

Derivation of the Redfield relaxation equation

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July 2, 2014

Abstract

An old set of notes from the time I taught courses in non-linear optics, and used the density operator approach (see S. Mukamel's book: "Principles of Nonlinear Optical Spectroscopy"). Somehow ResearchGate found it, or found it mentioned, on the web somewhere. The first part is a rather detailed and traditional derivation of the equation, followed by an answer to the question asked in the introduction for two different systems. If I remember well a question that came up during the course in relation to hole burning experiments. I studied the derivation first in the late 1980's when I worked on quadrupolar NMR relaxation of probe molecules in liquid crystals due to coupling to director fluctuations, which explains the remark on frequency dependence of the relaxation times at the end. I've always found the derivation weird (first solve the differential equation, then take the time derivative of the approximate solution to get a differential equation again, but it is a form of "coarse graining" that leads to dissipation), Somewhere I also have a derivation using a projection operator formalism. If I can find it I'll post it. I realize now that there probably is a simple argument for relation (1.1) somewhere. Although I was slightly surprised that it also worked for electronic transitions, since those lack symmetries spin systems have, in particular when taking state dipole moments into account. The term I included, related to the difference dipole moment of ground and excited state is mostly incorrectly ignored in more recent applications. I also found some sheets (dated 1999) with just the essential seven steps of the derivation, (using Mukamel's notation), and a few remarks, which I appended, starting on page 10. An (incomplete) literature list of papers having to do with relaxation, and/or relaxation in quantum systems, is also appended. There is also talk of simulations for excitonically coupled systems, which I haven't been able to locate yet. When I find them, or the student report alluded to at the end, I'll update this manuscript to include those. In the mean time I have much more to say about this and related topics, but since there was a request for this paper I uploaded it anyway.

If you have questions or remarks about it, or about related topics, my email address is at the bottom of this page. I did not bother to edit it, so please ignore any typo's or grammatical errors.

1 Introduction

To understand where the familiar expression

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1} \quad (1.1)$$

comes from, and to see if it is correct, we go here through the derivation of the Redfield equation, first in general, then for a magnetic system (NMR relaxation) and finally for an electronic transition.

2 The derivation

Starting point, as ever, is the Liouville equation for the density operator $\rho(t)$, which we write in the following form:

$$\frac{\partial \rho(t)}{\partial t} = -2\pi i [\mathcal{H}, \rho(t)] \quad (2.1)$$

where we used units such that $\hbar = 1$, $c = 1$. The Hamiltonian consists of two terms, the unperturbed part \mathcal{H}_0 , with eigenvalues ϵ_n and corresponding eigenfunctions $|n\rangle$, and a random perturbation \mathcal{H}_r , which couples system operators A_k to external fluctuating fields $E_k(t)$:

$$\mathcal{H}_r = \sum_k A_k E_k(t) \quad (2.2)$$

The fluctuating field properties are independent of the system, and the idea is to express everything in correlation functions of these fluctuating fields. We will work out some examples in later sections.

The first step is to go to the interaction picture:

$$\rho_I(t) = e^{2\pi i \mathcal{H}_0 t} \rho(t) e^{-2\pi i \mathcal{H}_0 t} \quad (2.3)$$

so that we can write

$$\frac{\partial \rho_I(t)}{\partial t} = -2\pi i [\mathcal{H}_{r,I}(t), \rho_I(t)] \quad (2.4)$$

This is a rather essential step, since we will assume that ρ_I varies slowly in time. If there was no perturbation, we would not have any variation at all, so the perturbation is assumed to make slow changes in $\rho_I(t)$. The time dependence in $\mathcal{H}_{r,I}(t)$ now comes from two sources: the fluctuating field and the operators $A_{k,I}$ which have now acquired a time dependence as well.

We now solve eq. (2.4) by iteration to second order: the formal (integral) solution is

$$\rho_I(t) = \rho_I(0) - 2\pi i \int_0^t d\tau [\mathcal{H}_{r,I}(\tau), \rho_I(\tau)] \quad (2.5)$$

which can be used as the starting point of a series expansion:

$$\rho_I(t) = \rho_I(0) - 2\pi i \int_0^t d\tau [\mathcal{H}_{r,I}(\tau), \rho_I(0)] - 4\pi^2 \int_0^t d\tau \int_0^\tau d\tau' [\mathcal{H}_{r,I}(\tau), [\mathcal{H}_{r,I}(\tau'), \rho_I(0)]] + \dots \quad (2.6)$$

Next we take the time derivative of this equation to get:

$$\frac{d\rho_I(t)}{dt} = -2\pi i [\mathcal{H}_{r,I}(t), \rho_I(0)] - 4\pi^2 \int_0^t d\tau [\mathcal{H}_{r,I}(t), [\mathcal{H}_{r,I}(\tau), \rho_I(0)]] + \dots \quad (2.7)$$

Then we take an ensemble average over the fluctuations in the external fields, and assume that $\langle E_k(t) \rangle = 0$, and that the fluctuations are uncorrelated with $\rho_I(0)$. This makes the first term vanish, and for the rest we get:

$$\frac{d\rho_I(t)}{dt} = -4\pi^2 \int_0^t d\tau \langle [\mathcal{H}_{r,I}(t), [\mathcal{H}_{r,I}(\tau), \rho_I(0)]] \rangle \quad (2.8)$$

