2.3 Generalized master equation (GME) for the RDM

In the two examples just discussed, we have calculated explicitly the time evolution of the RDM for a closed isolated system. We have calculated

$$\hat{\rho}_{red}(t) \equiv \mathrm{Tr}_B \{ \hat{\rho}_{tot}(t) \}.$$

The main results were: i) the appearance of mixed states within the time evolution, ii) the emergence of irreversibility in presence of an infinite unobserved subsystem. The systems considered here were, though, very idealized.

▲ Can we derive an equation of motion for $\hat{\rho}_{red}$ in a general context, whose solution is $\hat{\rho}_{red}(t)$?

2.3.1 System-bath model

The most generic framework for the derivation of a RDM is the one of a system-bath model: i.e.

$\Phi_1 \dashrightarrow S$ small subsystem characterized by $\hat{H}_S$ SYSTEM

$\Phi_2 \longrightarrow B$ large subsystem " " $\hat{H}_B$ BATH

The SYSTEM and the BATH interact via the Hamiltonian $\hat{V}$ which implies transfer of energy and/or particles between the two subsystems. The total Hamiltonian is given by

$$\hat{H} = \underbrace{\hat{H}_S + \hat{H}_B}_{= \hat{H}_0} + \hat{V} \qquad (2.25)$$

Notice: The BATH it is so large that it remains in thermal equilibrium despite the energy and/or particles exchanged with S through $\hat{V}$.

The Liouville-von Neumann equation for $\hat{\rho}_{tot}$ in interaction picture can be recast into the integro differential equation:

$$\dot{\hat{\rho}}_I(t) = -\frac{i}{\hbar}\left[\hat{V}_I(t), \hat{\rho}_I(0)\right] - \frac{1}{\hbar^2}\int_0^t dt' \left[\hat{V}_I(t), \left[\hat{V}_I(t'), \hat{\rho}_I(t')\right]\right] \quad (1.27)$$

which yields for the RDM, $\hat{\rho}_{red}(t) = Tr_B\, \hat{\rho}(t)$ in I-picture:

$$\dot{\hat{\rho}}_{I,red}(t) = -\frac{i}{\hbar} Tr_B\left\{\left[\hat{V}_I(t), \hat{\rho}_I(0)\right]\right\} - \frac{1}{\hbar^2}\int_0^t dt'\, Tr_B\left\{\left[\hat{V}_I(t), \left[\hat{V}_I(t'), \hat{\rho}_I(t')\right]\right]\right\} \quad (2.2\ldots$$

Eq. (2.26) is still <u>not</u> a closed equation for $\hat{\rho}_{red,I}$. Two points should still be solved

$\boxed{A}$ $\quad \hat{\rho}_{I,red} = \hat{\rho}_{red,I} \quad (2.27)$

<u>proof</u>.

$$\hat{\rho}_{I,red}(t) = Tr_B\left\{U_0^+(t)\, \hat{\rho}_{tot}(t) U_0(t)\right\} = Tr_B\left\{U_B^+(t)\, U_S^+(t)\, \hat{\rho}_{tot}(t)\, U_S(t)\, U_B(t)\right\}$$

The last equality follows from the observation that $[H_S(t), H_B(t')] = 0 \;\; \forall\, t, t'$ even assuming explicitly time dependent Hamiltonians for the system and the bath.

$$U_S(t) = T_{\leftarrow} \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, H_S(t')\right] \qquad U_B(t) = T_{\leftarrow} \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, H_B(t')\right]$$

as follows from the condition $i\hbar\, \partial_t U_{S/B}(t) = H_{S/B}(t)\, U(t)$ and $U_{S/B}(0) = \mathbb{1}$.

$U_0(t)$ is defined instead by $i\hbar\, \partial_t U_0 = (H_S(t) + H_B(t))\, U_0(t)$ and $U_0(0) = \mathbb{1}$.

Suppose $\quad U_0(t) = U_S(t)\, U_B(t)$

$$i\hbar\, \partial_t\left[U_S(t)\, U_B(t)\right] = H_S(t) U_S(t) U_B(t) + U_S(t) H_B(t) U_B(t) = (H_S(t) + H_B(t))\, U_S(t) U_B(t).$$

Analogously it works for $U_B(t)U_S(t)$. Moreover $U_S(0)U_B(0) = \mathbb{1}$ as it follows from the initial conditions for U_S and U_B separately. But the propagator is unique $\Rightarrow$ $U_S U_B$ $(=U_B U_S)$ makes the job.

