

Simulations on the two-level system

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1 Introduction

The two-level system, coupled to external fields can show an extraordinary set of different behaviors, which in part can be derived analytically, but in this document we want to mainly explore it numerically by direct numerical simulation of the quantum Liouville equation. The two-level system is characterized by its Hamiltonian

$$\mathcal{H} = \epsilon |1\rangle \langle 1| \quad (1.1)$$

that is, we choose the energy of the ground state zero. The second important operator for the 2LS is the dipole operator, which in its most general form can be written as

$$\hat{\vec{\mu}} = \vec{\mu}_g |0\rangle \langle 0| + \vec{\mu}_e |1\rangle \langle 1| + \vec{\mu} |0\rangle \langle 1| + \vec{\mu}^* |1\rangle \langle 0| \quad (1.2)$$

This allows the system to have a ground state dipole moment $\vec{\mu}_g$, an excited state dipole moment $\vec{\mu}_e$, and a transition dipole moment $\vec{\mu}$, which may be complex, to account for circular dichroism, or magnetic transitions. They are also vectors, which can have different directions in the molecular frame, and hence in space. These are the operators that couple the state of the molecule to the externally applied field.

The external fields we will consider are both time-dependent light fields, but also static Stark fields, and fluctuating polarization fields. For the second exact solutions can be derived, for the other two the usual methods are series expansion, to get linear and non-linear optics, the rotating wave approximation in strong resonant fields, and for instance Redfield theory for the fluctuating polarization fields. The 2LS can also induce fields in the medium, and create reaction fields at its own position, leading to possible symmetry breaking effects. The generic form of the coupling Hamiltonian is

$$\mathcal{H}_{\text{int}} = -\hat{\vec{\mu}} \cdot \vec{E} \quad (1.3)$$

A note about units

We will express everything in cm^{-1} , that is we use units such that $h = c = 1$. Typical values we will use for transition energies are 12500 cm^{-1} , which corresponds to 800 nm light. The frequency of the transition corresponds with an oscillation period of 2.67 fs.

Transition dipole moments are of the order of 6D for a decent transition at that frequency (oscillator strength ~ 0.5). Typical difference dipole moments are 1-2D. Typical field strengths in static (Stark) fields can be 1 MV/cm, which give a 1D dipole an energy of 16.8 cm^{-1} , for a 6D dipole this gives an energy of about 100 cm^{-1} . Laser fields, especially in strongly focussed short pulsed lasers can be as high or higher than that, and internal fields close to charged groups can be even higher.

The interaction energy between two 1D dipoles at 1 nm distance is 5.035 cm^{-1} . Since this depends strongly on the distance the interaction energies can be quite large: at 0.5 nm two 6D dipoles have an interaction energy of 1450 cm^{-1} , which is no longer small compared to electronic excitation energies. The field at 1 nm from an elementary charge is 14.3 MV/cm.

2 Simulation set-up

The simulations are performed using the Liouville equation, since this allows us to investigate damping mechanisms, and coupling to classical systems in a more-or-less consistent fashion.

The equation is in Liouville space notation:

$$\frac{\partial |\rho\rangle\rangle}{\partial t} = -2\pi i \mathcal{L} |\rho\rangle\rangle \quad (2.1)$$

We will use the convention that $|\rho\rangle\rangle$ is a vector with four components, numbered in base 2 order: $|0\rangle\rangle \equiv |00\rangle\rangle \equiv |0\rangle\rangle$, and so on. Operators on Hilbert space become vectors in Liouville space, and the commutator relation between Hilbert space operators becomes an operator in Liouville space. The inner product of two operators is denoted as

$$\langle\langle A | B \rangle\rangle = \text{Tr}[A^\dagger B] = \sum_n (A^\dagger B)_{nn} = \sum_{n,m} A_{mn}^* B_{mn} = (A_0^*, A_1^*, A_2^*, A_3^*) \begin{pmatrix} B_0 \\ B_1 \\ B_2 \\ B_3 \end{pmatrix} \quad (2.2)$$

where we again note that the vector index $k = m * 2 + n$. Note also that taking the Hermitian conjugate for the operators correspond to turning the row vector in a column vector and taking the complex conjugates of the elements.

The Hamiltonian operator becomes

$$\mathcal{H} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \epsilon \end{pmatrix} \quad (2.3)$$

and the interaction Hamiltonian $-\hat{\vec{\mu}} \cdot \vec{E}$:

$$\mathcal{H}_{\text{int}} = -\hat{\vec{\mu}} \cdot \vec{E} = - \begin{pmatrix} \vec{\mu}_g \cdot \vec{E} \\ \vec{\mu} \cdot \vec{E} \\ \vec{\mu} \cdot \vec{E} \\ \vec{\mu}_e \cdot \vec{E} \end{pmatrix} \quad (2.4)$$

Since we are not going to use the complex dipole moments for some time, we neglect the complex conjugate in the transition moment.

There is a simple way to determine Liouville space operators from the commutation relation:

$$-2\pi i [\mathcal{H}, \rho] = -2\pi i \mathcal{L} \quad (2.5)$$

The components of the matrix \mathcal{L} can be determined from

$$\mathcal{L}_{ij,kl} = \mathcal{H}_{ik} \delta_{jl} - \mathcal{H}_{lj} \delta_{ik} \quad (2.6)$$

and of course we can turn the double indices of \mathcal{L} into single indices again with the above rule. Using this we find for the total Liouvillian the following matrix

$$\mathcal{L}_{ij} = \begin{pmatrix} 0 & \vec{\mu} \cdot \vec{E} & -\vec{\mu} \cdot \vec{E} & 0 \\ \vec{\mu} \cdot \vec{E} & -\epsilon + \Delta\vec{\mu} \cdot \vec{E} & 0 & -\vec{\mu} \cdot \vec{E} \\ -\vec{\mu} \cdot \vec{E} & 0 & \epsilon - \Delta\vec{\mu} \cdot \vec{E} & \vec{\mu} \cdot \vec{E} \\ 0 & -\vec{\mu} \cdot \vec{E} & \vec{\mu} \cdot \vec{E} & 0 \end{pmatrix} \quad (2.7)$$

where $\Delta\vec{\mu} = \vec{\mu}_e - \vec{\mu}_g$ is the difference dipole moment.