Since the fluctuating fields are independent of the operators, we can separate the two parts:

$$\frac{d\rho_I(t)}{dt} = -4\pi^2 \sum_{n,m} \int_0^t d\tau \langle E_n(t) E_m(\tau) \rangle [A_n(t), [A_m(\tau), \rho_I(0)]] \quad (2.9)$$

where the time-dependence in the operators A_n indicates that they have to be evaluated in the interaction picture. Now we assume that the ensemble we average over is stationary, so that

$$\frac{d\rho_I(t)}{dt} = -4\pi^2 \sum_{n,m} \int_0^t d\tau \langle E_m E_n(t - \tau) \rangle [A_n(t), [A_m(\tau), \rho_I(0)]] \quad (2.10)$$

subsequently changing the integration variable to $t - \tau$ then gives:

$$\frac{d\rho_I(t)}{dt} = -4\pi^2 \sum_{n,m} \int_0^t d\tau \langle E_m E_n(\tau) \rangle [A_n(t), [A_m(t - \tau), \rho_I(0)]] \quad (2.11)$$

The next step is to assume that the correlation functions $\langle E_m E_n(\tau) \rangle$ are decaying rapidly, so that it has vanished before $\rho_I(0)$ starts to change appreciably. We may then replace the integration limit by $+\infty$ to get

$$\frac{d\rho_I(t)}{dt} = -4\pi^2 \sum_{n,m} \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle [A_n(t), [A_m(t - \tau), \rho_I(0)]] \quad (2.12)$$

We will in the next sections present a model for the correlation functions. For the moment we only need the assumption that they decay in some characteristic time τ_c , so that for times longer than τ_c we may replace $\rho_I(0)$ by $\rho_I(t)$, and have again a differential equation for $\rho_I(t)$, which is valid for times longer than τ_c .

It remains to work out the commutator terms in some set of basis functions, for which we use the eigenfunctions of the Hamiltonian \mathcal{H}_0 .

Thus we get

$$\frac{d}{dt}(\rho_I)_{\alpha\alpha'} = -4\pi^2 \sum_{n,m} \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle \langle \alpha | [A_n(t), [A_m(t - \tau), \rho_I]] | \alpha' \rangle \quad (2.13)$$

where we for the moment left out the t argument of the density operator.
The commutator expression has four terms which we consider separately:

$$\langle \alpha | A_n(t) A_m(t - \tau) \rho_I | \alpha' \rangle = \sum_{\beta, \beta'} \langle \alpha | A_n(t) | \beta \rangle \langle \beta | A_m(t - \tau) | \beta' \rangle \langle \beta' | \rho_I | \alpha' \rangle \quad (2.14)$$

We will denote the eigenvalues of \mathcal{H}_0 by the same greek symbols that occur in the ket. Using (2.3) it is easy to see that (2.14) is equal to

$$\sum_{\beta, \beta'} e^{2\pi i(\alpha - \beta)t} e^{2\pi i(\beta - \beta')(t - \tau)} (A_n)_{\alpha\beta} (A_m)_{\beta\beta'} (\rho_I)_{\beta'\alpha'} \quad (2.15)$$

Several variable changes and the introduction of a dummy summation lead to the following result:

$$\langle \alpha | A_n(t) A_m(t - \tau) \rho_I | \alpha' \rangle = \sum_{\beta, \beta'} \left[\delta_{\alpha'\beta'} \sum_{\gamma} e^{2\pi i(\beta - \gamma)\tau} e^{2\pi i(\alpha - \beta)t} (A_m)_{\gamma\beta} (A_n)_{\alpha\gamma} \right] (\rho_I)_{\beta\beta'} \quad (2.16)$$

The other terms are treated similarly. The second term gives:

$$- \langle \alpha | A_n(t) \rho_I A_m(t - \tau) | \alpha' \rangle = - \sum_{\beta, \beta'} e^{2\pi i(\alpha' - \beta')\tau} e^{2\pi i(\alpha - \beta + \beta' - \alpha')t} (A_m)_{\beta'\alpha'} (A_n)_{\alpha\beta} (\rho_I)_{\beta\beta'} \quad (2.17)$$

The third term is equal to:

$$- \langle \alpha | A_m(t - \tau) \rho_I A_n(t) | \alpha' \rangle = - \sum_{\beta, \beta'} e^{2\pi i(\beta - \alpha)\tau} e^{2\pi i(\alpha - \beta + \beta' - \alpha')t} (A_m)_{\alpha\beta} (A_n)_{\beta'\alpha'} (\rho_I)_{\beta\beta'} \quad (2.18)$$

and the final term gives:

$$\langle \alpha | \rho_I A_m(t - \tau) A_n(t) | \alpha' \rangle = \sum_{\beta, \beta'} \left[\delta_{\alpha\beta} \sum_{\gamma} e^{2\pi i(\gamma - \beta')\tau} e^{2\pi i(\beta' - \alpha)t} (A_m)_{\beta'\gamma} (A_n)_{\gamma\alpha'} \right] (\rho_I)_{\beta\beta'} \quad (2.19)$$

