \int_0^\infty g_{km}(\tau) \hat{Q}_k^R(t) \hat{Q}_m^{R\dagger}(t-\tau) d\tau \right] \hat{\sigma}(t) \quad (23)$$

After using Equations (10) to return back to the Schrödinger representation, we get:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i\hat{H}_0 \hat{\rho}(t) - \sum_{km} \int_0^\infty g_{km}(\tau) \hat{Q}_k e^{-i\hat{H}_0\tau} \hat{Q}_m^\dagger e^{i\hat{H}_0\tau} d\tau \hat{\rho}(t) \quad (24)$$

The master equation now has the following form:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i\hat{H}_0 \hat{\rho}(t) + \hat{R} \hat{\rho}(t) \quad (25)$$

In which the *relaxation superoperator* is defined as:

$$\hat{R} = - \sum_{km} \int_0^\infty g_{km}(\tau) \hat{Q}_k e^{-i\hat{H}_0\tau} \hat{Q}_m^\dagger e^{i\hat{H}_0\tau} d\tau \quad (26)$$

The derivation above can be repeated in Hilbert space to yield:

$$\begin{aligned} \frac{\partial \hat{\rho}(t)}{\partial t} &= -i[\hat{H}_0, \hat{\rho}(t)] - \sum_{km} \int_0^\infty g_{km}(\tau) [\hat{Q}_k, [e^{i\hat{H}_0\tau} \hat{Q}_m^\dagger e^{-i\hat{H}_0\tau}, \hat{\rho}(t)]] d\tau \\ \frac{\partial \hat{\rho}(t)}{\partial t} &= -i[\hat{H}_0, \hat{\rho}(t)] + \hat{R} \hat{\rho}(t), \quad \hat{R} \hat{\rho}(t) = - \sum_{km} \int_0^\infty G_{km}(\tau) [\hat{Q}_k, [e^{i\hat{H}_0\tau} \hat{Q}_m^\dagger e^{-i\hat{H}_0\tau}, \hat{\rho}(t)]] d\tau \end{aligned} \quad (27)$$

In practice most calculations are done in Liouville space.

Thermal equilibrium

At thermal equilibrium all energy levels are populated according to the Boltzmann law and all correlations between different molecules of the ensemble vanish. Hamiltonian diagonalization yields:

$$\hat{H} |\psi_k\rangle = E_k |\psi_k\rangle \quad (28)$$

with the population fraction in the state n being equal to:

$$p_n = \exp\left(-\frac{E_n}{kT}\right) / \sum_m \exp\left(-\frac{E_m}{kT}\right) \quad (29)$$

Noting that population probabilities are the diagonal terms of the density matrix and that the off-diagonal terms vanish by definition, we get the following expression for the equilibrium density matrix:

$$\hat{\rho}_{\text{eq}} = \sum_n \exp\left(-\frac{E_n}{kT}\right) |\psi_n\rangle \langle \psi_n| / \sum_m \exp\left(-\frac{E_m}{kT}\right) = \exp\left(-\frac{\hat{H}}{kT}\right) / \text{Tr}\left[\exp\left(-\frac{\hat{H}}{kT}\right)\right] \quad (30)$$

Very notably, the relaxation theory described above does *not* relax the system to this state – under Equation (25) the system relaxes to zero density matrix. This problem is a consequence of classical description of the spatial degrees of freedom; two *ad hoc* solutions are available:

1. To replace $\hat{\rho}(t)$ with $\hat{\rho}(t) - \hat{\rho}_{\text{eq}}$ in the relaxation part of Equation (25), to produce:

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -i\hat{H}_0 \hat{\rho}(t) + \hat{R}[\hat{\rho}(t) - \hat{\rho}_{\text{eq}}] \quad (31)$$

which has the correct asymptotic behaviour in the long-time limit. A practical inconvenience is in the fact that this equation is no longer uniform. This may be remedied by doubling the problem dimension:

$$\frac{\partial}{\partial t} \begin{pmatrix} \hat{\rho}(t) \\ \hat{\rho}_{\text{eq}} \end{pmatrix} = \begin{pmatrix} -i\hat{H}_0 + \hat{R} & -\hat{R} \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \hat{\rho}(t) \\ \hat{\rho}_{\text{eq}} \end{pmatrix} \quad (32)$$

or (equivalently and more efficiently) by adding just one extra dimension:

$$\frac{d}{dt} \begin{pmatrix} 1 \\ \rho_1 \\ \vdots \\ \rho_n \end{pmatrix} = \begin{pmatrix} 0 & 0 & \cdots & 0 \\ -[\hat{R}\hat{\rho}_{\text{eq}}]_1 & -iH_{11} + R_{11} & \cdots & -iH_{1n} + R_{1n} \\ \vdots & \vdots & \ddots & \vdots \\ -[\hat{R}\hat{\rho}_{\text{eq}}]_n & -iH_{n1} + R_{n1} & \cdots & -iH_{nn} + R_{nn} \end{pmatrix} \begin{pmatrix} 1 \\ \rho_1 \\ \vdots \\ \rho_n \end{pmatrix} \quad (33)$$

Another practical inconvenience inherent in Equations (32) and (33) is in the careful control required over the matrix dimension, particularly if independently evolving subspaces are present.

2. To re-balance the forward and backward rates in the relaxation superoperator to ensure that it drives the system to the thermal equilibrium. It may be shown that the following modification

$$\hat{R} \rightarrow \hat{R} \exp\left(-\frac{\hat{H}^R}{kT}\right) \quad (34)$$

where \hat{H}^R is the Hamiltonian right-side multiplication superoperator, has the desired effect. This is the preferred method in practice (default in *Spinach*) because the master equation stays uniform and the problem dimension remains unchanged.

Relaxation superoperator in the rotating frame

Because most magnetic resonance experiments are carried out at high field, it is instructive to consider the interaction representation picture with respect to the carrier frequency part of the Zeeman interaction. The master equation derived above is:

$$\frac{d}{dt}\hat{\rho}(t) = -i\left(\hat{H}_Z + \hat{H}_{\text{INT}}\right)\hat{\rho}(t) + \hat{R}\hat{\rho}(t) \quad (35)$$

where the static Hamiltonian \hat{H}_0 has been partitioned into the Zeeman part \hat{H}_Z and the interaction part \hat{H}_{INT} . In the interaction representation with respect to \hat{H}_Z , the equation becomes:

$$\frac{d}{dt}\hat{\sigma}(t) = \left[-i\hat{H}_{\text{INT}}^{\text{R}}(t) + \hat{R}^{\text{R}}(t)\right]\hat{\sigma}(t) \quad (36)$$

in which the rotating frame operators are

$$\hat{\sigma}(t) = e^{i\hat{H}_Z t}\hat{\rho}(t) \quad \hat{H}_{\text{INT}}^{\text{R}}(t) = e^{i\hat{H}_Z t}\hat{H}_{\text{INT}}e^{-i\hat{H}_Z t} \quad \hat{R}^{\text{R}}(t) = e^{i\hat{H}_Z t}\hat{R}e^{-i\hat{H}_Z t} \quad (37)$$

with the result that those terms in $e^{i\hat{H}_Z t}\hat{R}e^{-i\hat{H}_Z t}$ that end up being static are retained, and the terms that acquire a frequency as a result of the rotating frame transformation may be discarded as non-secular because they are “averaged out” on the time scale of the experiment.

The simplest approximation (often used when cross-relaxation is unimportant) is to keep only the diagonal of the relaxation superoperator. The corresponding terms are called *self-relaxation rates* because they correspond to the decay of the populations of the individual states to the equilibrium. The T_1 and T_2 relaxation times are the inverse of the diagonal elements of \hat{R} corresponding to L_Z and \hat{L}_{\pm} states of each spin respectively:

$$\frac{1}{T_1} = \langle \hat{L}_Z | \hat{R} | \hat{L}_Z \rangle / \langle \hat{L}_Z | \hat{L}_Z \rangle \quad \frac{1}{T_2} = \langle \hat{L}_+ | \hat{R} | \hat{L}_+ \rangle / \langle \hat{L}_+ | \hat{L}_+ \rangle \quad (38)$$

The next level of sophistication is to include cross-relaxation between all longitudinal spin orders (all of which have a zero Zeeman frequency) – for historical reasons this is called a *Redfield kite* approximation (the matrix representation in a certain basis resembles a kite). This form is often used when simulating nuclear Overhauser effect spectra.

The most accurate (but somewhat dangerous in systems where small frequency differences are present) rotating frame form would include all cross-terms between states with identical Zeeman frequencies. That is called the *secular approximation* to the relaxation superoperator. If physical accuracy is the overriding concern, the simulation should be performed in the laboratory frame, which is free of all approximations beyond those introduced in the construction of the relaxation theory itself.