Once the time-dependence of $|\rho\rangle\rangle$ is determined we can find the physical properties of the system as a function of time. The energy is given by $E(t) = \langle\langle \mathcal{H} | \rho(t) \rangle\rangle$, and the polarization by $\vec{P}(t) = \langle\langle \vec{\mu} | \rho(t) \rangle\rangle$.

Damping

Redfield theory provides a realistic way to introduce damping into the system. A minor problem is that Redfield theory describes damping towards the equilibrium density matrix, for which we will take the ground state. According to Redfield theory the damping operator can be written as

$$\mathcal{L}_d = \begin{pmatrix} -i\Gamma & 0 & 0 & i\Gamma \\ 0 & -i\gamma & i\Gamma & 0 \\ 0 & i\Gamma & -i\gamma & 0 \\ i\Gamma & 0 & 0 & -i\Gamma \end{pmatrix} \quad (2.8)$$

In terms of T_1 and T_2 we can also write

$$\Gamma = \frac{1}{2T_1} \quad \text{and} \quad \gamma = \frac{1}{2T_1} + \frac{1}{T_2} = \frac{1}{T_2} \quad (2.9)$$

which means that γ must be always larger than Γ .

There is also a simplified form of this operator, which we will sometimes use to compare. It can be written as

$$\mathcal{L}_{d,s} = \begin{pmatrix} 0 & 0 & 0 & i\Gamma \\ 0 & -i\gamma & 0 & 0 \\ 0 & 0 & -i\gamma & 0 \\ 0 & 0 & 0 & -i\Gamma \end{pmatrix} \quad (2.10)$$

Another option is to couple the system to a damped harmonic oscillator; in that case we couple the expectation value of the polarization operator to a new coordinate x which is described by the equation of motion

$$m \frac{d^2 x}{dt^2} = -m\omega^2 x - \zeta \frac{dx}{dt} \quad (2.11)$$

This just means adding the term x to E in the Liouville operator. If we also want to have the back reaction, we can drive the oscillator equation by the expectation value of the polarization operator.

3 Simulations

Simulation programs can be found in the directory `cprogs/gsl_odeint`.

The first simulation we will perform is the one where we turn on an external static field at time zero. This should be rather trivial, were it not for the fact that we need to know what the equilibrium state is the system decays to.

The system can of course be solved exactly; we will take the permanent moments zero, which means that we have to diagonalize

$$\begin{pmatrix} 0 & \mu E \\ -\mu E & \epsilon \end{pmatrix} \quad (3.1)$$

The eigenvalues are

$$\lambda_{\pm} = \frac{1}{2} \left[\epsilon \pm \sqrt{\epsilon^2 + 4(\mu E)^2} \right] \quad (3.2)$$

For a 2LS with 6.3 D transition moment, and vacuum excitation energy of 12500 cm^{-1} in a 10 MV/cm field the energy eigenvalues are -89 and 12589 cm^{-1} .

The ground state of this system is the equilibrium state. This state can be determined by solving

$$\begin{pmatrix} 0 & \mu E \\ -\mu E & \epsilon \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \lambda_- \begin{pmatrix} a \\ b \end{pmatrix} \quad (3.3)$$

or

$$a = \frac{\mu E}{\sqrt{(\mu E)^2 + \lambda_-^2}} \quad \text{and} \quad b = \frac{-\lambda_-}{\sqrt{(\mu E)^2 + \lambda_-^2}} \quad (3.4)$$

The simulations are rather trivial, and we won't bother to show them. Basically they show decay to equilibrium energy and polarization. The final energy for the above numbers is indeed -89 cm^{-1} , and the final polarization is 1.05 D , which is then of course the ground state dipole moment. We note here for the record that the polarizability also changes.

Redfield simulations

The first simulation shown is where we use the Redfield matrix. This is mainly intended as a test of the program, since for the 2LS the decay using the Redfield equations can also be solved analytically. The numerical solution and the analytical agree completely.

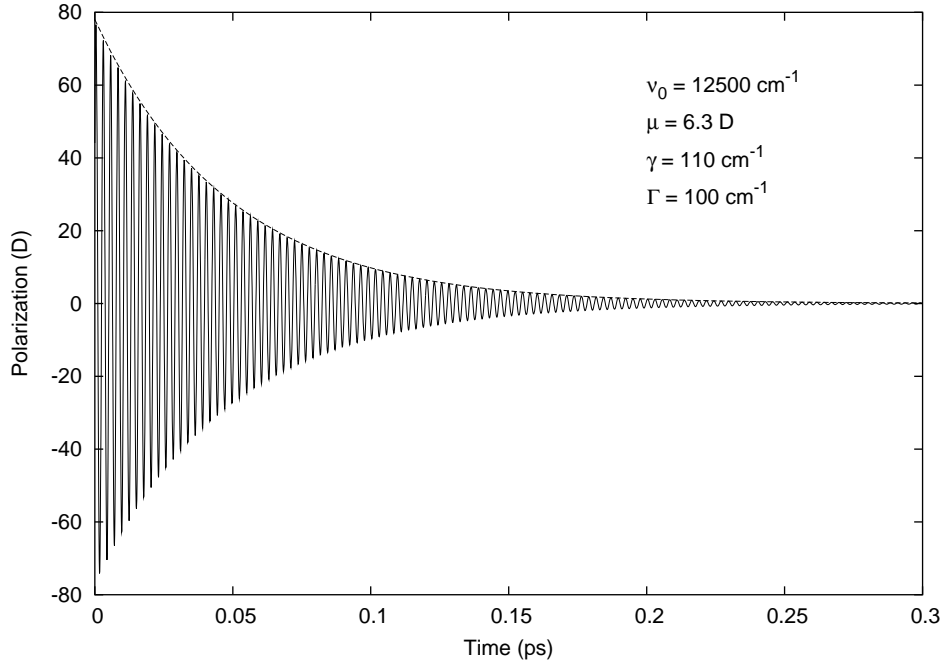


Figure 1: Simulation of the polarization decay of a 2LS using the Redfield matrix. The initial state is given by $|\rho\rangle\rangle = (0.5, 3.5 + 5i, 3.5 - 5i, 0.5)$. The decay time is $2\pi\gamma c$, where c is the speed of light. Also shown (dashed) is the decay curve with that decay time.