Going back to the original representation (Heisenberg picture) we note that all exponentials with t cancel, and we are left with

$$\begin{aligned} \frac{\partial \rho_{\alpha\alpha'}(t)}{\partial t} &= -2\pi i(\alpha - \alpha') \rho_{\alpha\alpha'}(t) - 4\pi^2 \sum_{n,m} \sum_{\beta, \beta'} \left[\delta_{\alpha'\beta'} \sum_{\gamma} \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle e^{2\pi i(\beta - \gamma)\tau} ((A_m)_{\gamma\beta} (A_n)_{\alpha\gamma}) \right. \\ &- \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle e^{2\pi i(\alpha' - \beta')\tau} (A_m)_{\beta'\alpha'} (A_n)_{\alpha\beta} - \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle e^{2\pi i(\beta - \alpha)\tau} (A_m)_{\alpha\beta} (A_n)_{\beta'\alpha'} \\ &+ \left. \delta_{\alpha\beta} \sum_{\gamma} \int_0^\infty d\tau \langle E_m E_n(\tau) \rangle e^{2\pi i(\gamma - \beta')\tau} (A_m)_{\beta'\gamma} (A_n)_{\gamma\alpha'} \right] \rho_{\beta\beta'}(t) \end{aligned} \quad (2.20)$$

This is the Redfield equation in its most general form. We now make the following simplifying assumption, that holds for isotropic systems with simple exponentially decaying correlation functions:

$$\langle E_m E_n(\tau) \rangle = \delta_{nm} \langle E^2 \rangle e^{-t/\tau_c} \equiv \delta_{nm} \langle E^2 \rangle e^{-2\pi\zeta t} \quad (2.21)$$

that is: all field components decay in the same way, and have the same equilibrium average.

In that case the integrals become particularly simple:

$$\int_0^\infty d\tau \langle E_m E_n(\tau) \rangle e^{2\pi i \omega \tau} = \delta_{nm} \frac{\langle E^2 \rangle}{2\pi(\zeta - i\omega)} \equiv \delta_{nm} \frac{1}{2\pi} J(\omega) \quad (2.22)$$

Introducing this into eq. (2.30) then yields:

$$\begin{aligned} \frac{\partial \rho_{\alpha\alpha'}(t)}{\partial t} = & -2\pi i(\alpha - \alpha')\rho_{\alpha\alpha'}(t) - 2\pi \sum_{\beta, \beta'} \left[\delta_{\alpha'\beta'} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{\alpha\gamma} \right. \\ & \left. - [J(\alpha' - \beta') + J(\beta - \alpha)] A_{\beta'\alpha'} \cdot A_{\alpha\beta} + \delta_{\alpha\beta} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma\alpha'} \right] \rho_{\beta\beta'}(t) \end{aligned} \quad (2.23)$$

where the dot denotes an inner product, for instance:

$$A_{\beta'\alpha'} \cdot A_{\alpha\beta} = \sum_n (A_n)_{\beta'\alpha'} (A_n)_{\alpha\beta} \quad (2.24)$$

3 Spin relaxation in a fluctuating magnetic field

As our first example we treat spin relaxation in fluctuating magnetic fields. For a spin 1/2 in a magnetic field in the z -direction we can write the unperturbed Hamiltonian as:

$$\mathcal{H}_0 = -\epsilon I_z \quad (3.1)$$

The fluctuating perturbations we will write as

$$\mathcal{H}_r = -\vec{H} \cdot \vec{I} \quad (3.2)$$

where \vec{H} is proportional to the fluctuating magnetic field (gyromagnetic ratio and so on is absorbed in this field. Thus E^2 in expression (2.22) should be replaced by H^2 and the A -operators are now spin operators.

Let us denote the ground state as $|0\rangle$ and the excited state as $|1\rangle$ with respective energies of $-\frac{1}{2}\epsilon$ and $\frac{1}{2}\epsilon$.

We only have to calculate two elements of ρ since $\rho_{00} + \rho_{11} = 1$, the trace is one and should be conserved (this can easily be checked, in general we need $\sum_{\alpha} \rho_{\alpha\alpha} = 1$, and it is straightforward to show that $\frac{\partial}{\partial t} \sum_{\alpha} \rho_{\alpha\alpha} = 0$).

For the other two elements we have the relation $\rho_{01} = \rho_{10}^*$. For the ρ_{00} element we have:

$$\frac{\partial \rho_{00}}{\partial t} = -2\pi \sum_{\beta, \beta'} \left[\delta_{0\beta'} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{0\gamma} - [J(-\beta') + J(\beta)] A_{\beta'0} \cdot A_{0\beta} + \delta_{0\beta} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma 0} \right] \rho_{\beta\beta'} \quad (3.3)$$

The three spin matrices are

$$I_x = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad I_y = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (3.4)$$

It is straightforward to show that

$$(\vec{I})_{\gamma\beta} \cdot (\vec{I})_{0\gamma} = \frac{1}{2} \delta_{\beta 0} \delta_{\gamma 1} + \frac{1}{4} \delta_{\beta 0} \delta_{\gamma 0} \quad (3.5)$$

and that

$$(\vec{I})_{\beta'0} \cdot (\vec{I})_{0\beta} = \frac{1}{2}\delta_{\beta 1}\delta_{\beta'1} + \frac{1}{4}\delta_{\beta 0}\delta_{\beta'0} \quad (3.6)$$

and finally that

$$(\vec{I})_{\beta'\gamma} \cdot (\vec{I})_{\gamma 0} = \frac{1}{2}\delta_{\beta'0}\delta_{\gamma 1} + \frac{1}{4}\delta_{\beta'0}\delta_{\gamma 0} \quad (3.7)$$