$$\mathrm{Tr}_B\left\{ U_B^+(t)\, U_S^+(t)\, \hat{\rho}_{tot}(s)\, U_S(t) U_B(t)\right\} =$$

$$= \sum_{ijk} \langle \phi_k^{(B)} | U_B^+(t) | \phi_i^{(B)}\rangle\langle \phi_i^{(B)} | U_S^+(t)\, \hat{\rho}_{tot}(t)\, U_S(t) | \phi_j^{(B)}\rangle\langle \phi_j^{(B)} | U_B(t) | \phi_k^{(B)}\rangle$$

$$= \sum_{ij} \overbrace{\langle \phi_j^{(B)} | \underbrace{U_B(t) U_B^+(t)}_{\mathbb{1}_B} | \phi_i^{(B)}\rangle}^{\delta_{ij}} \langle \phi_i^{(B)} | U_S^+(t)\, \hat{\rho}_{tot}(t)\, U_S(t) | \phi_j^{(B)}\rangle$$

$$= \sum_i U_S^+(t) \langle \phi_i^{(B)} | \hat{\rho}_{tot}(t) | \phi_i^{(B)}\rangle U_S(t) = \hat{\rho}_{red,I}$$

$\boxed{B}$ How does $\hat{\rho}_{red,I}$ appears on the RHS of (2.26) ?

We assume first of all that at until the initial time $t=0$ the system and the bath are uncorrelated $\Rightarrow$ $\hat{\rho}_{tot}(0) = \hat{\rho}_S \otimes \hat{\rho}_B$ with $\mathrm{Tr}_{S/B}\, \hat{\rho}_{S/B} = 1$. Additionally B is in thermal equilibrium:

$$\hat{\rho}_B(0) = \frac{e^{-\beta(\hat{H}_B - \mu \hat{N}_B)}}{Z_B} \qquad (1.296)$$

and its state is defined by the temperature $T = \frac{1}{k_B \beta}$ and chemical potential μ. Moreover

$$\rho_I(t) = U_I(t)\, \rho_S(0) \otimes \rho_B(0)\, U_I(t) = \rho_S(0) \otimes \rho_B(0) + \left(-\frac{i}{\hbar}\right)\int_0^t dt' \left[V_I(t'), \rho_S(0) \otimes \rho_B\right] + O(\hat{V}^2)$$

$$\Rightarrow \mathrm{Tr}_B\{\rho_I(t)\} \otimes \rho_B(0) = \rho_S(0) \otimes \rho_B(0) + O(\hat{V})$$

We can thus conclude

$$\rho_I(t) = \mathrm{Tr}_B\{\rho_I(t)\} \otimes \rho_B(0) + O(\hat{V}) \qquad (2.28)$$

The statement above is almost trivial if one understands it as: the coupling $\hat{V}$ introduces entanglements between system and bath, which we formally separate from the disentangled evolution $\rho_{red} \otimes \rho_B$.
At a still formally exact level we can write:

$$\hat{\rho}_I(t) = \mathrm{Tr}_B\{\hat{\rho}_I(t)\} \otimes \hat{\rho}_B(0) + \Delta\hat{\rho}.$$

And, consequently the equation:

$$\begin{aligned}\dot{\hat{\rho}}_{red,I}(t) = & -\frac{i}{\hbar}\mathrm{Tr}_B\{[\hat{V}_I(t), \hat{\rho}_S(0)\otimes\hat{\rho}_B(0)]\} \\ & -\frac{1}{\hbar^2}\int_0^t dt' \, \mathrm{Tr}_B\{[\hat{V}_I(t), [\hat{V}_I(t'), \hat{\rho}_{red,I}(t')\otimes\hat{\rho}_B(0)]]\} \\ & -\frac{1}{\hbar^2}\int_0^t dt' \, \mathrm{Tr}_B\{[\hat{V}_I(t), [\hat{V}_I(t'), \Delta\hat{\rho}]]\} \end{aligned} \qquad (2.29)$$

In a perturbative approach which stops at the II order in the interaction, the last line in (2.29) can be neglected and a GME is formally derived.

<u>Notice</u>: - In the case of higher order perturbative approaches $\Delta\hat{\rho}$ cannot be neglected.

- Eq. (2.29), even in its perturbative sense ($\Delta\hat{\rho}\to 0$) has memory since $\dot{\hat{\rho}}_{red,I}(t)$ depends on $\rho_{red,I}(t')$ with $0\le t'\le t$.

2.3.2 Bath correlation functions

Let's assume a bilinear system-bath interaction:

$$\hat{V} = \sum_i \hat{Q}_i \hat{F}_i \tag{2.30}$$

where $\hat{Q}_i$ only acts on the system and $\hat{F}_i$ on the bath B. In the interaction picture we obtain:

$$\hat{V}_I(t) = \hat{U}_0^+(t)\hat{V}\hat{U}_0(t) = \hat{U}_B^+(t)\hat{U}_S^+(t) V \hat{U}_S(t)\hat{U}_B(t) =$$

$$= \sum_i \hat{Q}_i(t)\hat{F}_i(t) = \sum_i \hat{U}_B^+(t)\hat{F}_i\hat{U}_B(t)\hat{U}_S^+(t)\hat{Q}_i\hat{U}_S(t) \tag{2.31}$$

The last equality in (2.31) is obtained under the conditions $[\hat{F}_i, \hat{U}_S(t)] = [\hat{Q}_i, \hat{U}_B(t)] = 0$ which is very natural for $\hat{H}_S$ and $\hat{H}_B$ which CONSERVE the particle number in S and B respectively => are formed by terms containing an even number of creation, annihilation operators.