An interesting exercise is to simulate the Redfield method directly. That is, we couple the 2LS to a fluctuating damped harmonic oscillator, and study the influence of such an oscillator on the 2LS. To do that we first simulate a damped harmonic oscillator with a random force.

Now here we start running into problems. Initial simulations indicate that the energy of the 2LS decreases to $-\infty$. Now several things may be going on here, including what we have seen for coupled oscillators, namely that the system can become unstable for large coupling. There is an additional problem which can probably best illustrated by looking at the harmonic oscillators again.

Starting point in that case is of course again the Liouville equation, but now coupled to a classical variable x :

$$\frac{\partial |\rho\rangle\rangle}{\partial t} = -2\pi i \mathcal{L}_0 |\rho\rangle\rangle - 2\pi i \alpha x \mathcal{P} |\rho\rangle\rangle \quad (3.5)$$

where \mathcal{P} is the Liouville operator corresponding to the dipole operator. The equation of motion for x contains the expectation value of the dipole operator as the driving force:

$$m \frac{d^2 x}{dt^2} + m\omega^2 x + \zeta \frac{dx}{dt} = F_r(t) - \alpha \langle \hat{\mu} \rangle \quad (3.6)$$

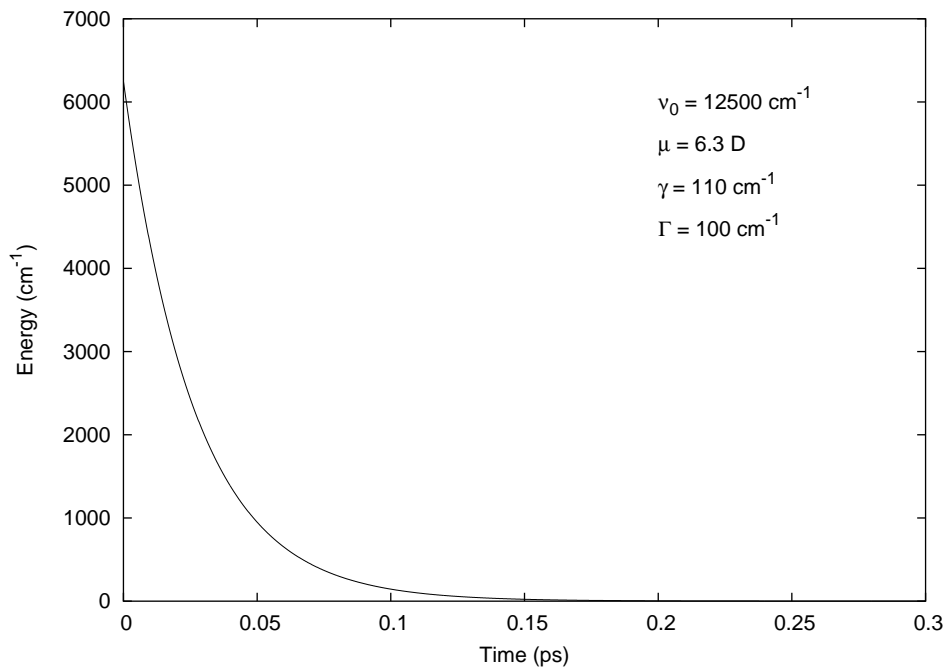


Figure 2: Simulation of the energy decay of a 2LS using the Redfield matrix. The initial state is given by $|\rho\rangle\rangle = (0.5, 3.5 + 5i, 3.5 - 5i, 0.5)$. The decay time is $2\pi\Gamma c$, where c is the speed of light.

We have to convert this to reasonable numbers. Dividing by the mass gives

$$\frac{d^2x}{dt^2} + \omega^2x + \frac{\zeta}{m} \frac{dx}{dt} = -\frac{\alpha}{m} \langle \hat{\mu} \rangle \quad (3.7)$$

where we left out the random force for the moment. For electronic transitions this mechanism can't do too well, but for the excitonic states, or for vibrations it should work. We should get some reasonable numbers for the coupling, and the masses. It should also work for NMR where the energy difference of the quantum system is rather small. The interaction between the two systems is of course again dipolar, so we can take anything for that. Maybe we should think about the proton transfer reactions for this case, or just at two coupled oscillators.

Two coupled oscillators with 1D dipole moments at 1 nm have an interaction energy of 5.035 cm^{-1} times a factor between -2 and 2, depending on the angles.

4 Equilibrium

The coupled quantum-classical Hamiltonian can be written as

$$\mathcal{H} = \epsilon |1\rangle \langle 1| + \alpha x [|0\rangle \langle 1| + |1\rangle \langle 0|] + \frac{1}{2}Ax^2 \quad (4.1)$$

The free energy of such a system can be found from

$$G = -k_B T \ln \int dx \text{Tr} [e^{-\beta \mathcal{H}}] \quad (4.2)$$

This can be calculated in the following way: first we diagonalize the operator part, then we take the trace, and finally we integrate. The eigenvalues of

$$\begin{pmatrix} 0 & \alpha x \\ \alpha x & \epsilon \end{pmatrix} \quad (4.3)$$

Eigenvalues are

$$\lambda_{\pm}(x) = \frac{1}{2} \left[\epsilon \pm \sqrt{\epsilon^2 + 4(\alpha x)^2} \right] \quad (4.4)$$

The matrix that diagonalizes this part of the Hamiltonian ($U^\dagger \mathcal{H} U$) can be written as

$$U = \begin{pmatrix} c(x) & s(x) \\ -s(x) & c(x) \end{pmatrix} \quad (4.5)$$

So, this needs to satisfy

$$\mathcal{H}U = U\Lambda \quad \text{or} \quad \begin{pmatrix} 0 & \alpha x \\ \alpha x & \epsilon \end{pmatrix} \begin{pmatrix} c(x) & s(x) \\ -s(x) & c(x) \end{pmatrix} = \begin{pmatrix} c(x) & s(x) \\ -s(x) & c(x) \end{pmatrix} \begin{pmatrix} \lambda_-(x) & 0 \\ 0 & \lambda_+(x) \end{pmatrix} \quad (4.6)$$