Introducing this into the above expression (3.3) gives:

$$\frac{\partial \rho_{00}}{\partial t} = -\pi[J(\epsilon) + J(-\epsilon)] \sum_{\beta, \beta'} [\delta_{\beta 0}\delta_{0\beta'} - \delta_{\beta 1}\delta_{\beta'1}] \rho_{\beta\beta'} \quad (3.8)$$

so that

$$\frac{\partial \rho_{00}(t)}{\partial t} = -\pi[J(\epsilon) + J(-\epsilon)][\rho_{00}(t) - \rho_{11}(t)] \quad (3.9)$$

Introduction of the expression for J , eq. (2.22) then gives after a lengthy calculation:

$$\frac{\partial \rho_{00}(t)}{\partial t} = -\frac{2\pi\zeta \langle H^2 \rangle}{\epsilon^2 + \zeta^2} [\rho_{00}(t) - \rho_{11}(t)] \quad (3.10)$$

We also note that

$$\frac{\partial \rho_{00}(t)}{\partial t} = \frac{\partial \rho_{00}(t) + \rho_{11}(t) - \rho_{11}(t)}{\partial t} = -\frac{\partial \rho_{11}(t)}{\partial t} \quad (3.11)$$

so that

$$\frac{\partial [\rho_{00}(t) - \rho_{11}(t)]}{\partial t} = -\frac{4\pi\zeta \langle H^2 \rangle}{\epsilon^2 + \zeta^2} [\rho_{00}(t) - \rho_{11}(t)] \quad (3.12)$$

Since the z -magnetization is defined as $M_z = \text{Tr}[I_z \rho]$, we have the following equation for the z -magnetization:

$$\frac{\partial M_z(t)}{\partial t} = -\frac{4\pi\zeta \langle H^2 \rangle}{\epsilon^2 + \zeta^2} M_z(t) \equiv -\frac{2\pi}{T_1} M_z(t) \quad (3.13)$$

Next we study the equation for the coherences. From eq. (2.23) we get:

$$\begin{aligned} \frac{\partial \rho_{01}(t)}{\partial t} &= 2\pi i \epsilon \rho_{01}(t) - 2\pi \sum_{\beta, \beta'} \left[\delta_{\beta'1} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{0\gamma} \right. \\ &\quad \left. - \left[J\left(\frac{1}{2}\epsilon - \beta'\right) + J\left(\beta + \frac{1}{2}\epsilon\right) \right] A_{\beta'1} \cdot A_{0\beta} + \delta_{\beta 0} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma 1} \right] \rho_{\beta\beta'}(t) \end{aligned} \quad (3.14)$$

The first operator term was already calculated in eq. (3.5). For the second we get:

$$(\vec{I})_{\beta'1} \cdot (\vec{I})_{0\beta} = -\frac{1}{4}\delta_{\beta'1}\delta_{\beta 0} \quad (3.15)$$

and the third term gives:

$$(\vec{I})_{\beta'\gamma} \cdot (\vec{I})_{\gamma 1} = \frac{1}{2}\delta_{\beta'1}\delta_{\gamma 0} + \frac{1}{4}\delta_{\beta'1}\delta_{\gamma 1} \quad (3.16)$$

Introducing this into eq. (3.14) gives:

$$\frac{\partial \rho_{01}(t)}{\partial t} = 2\pi i \epsilon \rho_{01}(t) - 2\pi \sum_{\beta, \beta'} \delta_{\beta'1}\delta_{\beta 0} [J(-\epsilon) + J(0)] \rho_{\beta\beta'}(t) \quad (3.17)$$

so that:

$$\frac{\partial \rho_{01}(t)}{\partial t} = 2\pi i \epsilon \rho_{01}(t) - 2\pi [J(-\epsilon) + J(0)] \rho_{01}(t) \quad (3.18)$$

Taking the complex conjugate of this equation gives us the equation for ρ_{10} :

$$\frac{\partial \rho_{10}(t)}{\partial t} = -2\pi i \epsilon \rho_{10}(t) - 2\pi [J(\epsilon) + J(0)] \rho_{10}(t) \quad (3.19)$$

where we also used that $J^*(\epsilon) = J(-\epsilon)$. Now we can calculate the magnetization in the x - and y -direction:

$$M_x(t) = \text{Tr}[I_x \rho(t)] = \frac{1}{2}(\rho_{01} + \rho_{10}) \quad (3.20)$$

Using eqs. (3.18) and (3.19) we get for this quantity:

$$\frac{\partial M_x(t)}{\partial t} = 2\pi (\epsilon + \text{Im}[J(\epsilon)]) M_y(t) - 2\pi (J(0) + \text{Re}[J(\epsilon)]) M_x(t) \quad (3.21)$$

where $M_y(t) = \frac{i}{2}(\rho_{01} - \rho_{10})$. We note that the imaginary part of the spectral density causes a frequency shift, which is usually neglected in NMR. The relaxation time T_2 is now given by:

$$\frac{1}{T_2} = J(0) + \text{Re}[J(\epsilon)] = \frac{\langle H^2 \rangle}{\zeta} + \frac{\langle H^2 \rangle}{\zeta^2 + \epsilon^2} = \frac{1}{2T_1} + \frac{\langle H^2 \rangle}{\zeta} \equiv \frac{1}{2T_1} + \frac{1}{T_2'} \quad (3.22)$$

For $M_y(t)$ we can derive a similar equation:

$$\frac{\partial M_y(t)}{\partial t} = -2\pi (\epsilon + \text{Im}[J(\epsilon)]) M_x(t) - \frac{2\pi}{T_2} M_y(t) \quad (3.23)$$

Finally we note that the Redfield equation is also applicable to the difference between the density operator and the equilibrium density operator. That is, eq. (2.23) supposedly holds also for $\rho_{\beta\beta'} - \rho_{\beta\beta'}^{\text{eq}}$.