By inserting (2.31) into (2.29) and using the cyclic property of the (partial) trace in the Bath subspace, one finds:

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{i}{\hbar}\sum_i \left[\hat{Q}_i(t), \hat{\rho}_S(0)\right] \mathrm{Tr}_B\left\{\hat{F}_i(t)\,\hat{\rho}_B(0)\right\}$$

$$-\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \left[\hat{Q}_i(t)\hat{Q}_j(t')\hat{\rho}_{red,I}(t') - \hat{Q}_j(t')\hat{\rho}_{red,I}\hat{Q}_i(t)\right]\mathrm{Tr}_B\left\{\hat{F}_i(t)\hat{F}_j(t')\,\hat{\rho}_B\right\}$$

$$-\left[\hat{Q}_i(t)\hat{\rho}_{red,I}(t')\hat{Q}_j(t') - \hat{\rho}_{red,I}\hat{Q}_j(t')\hat{Q}_i(t)\right]\mathrm{Tr}_B\left\{\hat{F}_j(t')\hat{F}_i(t)\,\hat{\rho}_B\right\}$$

$$+ O(\hat{V}^3) \tag{2.32}$$

Consider now the expectation values

$$\langle \hat{F}_i(t)\rangle_B \equiv \mathrm{Tr}_B\left\{\hat{F}_i(t)\,\rho_B\right\} \quad \text{and}$$

$$\langle \hat{F}_i(t)\hat{F}_j(t')\rangle_B \equiv \mathrm{Tr}_B\left\{\hat{F}_i(t)\hat{F}_j(t')\,\rho_B\right\}$$

i)

$$\langle \hat{F}_i(t) \rangle_B = \sum_{Nn, Mm} \langle Nn | F_i(t) | Mm \rangle \langle Mm | \rho_B | Nn \rangle$$

$$= \sum_{Nn} \frac{1}{Z} \langle Nn | F_i | Nn \rangle \, e^{-\beta(E_{N,n} - N\mu)} = \langle \hat{F} \rangle_B$$

In case $\langle \hat{F} \rangle_B \neq 0$ one can redefine the interaction Hamiltonian as $\tilde{V} = \sum_i (\hat{F}_i - \langle \hat{F}_i \rangle) \hat{Q}_i$ and $\tilde{H}_S = \hat{H}_S + \sum_i \langle F_i \rangle \hat{Q}_i$. It is thus not a loss of generality to ensure $\langle F_i \rangle = 0$ and neglect the linear order in $\hat{V}$ in (2.32)

ii)

$$\langle \hat{F}_i(t) \hat{F}_j(t') \rangle_B = \mathrm{Tr}_B \{ \hat{F}_i(t) \hat{F}_j(t') \hat{\rho}_B \} =$$

$$= \mathrm{Tr}_B \{ \hat{U}_B^+(t) \hat{F}_i \hat{U}_B(t) \hat{U}_B^+(t') \hat{F}_j \hat{U}_B(t') \hat{\rho}_B \} = \quad \rho_B \text{ is not evolving in time}$$

$$\overset{\text{cyclic property of } \mathrm{Tr}_B}{=} \mathrm{Tr}_B \{ \hat{U}_B(t') \hat{U}_B^+(t) \hat{F}_i \hat{U}_B(t) \hat{U}_B^+(t') \hat{F}_j \hat{\rho}_B \} =$$

$$= \mathrm{Tr}_B \{ \hat{F}_i(t-t') \hat{F}_j \hat{\rho}_B \} = \langle \hat{F}_i(t-t') \hat{F}_j \rangle_B \qquad (2.33)$$

The function $\langle \hat{F}_i(t) \hat{F}_j(t') \rangle_B$ – the bath correlation function – only depends on the time difference. Summarizing:

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{1}{\hbar^2} \sum_{ij} \int_0^t dt' \{ [\hat{Q}_i(t), \hat{Q}_j(t') \rho_{red,I}(t')] \, F_{ij}^{(B)}(t-t')$$

$$- [\hat{Q}_i(t), \rho_{red,I}(t') \hat{Q}_j(t')] \, F_{ji}^{(B)}(t'-t) \} + O(V^3)$$

where $F_{ij}^{(B)}(\tau) = \mathrm{Tr}_B \{ \hat{F}_i(\tau) \hat{F}_j(0) \hat{\rho}_B \}$. $\qquad (2.34)$