This fixes s and c , using

$$t = \frac{s}{c} = \frac{\sqrt{\epsilon^2 + 4(\alpha x)^2} - \epsilon}{2\alpha x} \quad \text{with} \quad s = \frac{t}{\sqrt{1+t^2}}, \quad c = \frac{1}{\sqrt{1+t^2}} \quad (4.7)$$

note that t goes to zero when $\alpha \rightarrow 0$. This means that we can write for the trace:

$$\text{Tr} [e^{-\beta \mathcal{H}}] = \text{Tr} [U e^{-\beta U^\dagger \mathcal{H} U} U^\dagger] = \text{Tr} [U e^{-\beta \Lambda} U^\dagger] = e^{-\beta \lambda_-(x)} + e^{-\beta \lambda_+(x)} \quad (4.8)$$

So the partition function becomes:

$$Q = \int_{-\infty}^{\infty} dx \left[e^{-\beta \lambda_-(x)} + e^{-\beta \lambda_+(x)} \right] e^{-\frac{1}{2}\beta A x^2} \quad (4.9)$$

This should allow us to find probabilities, for instance the probability of finding x :

$$P(x) = \frac{\text{Tr} [e^{-\beta \mathcal{H}}]}{Q} = \frac{[e^{-\beta \lambda_-(x)} + e^{-\beta \lambda_+(x)}] e^{-\frac{1}{2}\beta A x^2}}{\int_{-\infty}^{\infty} dx [e^{-\beta \lambda_-(x)} + e^{-\beta \lambda_+(x)}] e^{-\frac{1}{2}\beta A x^2}} \quad (4.10)$$

The probability $P(x)$ can have some interesting behavior. Assume that the temperature is rather low compared to the electronic excitation energy. In that case

$$\beta(Ax^2 + 2\lambda_+) = \beta(Ax^2 + \epsilon + \sqrt{\epsilon^2 + (2\alpha x)^2}) \quad (4.11)$$

is large for all values of x , and we can approximate $P(x)$ by:

$$P(x) \approx \frac{e^{-\frac{1}{2}\beta [Ax^2 - \sqrt{\epsilon^2 + (2\alpha x)^2}]}{\int_{-\infty}^{\infty} dx e^{-\frac{1}{2}\beta [Ax^2 - \sqrt{\epsilon^2 + (2\alpha x)^2}]} \quad (4.12)$$

The denominator is of course just a normalization constant, so we can just look at the behavior of the exponential, which we can write in the form

$$e^{-\frac{1}{2}\beta A [x^2 - \sqrt{\epsilon^2/A^2 + (2\alpha x/A)^2}]} \quad (4.13)$$

Taking the derivative of the function occurring in the exponential we get

$$2x - \frac{2x(2\alpha/A)^2}{2\sqrt{\epsilon^2/A^2 + (2\alpha x/A)^2}} = \frac{x}{\sqrt{\epsilon^2/A^2 + (2\alpha x/A)^2}} \left[2\sqrt{\epsilon^2/A^2 + (2\alpha x/A)^2} - (2\alpha/A)^2 \right] \quad (4.14)$$

The zeroes of this function are $x = 0$, and possible solutions of

$$\sqrt{\epsilon^2/A^2 + (2\alpha x/A)^2} - 2(\alpha/A)^2 = 0 \quad (4.15)$$

This equation also has two solutions:

$$x^2 = \left(\frac{A}{2\alpha}\right)^2 \left[4\left(\frac{A}{\alpha}\right)^4 - \left(\frac{\epsilon}{A}\right)^2 \right] \quad (4.16)$$

which are real for $\alpha^2 \geq \epsilon A/2$. Note that the temperature is irrelevant here.

A note about units again. The potential energy of an oscillator is $\frac{1}{2}m\omega_s^2 x^2$, where ω_s is the solvent frequency. We will see below that frequencies are of the order of 1–100 ps⁻¹. Division by c^2 turns this in wavenumbers. That means the position is scaled by $\sqrt{mc^2}$. So, let us write the energy of the oscillator as

$$\frac{1}{2}m\omega_s^2 x^2 = \frac{1}{2}m\omega_s^2 x_0^2 \left(\frac{x}{x_0}\right)^2 \quad (4.17)$$

where we take $x_0 = 1$ nm. For a solvent frequency of 1 ps⁻¹, and 1 proton mass we get

$$A = m_p \omega_s^2 x_0^2 = 1.67 \times 10^{-27} \times 10^{24} \times 10^{-18} \text{ J} = 1.67 \times 10^{-21} \text{ J} \approx 84 \text{ cm}^{-1} \quad (4.18)$$

This result of course depends on the mass of the oscillator, but we get numbers of the same order of magnitude. Only now we measure the deviation of the oscillator in nm. For the coupling similar considerations hold. We could also express the deviation in terms of the mass: for the same energies, but bigger masses, the deviation is just smaller.

There is a related issue for the dynamical equations. The equations of motion for the (undamped) system are

$$\frac{dx}{dt} = \frac{p}{m} \quad (4.19)$$

and

$$\frac{dp}{dt} = -m\omega^2 x = -(m\omega^2 x_0^2) \left(\frac{x}{x_0}\right) \quad (4.20)$$

This last equation can also be written as (we keep the constants h and c for the moment):

$$\frac{dp x_0 / h}{dct} = -\frac{m\omega^2 x_0^2}{hc} \left(\frac{x}{x_0}\right) = -A \left(\frac{x}{x_0}\right) \quad (4.21)$$

Note that $p x_0 / h$ is dimensionless. Now the time is scaled to cm (as is used in the program), but it also means that the equation for the momentum has to be changed to:

$$\frac{dx/x_0}{dct} = \frac{p x_0 / h}{m x_0^2 c / h} \quad (4.22)$$

Taking again the mass of the proton, we get for the numerical value of the constant in this equation:

$$\frac{m_p x_0^2 c}{h} = \frac{1.67 \times 10^{-27} \times 10^{-18} \times 2.9979 \times 10^8}{6.626 \times 10^{-34}} = 7.6 \times 10^{-2} \text{ cm} \quad (4.23)$$

The above calculation means that above a certain interaction strength spontaneous symmetry breaking occurs: the system acquires a permanent dipole moment. We have assumed here that the solvent frequency does not depend on the temperature, but in reality it probably does.