Reverting to Liouville space notation, we can write eq. (2.23) in the following form:

$$\frac{\partial |\rho(t)\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 |\rho(t)\rangle\rangle - 2\pi i \mathcal{L}_d |\rho(t)\rangle\rangle \quad (3.24)$$

where $|\rho(t)\rangle\rangle$ now denotes the difference between $|\rho(t)\rangle\rangle$ and $|\rho^{\text{eq}}\rangle\rangle$ and the operators \mathcal{L}_0 and \mathcal{L}_d are given by:

$$\mathcal{L}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathcal{L}_d = \begin{pmatrix} -\frac{i}{2T_1} & 0 & 0 & \frac{i}{2T_1} \\ 0 & -\frac{i}{T_2} & 0 & 0 \\ 0 & 0 & -\frac{i}{T_2} & 0 \\ \frac{i}{2T_1} & 0 & 0 & -\frac{i}{2T_1} \end{pmatrix} \quad (3.25)$$

If we want to compare this to the equations used in nlo.tex, we can identify $1/2T_1$ with Γ , and $1/T_2$ with γ . Then there are still small differences due to the fact that here we look at the difference density operator. More importantly are the 00 and 30 elements of \mathcal{L}_d which are nonzero here.

We will see how this holds up for electronic transitions.

4 Electronic transitions

Since eq. (2.23) is general, it can also be used for electronic transitions. Now we usually take the unperturbed Hamiltonian as $\mathcal{H}_0 = \epsilon |1\rangle \langle 1|$, and the interaction with external fluctuating fields can be written as

$$\mathcal{H}_r = -\hat{\vec{\mu}} \cdot \vec{E}_r(t) \quad (4.1)$$

The difference with the NMR case is that the dipole transitions can be different for the various field components. That is, the coupling is between transition dipole moment and external field, and/or between ground and excited state dipole moments and the fields. We consider both cases separately.

If we only have a transition dipole moment, we can write (4.1) as:

$$\mathcal{H}_r = -\vec{\mu} \cdot \vec{E}_r(t) [|0\rangle \langle 1| + |1\rangle \langle 0|] = -\vec{\mu} \cdot \vec{E}_r(t) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (4.2)$$

where the matrix representation shows that this is closely related to just the I_x operator for NMR.

Again we consider population and coherence terms separately. For the population we again get (3.3), although we now immediately assume that the equation holds for the difference between time-dependent density operator and equilibrium density operator. The expressions for the operator products are simpler:

$$\begin{aligned} A_{\gamma\beta} \cdot A_{0\gamma} &= \delta_{\gamma 1} \delta_{\beta 0} \\ A_{\beta'0} \cdot A_{0\beta} &= \delta_{\beta' 1} \delta_{\beta 1} \\ A_{\beta'\gamma} \cdot A_{\gamma 0} &= \delta_{\gamma 1} \delta_{\beta' 0} \end{aligned} \quad (4.3)$$

Introducing this into eq. (3.3) gives:

$$\frac{\partial \rho_{00}(t)}{\partial t} = -2\pi [J(\epsilon) + J(-\epsilon)] [\rho_{00}(t) - \rho_{11}(t)] \quad (4.4)$$

where now, under assumptions of isotropic systems and exponential decay, we get for J :

$$J(\omega) = \langle E^2 \rangle \frac{1}{\zeta - i\omega} \quad (4.5)$$

where, as before, we absorbed the magnitude of the transition moment in the field, so that we can again define

$$\frac{\partial \rho_{00}(t)}{\partial t} = -\frac{\pi}{T_1} [\rho_{00}(t) - \rho_{11}(t)] \quad (4.6)$$

where now

$$\frac{1}{T_1} = \frac{4\zeta \langle E^2 \rangle}{\zeta^2 + \epsilon^2} \quad (4.7)$$

The difference of the factor of 2 here is a consequence of the difference between the coupling operators in the NMR and the electronic case, we defined T_1 in this way so that the population difference operator (corresponding to M_z) decays as:

$$\frac{\partial [\rho_{00}(t) - \rho_{11}(t)]}{\partial t} = -\frac{2\pi}{T_1} [\rho_{00}(t) - \rho_{11}(t)] \quad (4.8)$$

which is now the same as eq. (3.13).

