Problem Set 4: Simulations in Liouville Space

In this Problem Set, we will build on Problem Set 2, but will carry out the simulations in Liouville space. In a first step, we will simulate a spin-1/2 system both with and without relaxation using a random field approach. Then we will simulate a two-spin system and see what happens to the spectrum, if one of the spins relaxes very fast.

Problem 1: A simple isotropic spin-½ system in Liouville space without relaxation

The matlab script `ex_1_one_spin_liouville_pulse_acquire_unitary` gives you the basic structure for this simulation. But some of the code was removed. Your task is to fill in the gaps.
Most of the script is analogous the Problem Set 2, and will not be discussed in detail again. The main difference comes in section 5), where you have to convert all operators given in section 4) to Liouville space. There are two things you have to consider.
1) Are you dealing with a (commutation) superoperator, or with a state vector in Liouville space?
2) The ordering of the elements.
As given in the script, the Hamiltonian commutation superoperator can be written as

$$\left[\hat{H},\bullet\right] = \hat{\hat{H}} = \hat{H}\otimes\mathbb{1} - \mathbb{1}\otimes\hat{H}^T \qquad . \tag{1}$$

This implies a certain ordering when converting an operator $\hat{A}$ in Hilbert space to a vector $|A\rangle$ in Liouville space, namely

$$\hat{A} = \begin{pmatrix} a_{11} & a_{12} & \vdots & a_{1N} \\ a_{21} & a_{22} & & \\ \dots & & \ddots & \\ a_{N1} & & & a_{NN} \end{pmatrix} \rightarrow |A\rangle = \begin{pmatrix} a_{11} \\ a_{12} \\ \vdots \\ a_{1N} \\ a_{21} \\ \vdots \\ a_{NN} \end{pmatrix} \tag{2}$$

use the MATLAB functions `reshape` and, if needed, `transpose` to convert the operators into state vectors. Double check that the ordering of elements is correct.
After this, you have to construct the propagators, and apply them to the density operator. Think about the differences between Hilbert space and Liouville space. The same applies to the detection event.
Run the code to make sure everything works and gives the expected results.

Problem 2: A simple isotropic spin-½ system in Liouville space with random-field relaxation

The matlab script `ex_2_one_spin_rand_field_pulse_acquire` gives you the basic structure for this simulation. It is essentialy the same as in the first problem, so you will have to insert everything that you had to insert in Problem 1 again. The difference is that now we would like to explicitly include Relaxation .

For this, we build a Relaxation superoperator of the form

$$\hat{\hat{R}} = k_z \left[\hat{I}_z, \left[\hat{I}_z, \bullet\right]\right] + k_{xy} \left(\left[\hat{I}_x, \left[\hat{I}_x, \bullet\right]\right] + \left[\hat{I}_y, \left[\hat{I}_y, \bullet\right]\right]\right) \tag{3}$$

The rate constants k_z and k_{xy} describe randomly fluctuating fields along the given directions. We will see in the lecture how they relate to fluctuation amplitudes and spectral densities, but we will take them as given for this exercise. Later, we will also see how they relate to the relaxation times T_1 and T_2.
After copying the results your results from Problem 1, you have to build matrix representations of the double commutators in section 5) of the exercise script. For this, remember that you know how to construct a commutation superoperator, and then notice that the double commutator is nothing else than applying the commutation superoperator twice.
Last but not least, we would like the system to relax towards $|I_z\rangle$. Think about how to achieve this in the propagation loop.
Run the simulation, play with the parameters, and check if you can see both transverse and longitudinal relaxation.

Problem 3: Basis of the relaxation superoperator

Have a look at the matrix representation of the Relaxation superoperator in Problem 2. What basis is it in? Do you have an intuitive understanding of the elements and what they mean?
In section 9) of the script of Problem 2), we generate a unitary operation, i.e. a Basis transformation, that transforms the operators and state vectors from the usual product basis (i.e. $|\alpha\alpha\rangle, |\alpha\beta\rangle, ...$) to a basis set spanned by the Cartesian operators $\{|\mathbb{1}\rangle, |I_x\rangle, |I_y\rangle, |I_z\rangle\}$.
Look again at the relaxation superoperator, now in the new frame. What do the different elements mean? Can you guess or derive how the constants k_z and k_{xy} relate to these matrix elements? Does it make physical sense?

Problem 4 (optional): Heteronuclear two-spin system in Liouville space

The matlab script `ex_4_two_spin_rand_field_pulse_acquire` gives you the basic structure for this simulation. It is again essentially the same as in Problem 2. But now we look at the spectrum of one spin as a function of the relaxation times of a coupled heteronuclear spin.

After you inserted all the left out operators, play with the relaxation times of spin 2, i.e. `k_xy_2` and `k_z_2`. Under which conditions does the doublet in the spectrum of spin 1 collapse to a singlet?