Before attempting some real numerical calculations, we'll also calculate the probability of finding a state $|\psi\rangle$. The most general state can be written as

$$|\psi\rangle = \cos\theta |0\rangle + e^{i\phi} \sin\theta |1\rangle \quad (4.24)$$

The probability of finding this state, and position x of the oscillator is of course

$$P(\theta, \phi, x) = \frac{1}{Q} \langle \psi | e^{-\beta \mathcal{H}} | \psi \rangle \quad (4.25)$$

The matrix element can be calculated using the above transformation:

$$\langle \psi | e^{-\beta \mathcal{H}} | \psi \rangle = \langle \psi | U^\dagger U e^{-\beta \mathcal{H}} U^\dagger U | \psi \rangle \quad (4.26)$$

which can be expanded to

$$(\cos \theta, e^{-i\phi} \sin \theta) \begin{pmatrix} c(x) & -s(x) \\ s(x) & c(x) \end{pmatrix} \begin{pmatrix} e^{-\beta \lambda - (x)} & 0 \\ 0 & e^{-\beta \lambda + (x)} \end{pmatrix} \begin{pmatrix} c(x) & s(x) \\ -s(x) & c(x) \end{pmatrix} \begin{pmatrix} \cos \theta \\ e^{i\phi} \sin \theta \end{pmatrix} e^{-\frac{1}{2} \beta A x^2} \quad (4.27)$$

This works out to:

$$\left[e^{-\beta \lambda - (x)} [c(x)^2 \cos^2 \theta + s(x)^2 \sin^2 \theta] + e^{-\beta \lambda + (x)} [s(x)^2 \cos^2 \theta + c(x)^2 \sin^2 \theta] \right] e^{-\frac{1}{2} \beta A x^2} \quad (4.28)$$

So we note that the ϕ -dependence drops out, which is not unexpected. Using this probability we can of course calculate all other probabilities, such as the probability of finding θ , or x , and conditional probabilities, such as $P(\theta|x)$. Note that if we integrate over θ we get the integral Q , as in eq. (4.10).

Let's try to find some reasonable numbers. For the excitation energy of the 2LS we take again 12500 cm^{-1} , and at room temperature $k_B T = \beta^{-1}$ is about 200 cm^{-1} . The problem is what to take for the coupling and for the frequency of the oscillator. The frequency of the oscillator (if we think of polarization being the cause) can be related to the solvent frequency ω_s , for which in earlier papers we took values between 1 and 100 ps^{-1} . This corresponds to values between 30 and 3000 cm^{-1} . The coupling can of course be anything, mainly depending on the cavity radius if we think of an Onsager cavity type model. We've calculated before that the energy of a dipole in its own reaction field can easily be 1000 cm^{-1} , so again we have a large range of values that can be covered.

Let's look at some limiting behavior. If we don't couple the 2LS to an oscillator, α goes to zero, U becomes the unit matrix, and we get

$$P(\theta) = \frac{\cos^2 \theta + e^{-\beta \epsilon} \sin^2 \theta}{1 + e^{-\beta \epsilon}} \quad (4.29)$$

This at least seems correct. In the zero temperature limit it goes to $\cos^2 \theta$, whereas for infinite temperature it approaches $1/2$, as it should.

The expectation value of the dipole operator can be found from

$$\langle \hat{\mu} \rangle = \frac{\mu}{Q} \int_{-\infty}^{\infty} dx [\langle 0 | e^{-\beta \mathcal{H}} | 1 \rangle + \langle 1 | e^{-\beta \mathcal{H}} | 0 \rangle] = \frac{\mu}{Q} \int_{-\infty}^{\infty} dx s(x) c(x) [e^{-\beta \lambda -} - e^{-\beta \lambda +}] e^{-\frac{1}{2} A x^2} \quad (4.30)$$

In figure 3 we show the probability density $P(x)$ for two sets of parameter values, one below, and one above the point where phase separation occurs.

Something similar to this should happen to $P(\theta)$ as well, but we can't see it from the average dipole moment, because it still has the same probability of pointing each way.

So, although the equilibrium situation can be complicated, there appears no problem with large coupling, as in the case of two coupled oscillators which can become unstable for large coupling. Nevertheless, dynamically the system does not perform as expected.

5 Coupled classical–quantum Liouville equation

Initial simulations of the coupled quantum–classical system do not appear to work properly. The population of the quantum system does not decay to the ground state, and the coherences do not appear to decay at all.

We first try to look at the equations themselves. The density operator elements satisfy the following equations:

$$\begin{aligned} \frac{\partial \rho_0}{\partial t} &= 2\pi i \alpha x \rho_1 - 2\pi i \alpha x \rho_2 \\ \frac{\partial \rho_1}{\partial t} &= 2\pi i \alpha x \rho_0 + 2\pi i \epsilon \rho_1 - 2\pi i \alpha x \rho_3 \end{aligned}$$