For the coherence equation, eq. (3.14) we need in addition

$$\begin{aligned} A_{\beta'1} \cdot A_{0\beta} &= \delta_{\beta'0} \delta_{\beta1} \\ A_{\beta'\gamma} \cdot A_{\gamma1} &= \delta_{\gamma0} \delta_{\beta'1} \end{aligned} \quad (4.9)$$

$$\frac{\partial \rho_{01}(t)}{\partial t} = 2\pi i \epsilon \rho_{01}(t) - 4\pi [J(-\epsilon) \rho_{01}(t) - J(\epsilon) \rho_{10}(t)] \quad (4.10)$$

Neglecting again the imaginary parts of the spectral density, which only contribute to a shift in energy, we get

$$\frac{\partial \rho_{01}(t)}{\partial t} = 2\pi i \epsilon \rho_{01}(t) - 4\pi J'(\epsilon) [\rho_{01}(t) - \rho_{10}(t)] = 2\pi i \epsilon \rho_{01}(t) - \frac{\pi}{T_1} [\rho_{01}(t) - \rho_{10}(t)] \quad (4.11)$$

The other matrix element evolves as:

$$\frac{\partial \rho_{10}(t)}{\partial t} = -2\pi i \epsilon \rho_{10}(t) - \frac{\pi}{T_1} [\rho_{10}(t) - \rho_{01}(t)] \quad (4.12)$$

Before looking at other relaxation mechanisms, and the damping Liouvillian, we'll solve the resulting set of equations, and compare to the NMR case. To compare we use the same operators as above (although they now have different physical interpretations). We already derived the M_z equation above: eq. (4.8). For the coherence sum we get:

$$\frac{\partial [\rho_{01}(t) + \rho_{10}(t)]}{\partial t} = 2\pi i \epsilon [\rho_{01}(t) - \rho_{10}(t)] \quad (4.13)$$

and for the coherence difference:

$$\frac{\partial [\rho_{01}(t) - \rho_{10}(t)]}{\partial t} = 2\pi i \epsilon [\rho_{01}(t) + \rho_{10}(t)] - \frac{2\pi}{T_1} [\rho_{10}(t) - \rho_{01}(t)] \quad (4.14)$$

Differentiation of this last equation, and subsequent substitution of (4.13) gives:

$$\frac{\partial^2 [\rho_{01}(t) - \rho_{10}(t)]}{\partial t^2} + \frac{2\pi}{T_1} \frac{\partial [\rho_{01}(t) - \rho_{10}(t)]}{\partial t} + (2\pi \epsilon)^2 [\rho_{01}(t) - \rho_{10}(t)] = 0 \quad (4.15)$$

If $\epsilon \gg 1/2T_1$, which is usually the case for electronic transitions the eigenvalues of this equation can be approximated by

$$2\pi \left(\pm i \epsilon - \frac{1}{2T_1} \right) \quad (4.16)$$

so that the decay rate is again $1/2T_1$, as in the NMR case.

We note that the difference of a factor 2 in the relaxation rate is caused by the term $(2\pi \epsilon)^2$. If that term were zero, as it is for the population related terms, we would find one eigenvalue zero (which for the populations is related to conservation of the trace), and one term decaying as $1/T_1$.

Next we consider energy fluctuations due to coupling with ground- and/or excited state dipole moments.

We can write the random Hamiltonian as:

$$\mathcal{H}_r = -\vec{\mu}_g \cdot \vec{E}_r(t) |0\rangle \langle 0| - \vec{\mu}_e \cdot \vec{E}_r(t) |1\rangle \langle 1| \quad (4.17)$$

where $\vec{\mu}_g$ is the ground, and $\vec{\mu}_e$ the excited state dipole moment. We can write this also as:

$$\mathcal{H}_r = -(\vec{\mu}_e - \vec{\mu}_g) \cdot \vec{E}_r(t) |1\rangle \langle 1| \quad (4.18)$$

where we used that $|0\rangle \langle 0| + |1\rangle \langle 1|$ is the unit operator, which commutes with everything and hence cannot cause any relaxation.

Thus our A operator is now equal to $|1\rangle \langle 1|$, and we can calculate the various terms again. First the populations:

$$\frac{\partial \rho_{00}}{\partial t} = -2\pi \sum_{\beta, \beta'} \left[\delta_{0\beta'} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{0\gamma} - [J(-\beta') + J(\beta)] A_{\beta'0} \cdot A_{0\beta} + \delta_{0\beta} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma 0} \right] \rho_{\beta\beta'} \quad (4.19)$$

Since the only component of A is A_{11} this gives:

$$\frac{\partial \rho_{00}}{\partial t} = 0 \quad (4.20)$$

and we get no extra contribution to the population decay, as was to be expected. For the coherence we get:

$$\frac{\partial \rho_{01}(t)}{\partial t} = 2\pi i \epsilon \rho_{01}(t) - 2\pi J(0) \rho_{01}(t) \equiv 2\pi i \epsilon \rho_{01}(t) - \frac{2\pi}{T_2'} \rho_{01}(t) \quad (4.21)$$

We therefore find essentially the same results as in the NMR case, albeit with different interpretations, and for different reasons. The dipole moment to be used in T_2' is different also from the one to be used in T_1 : in the latter the transition dipole moment $\vec{\mu}$ enters, in the former the difference between ground- and excited state dipole moment $\Delta\mu = \vec{\mu}_e - \vec{\mu}_g$.

The damping Liouvillian thus becomes:

$$\mathcal{L}_d = \begin{pmatrix} -\frac{i}{2T_1} & 0 & 0 & \frac{i}{2T_1} \\ 0 & -\frac{i}{2T_1} - \frac{i}{T_2'} & \frac{i}{2T_1} & 0 \\ 0 & \frac{i}{2T_1} & -\frac{i}{2T_1} - \frac{i}{T_2'} & 0 \\ \frac{i}{2T_1} & 0 & 0 & -\frac{i}{2T_1} \end{pmatrix} \quad (4.22)$$

Although the energy shift is slightly different, but negligible anyway, we get for the relaxation time again

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2'} \quad (4.23)$$

Curious, but true.

As a final note, we have shown that the damping Liouvillian we have found here is quite different from the one we used in the simulations, so some adaptations are necessary there. In terms of the parameters γ (coherence damping) and Γ (population damping) introduced there, we can write the Liouville operator as:

$$\mathcal{L} = \begin{pmatrix} -i\Gamma & 0 & 0 & i\Gamma \\ 0 & -\epsilon - i\gamma & i\Gamma & 0 \\ 0 & i\Gamma & \epsilon - i\gamma & 0 \\ i\Gamma & 0 & 0 & -i\Gamma \end{pmatrix} \quad (4.24)$$

so that:

$$\frac{\partial}{\partial t} |\rho(t)\rangle\rangle = -2\pi i \mathcal{L} |\rho(t)\rangle\rangle \quad (4.25)$$

We'll have to start the simulations now with this new and improved damping matrix. Some care is needed, since the damping is supposed to work on the difference density operator, whereas the field acts on the density operator itself. Thus without external fields we can write eq. (4.25) where in fact $|\rho\rangle\rangle = |\rho\rangle\rangle - |\rho^{\text{eq}}\rangle\rangle$, which is valid since $[\mathcal{H}_0, \rho^{\text{eq}}] = 0$. However, this is not true for the external interaction term: $[\mathcal{H}_{\text{ext}}, \rho^{\text{eq}}] \neq 0$, since otherwise the interaction would never be able to get the system out of its equilibrium state. The simplest way to fix this is to add $2\pi i \mathcal{L}_d \rho^{\text{eq}}$ to the equation.

NB: in NMR there are cases when the frequency dependence of the spectral density can be measured, for instance in liquid crystals, due to slow components of the director fluctuations. Is that also possible for electronic transitions?

REDFIELD THEORY

$$\frac{\partial |\rho(t)\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 |\rho(t)\rangle\rangle - 2\pi i \mathcal{L}_r(t) |\rho(t)\rangle\rangle$$

Random Hamiltonian

$$\mathcal{H}_r(t) = \sum_k \hat{A}_k B_k(t)$$

\hat{A}_k : System operators

$B_k(t)$: Fluctuating bath functions.

Properties:

$$\langle B_k(t) \rangle = 0$$

$$\langle B_k(t) B_l(t + \tau) \rangle = \langle B_k(0) B_l(\tau) \rangle \equiv J_{kl}(\tau)$$

STEP ONE: formal solution in interaction picture:

$$|\rho_I(t)\rangle\rangle = |\rho_I(0)\rangle\rangle - 2\pi i \int_0^t d\tau \mathcal{L}_{r,I}(\tau) |\rho_I(\tau)\rangle\rangle$$

STEP TWO: expand to second order:

$$\begin{aligned} |\rho_I(t)\rangle\rangle &= |\rho_I(0)\rangle\rangle - 2\pi i \int_0^t d\tau \mathcal{L}_{r,I}(\tau) |\rho_I(0)\rangle\rangle \\ &\quad - 4\pi^2 \int_0^t d\tau \int_0^\tau d\tau' \mathcal{L}_{r,I}(\tau) \mathcal{L}_{r,I}(\tau') |\rho_I(0)\rangle\rangle \end{aligned}$$

STEP THREE: Take time derivative:

$$\frac{d}{dt} |\rho_I(t)\rangle\rangle = -2\pi i \mathcal{L}_{r,I}(t) |\rho_I(0)\rangle\rangle - 4\pi^2 \int_0^t d\tau \mathcal{L}_{r,I}(t) \mathcal{L}_{r,I}(\tau) |\rho_I(0)\rangle\rangle$$

STEP FOUR: Average over bath variables:

$$\frac{d}{dt} |\rho_I(t)\rangle\rangle = -4\pi^2 \int_0^t d\tau \langle \mathcal{L}_{r,I}(t) \mathcal{L}_{r,I}(\tau) \rangle |\rho_I(0)\rangle\rangle$$

STEP FIVE: stationarity and rapid decay of bath correlation functions:

$$\frac{d}{dt} |\rho_I(t)\rangle\rangle = -4\pi^2 \int_0^\infty d\tau \langle \mathcal{L}_{r,I}(0) \mathcal{L}_{r,I}(\tau - t) \rangle |\rho_I(0)\rangle\rangle$$

STEP SIX: Assume slow change in $|\rho_I(0)\rangle\rangle$ one time scale of decay:

$$\frac{d}{dt} |\rho_I(t)\rangle\rangle = -4\pi^2 \int_0^\infty d\tau \langle \mathcal{L}_{r,I}(0) \mathcal{L}_{r,I}(\tau - t) \rangle |\rho_I(t)\rangle\rangle$$

STEP SEVEN: work out correlation functions:

$$\begin{aligned} \frac{d\rho_{\alpha\alpha'}(t)}{dt} = & -2\pi i(\alpha - \alpha')\rho_{\alpha\alpha'}(t) - 2\pi \sum_{\beta,\beta'} \left[\delta_{\alpha'\beta'} \sum_{\gamma} J(\beta - \gamma) A_{\gamma\beta} \cdot A_{\alpha\gamma} \right. \\ & \left. - [J(\alpha' - \beta') + J(\beta - \alpha)] A_{\beta'\alpha'} \cdot A_{\alpha\beta} + \delta_{\alpha\beta} \sum_{\gamma} J(\gamma - \beta') A_{\beta'\gamma} \cdot A_{\gamma\alpha'} \right] \rho_{\beta\beta'}(t) \end{aligned}$$

This horrible equation is the Redfield equation. The term between brackets has both so-called secular terms (shifts in energy) as well as damping terms (decay of coherences and populations).