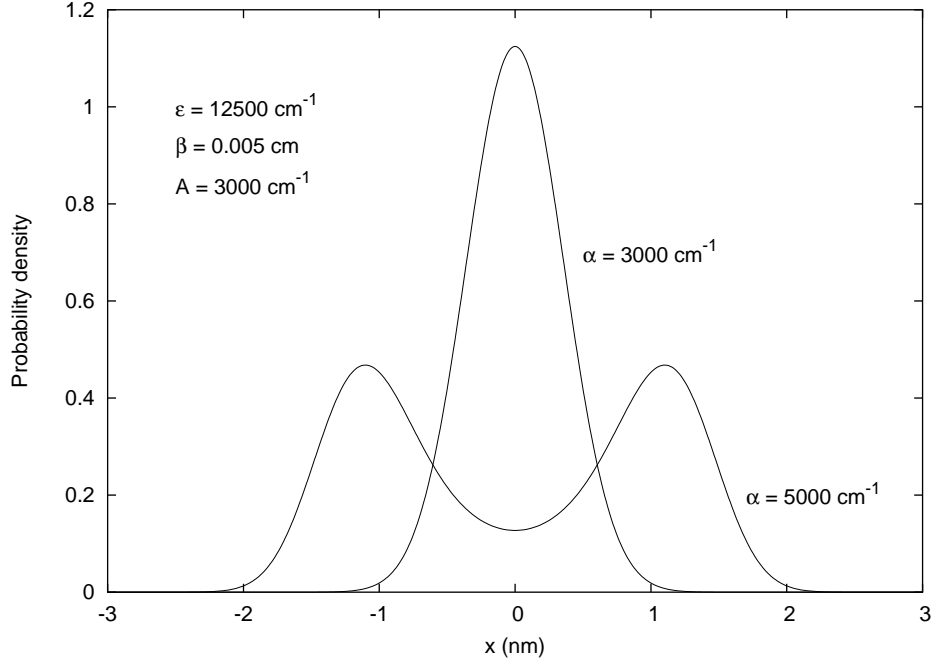


Figure 3: Probability density for finding the oscillator with position x . For $\alpha = 3000 \text{ cm}^{-1}$, which is below the phase separation coupling constant, a single peak is found, centered around 0. For $\alpha = 5000 \text{ cm}^{-1}$ we are above the transition point, and the density has two peaks, corresponding to two minima in the free energy. The free energy now has a maximum at $x = 0$.

$$\begin{aligned}\frac{\partial \rho_2}{\partial t} &= -2\pi i \alpha x \rho_0 - 2\pi i \epsilon \rho_2 + 2\pi i \alpha x \rho_3 \\ \frac{\partial \rho_3}{\partial t} &= -2\pi i \alpha x \rho_1 + 2\pi i \alpha x \rho_2\end{aligned}\quad (5.1)$$

The sum $\rho_0 + \rho_3$ should be constant, and indeed it is. Thus we can replace ρ_3 by $1 - \rho_0$. Furthermore separating the equations into real and imaginary parts, using that x and ρ_0 must be real, gives

$$\begin{aligned}\frac{\partial \rho_0}{\partial t} &= -4\pi \alpha x \rho_1'' \\ \frac{\partial \rho_1'}{\partial t} &= -2\pi \epsilon \rho_1'' \\ \frac{\partial \rho_1''}{\partial t} &= 2\pi \epsilon \rho_1' + 2\pi \alpha x (2\rho_0 - 1)\end{aligned}\quad (5.2)$$

Again this system does not show decay behavior of the coherences, and also the probability for finding the state $|0\rangle$ for instance, can be seen to exceed 1, or be below 0. This is not good.

To see where we possibly went wrong we consider the classical-quantum Liouville equation, where ρ is a matrix depending on the parameters x, p . The equation can be written as

$$\frac{\partial \rho}{\partial t} = -2\pi i [\mathcal{H}, \rho] - \{\mathcal{H}, \rho\} \quad (5.3)$$

with

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 + \alpha x \hat{\mu} + \epsilon |0\rangle \langle 0| \quad (5.4)$$

The Poisson bracket can then be written as:

$$\{\mathcal{H}, \rho\} = \frac{\partial \mathcal{H}}{\partial p} \frac{\partial \rho}{\partial x} - \frac{\partial \mathcal{H}}{\partial x} \frac{\partial \rho}{\partial p} = \frac{p}{m} \frac{\partial \rho}{\partial x} - (m\omega^2 x + \alpha \hat{\mu}) \frac{\partial \rho}{\partial p} \quad (5.5)$$

Let us first try to derive the equations of motion for x and p from this. For x we get

$$\frac{dx}{dt} = \text{Tr} \int d\Gamma x \frac{\partial \rho}{\partial t} = \frac{p}{m} \quad (5.6)$$

Obviously the commutator term vanishes because of the trace, and x is not an operator. The integral over Γ is a phase space integral, and can be performed using partial integration. Similarly we get

$$\frac{dp}{dt} = \text{Tr} \int d\Gamma p \frac{\partial \rho}{\partial t} = -m\omega^2 x - \alpha \langle \hat{\mu} \rangle \quad (5.7)$$

where $\langle \hat{\mu} \rangle$ is the expectation value of the dipole operator. Just integrating eq. (5.2) over phase space keeps the quantum mechanical part of this operator:

$$\frac{\partial \rho}{\partial t} = -2\pi i [\mathcal{H}_0, \rho] - 2\pi i \alpha x [\hat{\mu}, \rho] \quad (5.8)$$

since obviously the Poisson bracket now drops out. So far it all looks good. We did make an approximation here, however. The position coordinate is defined as

$$x = \text{Tr} \int dx x \rho \quad (5.9)$$

and it is not immediately obvious that this is the same as

$$\int dx x \rho = x \rho_Q \quad (5.10)$$

where ρ_Q is the quantum part of this operator, in other words $\rho_Q = \int dx x \rho$.

There is a limitation on the values that the matrix elements can take. This is obvious for the diagonal elements, they should add up to one, and represent probabilities, so that they cannot be less than zero, but also the off diagonal elements cannot exceed 0.5, both for their real and imaginary parts. This can be shown by looking at the probability of a state, for a given density matrix. Taking again the state (4.24), the probability of finding it is given by:

$$\langle \psi | \rho | \psi \rangle = \rho_{00} \cos^2 \theta + \rho_{11} \sin^2 \theta + \rho_{10} e^{-i\phi} \sin \theta \cos \theta + \rho_{01} e^{i\phi} \sin \theta \cos \theta \leq 1, \quad \forall \theta, \phi \quad (5.11)$$

which can be written in the form

$$\sin^2 \theta + \rho_{00} \cos 2\theta + \sin 2\theta [\rho'_{01} \cos \phi - \rho''_{01} \sin \phi] \leq 1, \quad \forall \theta, \phi \quad (5.12)$$