AN EXAMPLE

Electric field fluctuations coupled to transition dipole moment

$$\mathcal{H}_r(t) = -\vec{\mu} \cdot \vec{E}_r(t)$$

Bath correlation functions:

$$J(\omega) = \int_0^\infty dt e^{i\omega t} J(t) = \int_0^\infty dt e^{i\omega t} \langle \vec{E}_r(0) \cdot \vec{E}_r(t) \rangle$$

Resulting equations:

Populations

$$\frac{d\rho_{00}(t)}{dt} = -2\pi [J(\epsilon) + J(-\epsilon)] [\rho_{00}(t) - \rho_{11}(t)] \equiv -\frac{\pi}{T_1} [\rho_{00}(t) - \rho_{11}(t)]$$

Coherences

$$\frac{d\rho_{01}(t)}{dt} = -2\pi i \epsilon \rho_{01}(t) - \frac{\pi}{T_1} [\rho_{10}(t) - \rho_{01}(t)]$$

Damping matrix:

$$\mathcal{L}_d = \begin{pmatrix} -i/2T_1 & 0 & 0 & i/2T_1 \\ 0 & -i/2T_1 & i/2T_1 & 0 \\ 0 & i/2T_1 & -i/2T_1 & 0 \\ 2T_1 & 0 & 0 & -i/2T_1 \end{pmatrix}$$

Eigenvalue equations:

Populations

$$\lambda^2 + \frac{i}{T_1}\lambda = 0$$

Two eigenvalues:

$\lambda = 0$ Non-decaying trace of ρ : sum of populations is constant

$\lambda = -\frac{i}{T_1}$: Population difference decay constant

Coherences

$$\lambda^2 + \frac{i}{T_1}\lambda - \epsilon^2 = 0$$

Two eigenvalues:

$$\lambda_{1,2} = -\frac{i}{2T_1} \pm \sqrt{\epsilon^2 - \frac{1}{4T_1^2}}$$

In most cases (?) $\epsilon \gg \frac{1}{2T_1}$ so that

$$\lambda_{1,2} = \pm\epsilon - \frac{i}{2T_1}$$

Thus:

$-\frac{i}{2T_1}$: Coherence decay constant

NB: fluctuations that couple to ground or excited state dipole moments give an additional contribution to the coherence decay $1/2T_2'$, related to the zero frequency component of J .

LIOUVILLE EQUATION

$$\frac{\partial |\rho(t)\rangle\rangle}{\partial t} = -2\pi i \mathcal{L} |\rho(t)\rangle\rangle$$

with

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_d + \mathcal{L}_{\text{ext}}$$

TWO LEVEL SYSTEM

$$|\rho(t)\rangle\rangle = \begin{pmatrix} \rho_{00} \\ \rho_{01} \\ \rho_{10} \\ \rho_{11} \end{pmatrix}$$

System Liouvillian

$$\mathcal{L}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\epsilon & 0 & 0 \\ 0 & 0 & \epsilon & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$$

External field Liouvillian

$$\mathcal{L}_{\text{ext}} = -\vec{\mu} \cdot \vec{E}_{\text{ext}}(t) \begin{pmatrix} 0 & 1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ -1 & 0 & 0 & 1 \\ 0 & -1 & 1 & 0 \end{pmatrix}$$

Damping Liouvillian

$$\mathcal{L}_d = \begin{pmatrix} -i\Gamma & 0 & 0 & i\Gamma \\ 0 & -i\gamma & i\Gamma & 0 \\ 0 & i\Gamma & -i\gamma & 0 \\ i\Gamma & 0 & 0 & -i\Gamma \end{pmatrix} \quad \text{with} \quad \begin{cases} \gamma = \text{coherence damping} \\ \Gamma = \text{population decay} \end{cases}$$

Coupled two–level systems

$$|\rho(t)\rangle\rangle = |\rho_1(t)\rangle\rangle \otimes |\rho_2(t)\rangle\rangle$$

So now $|\rho(t)\rangle\rangle$ is a vector with 16 components.

All previous matrices have to be extended to 2–particle Liouville space (mainly a counting problem).

Dipole coupling is now added (This is a little tricky, since we have to begin in two–particle space, again mainly a counting problem, but usually done differently from the previous)

Thus we get a 16×16 Liouvillian matrix which is used for the simulations.

Problems:

1. decay to incorrect ground state (maybe inherent in Redfield approach, since there are basic inconsistencies in Redfield that cannot be removed: *cf.* D. Kohen, C.C. Marston, D.J. Tannor: Phase space approach to theories of quantum dissipation, J. Chem. Phys. 107, (1997), 5236.

2. How to extract the correct quantities: Solving the Liouville equation numerically is not an expansion method, so how to extract quantities related to for instance $\chi^{(1)}$, or $\chi^{(3)}$ is non–trivial.

What we hoped to see:

1. Energy transfer between monomers, echoes, fluorescence depolarization.

2. Decay (or not) to lowest excited state. (If not what must be added to get that?)

3. Estimates of simulation times, how to add vibrational states, and what is their influence?

What we did see:

Come to Abdon Pijpelink’s presentation on march 9, 1999.

WHY IS

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1}$$

?

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