It can be inferred from this equation that, apart from $\rho_{11} \leq 1$, also $\rho'_{01} \leq \frac{1}{2}$ and $\rho''_{01} \leq \frac{1}{2}$. This is a major cause of the simulations not working properly before. We accidentally started with higher values, and this leads to, now expectedly, incorrect behavior for the diagonal elements as well. There are additional restrictions. Suppose the density matrix is written as

$$\begin{pmatrix} \rho_0 & \rho_1 \\ \rho_1^* & 1 - \rho_0 \end{pmatrix} \quad (5.13)$$

The eigenvalues of this matrix are

$$\lambda_{1,2} = \frac{1}{2} \left[1 \pm \sqrt{1 + 4|\rho_1|^2 - 4\rho_0(1 - \rho_0)} \right] \quad (5.14)$$

The sum of these eigenvalues is one, as it should be, but in addition both these eigenvalues have to be larger than zero and smaller than one for them to represent probabilities. This leads to the condition

$$\sqrt{1 + 4|\rho_1|^2 - 4\rho_0(1 - \rho_0)} \leq 1 \quad (5.15)$$

from which we derive that

$$|\rho_1|^2 \leq \rho_0(1 - \rho_0) \quad (5.16)$$

This means that if in equilibrium $\rho_0 = 1$, the off-diagonal elements must also be zero. It also means that for a pure state (where the eigenvalues are 0 and 1) $|\rho_1|^2 = \rho_0(1 - \rho_0)$.

We will first do some simulations with the simplified system, described by the equations (5.2). We scale the time with $2\pi\epsilon$, so that the equations can be written as

$$\begin{aligned}\frac{\partial\rho_0}{\partial t} &= -2\alpha x\rho_1'' \\ \frac{\partial\rho_1'}{\partial t} &= -\rho_1'' \\ \frac{\partial\rho_1''}{\partial t} &= \rho_1' + \alpha x(2\rho_0 - 1)\end{aligned}\tag{5.17}$$

where α/ϵ is now replaced by α , which now measures the interaction energy relative to the electronic energy. The other equations are still

$$\frac{dx}{dt} = p\tag{5.18}$$

and

$$\frac{dp}{dt} = -Ax - \zeta p + \alpha\mu\rho_1'\tag{5.19}$$

An interesting question is of course regarding the stationary state of this set of equations, which we should be able to find by setting the right hand sides to 0. We introduced an additional parameter μ here, which can represent the mass of the oscillator.

We then get

$$\begin{aligned}\alpha x\rho_1'' &= 0 \\ \rho_1'' &= 0 \\ \rho_1' + \alpha x(2\rho_0 - 1) &= 0 \\ p &= 0 \\ -Ax - \zeta p + \alpha\mu\rho_1' &= 0\end{aligned}\tag{5.20}$$

The solution is

$$\begin{aligned}\rho_1'' &= 0 \\ p &= 0 \\ \rho_1' + \alpha x(2\rho_0 - 1) &= 0 \\ -Ax + \alpha\mu\rho_1' &= 0\end{aligned}\tag{5.21}$$

There is an infinite number of solutions, so how can we make it go to the correct equilibrium solution, and what is the solution found in the calculations, in particular: how does it depend on the initial conditions? From the simulations it even appears that there is no approach to this equilibrium at all in certain cases. One curious thing about the equations as they stand is the following: at all times $|\rho_1|^2 - \rho_0(1 - \rho_0)$ is a constant. This can be seen as follows: multiplying the second of eqs. (5.2) by ρ_1' gives

$$\rho_1' \frac{\partial\rho_1'}{\partial t} = \frac{1}{2} \frac{\partial\rho_1'^2}{\partial t} = -2\pi\epsilon\rho_1'\rho_1''\tag{5.22}$$

Similarly we find from the third of eqs. (5.2):

$$\rho_1'' \frac{\partial\rho_1''}{\partial t} = \frac{1}{2} \frac{\partial\rho_1''^2}{\partial t} = 2\pi\epsilon\rho_1'\rho_1'' + 2\pi\alpha x\rho_1''(2\rho_0 - 1)\tag{5.23}$$

so that

$$\frac{\partial|\rho_1|^2}{\partial t} = 4\pi\alpha x\rho_1''(2\rho_0 - 1)\tag{5.24}$$

Multiplying the first of eqs. (5.1) with ρ_0 gives

$$\frac{\partial \rho_0^2}{\partial t} = -8\pi\alpha x \rho_1'' \rho_0 \quad (5.25)$$

so that

$$\frac{\partial(\rho_0 - \rho_0^2)}{\partial t} = 4\pi\alpha x \rho_1'' (2\rho_0 - 1) \quad (5.26)$$

so that indeed

$$\frac{\partial[|\rho_1|^2 - \rho_0(1 - \rho_0)]}{\partial t} = 0 \quad (5.27)$$

and

$$\rho_0 - |\rho_1|^2 - \rho_0^2 \equiv \sigma \quad (5.28)$$

This holds regardless of what the time dependence of x is. The constant σ is determined by the initial values. If we are dealing with a pure state the eigenvalues are zero and one, and the state remains pure. It also means that a pure state can never develop into a mixed state by this mechanism. So how can Redfield theory be correct? And, is the same true if we also have permanent moments? (yes, see below).

Since we now have an additional constant of motion, this should also restrict the number of possible solutions to eqs. (5.21). From the last two equations we derive

$$\rho_1' \left[1 + \frac{\alpha^2}{A}(2\rho_0 - 1) \right] = \sqrt{\sigma + \rho_0^2 - \rho_0} \left[1 + \frac{\alpha^2}{A}(2\rho_0 - 1) \right] = 0 \quad (5.29)$$

This has three solutions for ρ_0 :

$$\rho_0 = \frac{1}{2} [1 \pm \sqrt{1 - 4\sigma}] \quad (5.30)$$

and

$$\rho_0 = \frac{1}{2} \left[1 - \frac{A}{\alpha^2} \right] \quad (5.31)$$

where the last solution can only apply if $A \leq \alpha^2$. Note that in the first case $\rho_1 = x = 0$, whereas in the second case ρ_0 and thus x is determined by the initial conditions. This is, however, no proof that the solutions will actually converge to any to these.

Since we now have an additional relation between the variables (albeit dependent on the initial conditions chosen), we can reduce the number of equations again.

6 Redfield revisited

The starting point of Redfield, or for that matter, Kubo theory is the quantum Liouville equation with coupling to external, classical, fields:

$$\frac{\partial \rho}{\partial t} = -2\pi i [\mathcal{H}_0, \rho] - 2\pi i \sum_k [A_k, \rho] E_k(t) \quad (6.1)$$

In this equation A_k is a set of system operators, and E_k are bath functions with a dynamics that may or may not be influenced by the state of the system. In most cases the interaction is supposed to be weak, and the effect of the quantum system on the bath neglected, so that the dynamics of the bath develops independently. For a 2LS there are a maximum of three system operators $|0\rangle\langle 0|$, $|0\rangle\langle 1|$, and $|1\rangle\langle 0|$, the fourth one is dependent on these due to completeness. Since we want to keep the bath functions real, we choose the following linear combinations for these operators, which makes them all hermitian:

$$A_0 = |0\rangle\langle 0| - |1\rangle\langle 1| \quad (6.2)$$

$$A_1 = |0\rangle\langle 1| + |1\rangle\langle 0| \quad (6.3)$$

and

$$A_2 = i[|0\rangle\langle 1| - |1\rangle\langle 0|] \quad (6.4)$$

Keeping the same notation for the density matrix (as a vector in Liouville space) as above, we can write down the equations of motion of the various components. To that end we use

$$\begin{aligned} \sum_k [A_k, |0\rangle\langle 0|] E_k &= -(E_1 + iE_2) |0\rangle\langle 1| + (E_1 - iE_2) |1\rangle\langle 0| \\ \sum_k [A_k, |0\rangle\langle 1|] E_k &= -(E_1 - iE_2) |0\rangle\langle 0| + 2E_0 |0\rangle\langle 1| + (E_1 - iE_2) |1\rangle\langle 1| \\ \sum_k [A_k, |1\rangle\langle 0|] E_k &= (E_1 + iE_2) |0\rangle\langle 0| - 2E_0 |1\rangle\langle 0| - (E_1 + iE_2) |1\rangle\langle 1| \\ \sum_k [A_k, |1\rangle\langle 1|] E_k &= (E_1 + iE_2) |0\rangle\langle 1| - (E_1 - iE_2) |1\rangle\langle 0| \end{aligned} \quad (6.5)$$

Thus we can write for the time evolution of the elements of the density operator

$$\frac{\partial}{\partial t} \begin{pmatrix} \rho_0 \\ \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} = -2\pi i \begin{pmatrix} 0 & -(E_1 + iE_2) & (E_1 - iE_2) & 0 \\ -(E_1 - iE_2) & -\epsilon + 2E_0 & 0 & (E_1 - iE_2) \\ (E_1 + iE_2) & 0 & \epsilon - 2E_0 & -(E_1 + iE_2) \\ 0 & (E_1 + iE_2) & -(E_1 - iE_2) & 0 \end{pmatrix} \begin{pmatrix} \rho_0 \\ \rho_1 \\ \rho_2 \\ \rho_3 \end{pmatrix} \quad (6.6)$$

Let's again calculate the time rate of change of $|\rho_1|^2 + \rho_0^2 - \rho_0$; we can use that $\rho_2 = \rho_1^*$:

$$\begin{aligned} \rho_1^* \frac{\partial \rho_1}{\partial t} + \rho_2^* \frac{\partial \rho_2}{\partial t} &= \rho_1^* \frac{\partial \rho_1}{\partial t} + \rho_1 \frac{\partial \rho_1^*}{\partial t} = \frac{\partial |\rho_1|^2}{\partial t} = \\ &= -2\pi i [2(E_1 + iE_2)\rho_0\rho_1 - 2(E_1 - iE_2)\rho_0\rho_1^* - (E_1 + iE_2)\rho_1 + (E_1 - iE_2)\rho_1^*] \end{aligned} \quad (6.7)$$

furthermore:

$$(2\rho_0 - 1) \frac{\partial \rho_0}{\partial t} = \frac{\partial \rho_0^2 - \rho_0}{\partial t} = -2\pi i [-2(E_1 + iE_2)\rho_0\rho_1 + 2(E_1 - iE_2)\rho_0\rho_1^* + (E_1 + iE_2)\rho_1 - (E_1 - iE_2)\rho_1^*] \quad (6.8)$$

Adding the last two equations indeed shows again that the quantity (can we call this the purity of the density matrix? for a pure state $\sigma = 0$, if the state is not pure $\sigma > 0$.)

$$\sigma = \rho_0 - \rho_0^2 - |\rho_1|^2 \quad (6.9)$$

is conserved under these dynamics, regardless of what the time-dependence of the externally applied fields is.

So, here is the problem. In thermal equilibrium the density matrix for a 2LS is a mixed state (unless the temperature is 0) given by

$$\rho_{eq} = \frac{1}{1 + e^{-\beta\epsilon}} \begin{pmatrix} 1 & 0 \\ 0 & e^{-\beta\epsilon} \end{pmatrix} \quad (6.10)$$

and supposedly every state must evolve to this. Now suppose we start in a pure state, for instance $|0\rangle\langle 0|$. For this state $\sigma = 1$. For the state the system is supposed to evolve to

$$\sigma = \frac{e^{-\beta\epsilon}}{(1 + e^{-\beta\epsilon})^2} > 0 \quad (6.11)$$

for any finite temperature. In the zero temperature limit it goes to zero. However, σ is conserved, so how can this happen? Probably there is something in the limiting procedures used in the derivation of Redfield, which changes this, but it certainly is a problem for direct simulation: the 2LS system, coupled to a damped HO will never relax to equilibrium. On the other hand, we can also state that also the interaction with an electromagnetic field will preserve the purity of the state, so if we start in thermal equilibrium, it can eventually return to this state by this mechanism. We probably do have a problem if we look at excited state vibrational distributions though, since it is unclear what type of state is created there.