

## 2.5 Alternative approaches to the GME for the RDM

### 2.5.1 The projector operator technique (Nakajima-Zwanzig 1958)

For the derivation of the GME according to the projector-operator technique one starts from the Liouville-von Neumann equation

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] \equiv \mathcal{L}\rho$$

The equation above admits a very simple solution if  $\mathcal{L}$  is not explicitly time dependent  $\rho(t) = e^{\mathcal{L}t} \rho_0$  where  $\rho_0 = \rho(t=0)$ .

Our interest, though, is in a perturbative approach to a system-bath model:

$$H = H_S + H_B + V$$

where  $V$  represents the coupling between the system and the bath.

For this reason we introduce the projector:

$$\left\{ \begin{array}{l} \mathcal{P}: \mathcal{P}\rho = \text{Tr}_B \{ \rho \} \otimes \rho_B \\ \mathcal{Q} = 1 - \mathcal{P} \end{array} \right. \quad (2.76)$$

where  $\rho_B$  is a reference bath state. Typically one assumes  $\rho_B$  to be the thermal equilibrium state of the bath.

Notice that the following equations hold:

$$\left\{ \begin{array}{l} \mathcal{P}^2 = \mathcal{P} \\ \mathcal{Q}^2 = \mathcal{Q} \end{array} \right. \quad (2.77)$$

from which it follows immediately  $\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$

proof of (2.77)

$$\rho^2 = \text{Tr}_B \{ \text{Tr}_B \{ \rho \} \otimes \rho_B \} \otimes \rho_B = \text{Tr}_B \{ \rho \} \overset{1}{\text{Tr}_B \rho_B} \otimes \rho_B = \rho$$

$$Q^2 = (1 - P)(1 - P) = 1 - 2P + P^2 = 1 - P = Q$$

Using the property  $P + Q = 1$  which follows directly from the definition of the projector operators  $P, Q$ , we can write:

$$\begin{cases} P\dot{\rho}(t) = P\mathcal{L}P\rho(t) + P\mathcal{L}Q\rho(t) \\ Q\dot{\rho}(t) = Q\mathcal{L}P\rho(t) + Q\mathcal{L}Q\rho(t) \end{cases} \quad (2.78)$$

The system of equations (2.78) is completely equivalent to the Liouville von Neumann equation. The second equation in (2.78) is formally solved by introducing the propagator

$$G_Q(t, s) = e^{Q\mathcal{L}(t-s)} \quad (2.79)$$

In fact we can rewrite the second of (2.78) as:

$$Q\dot{\rho} - Q\mathcal{L}Q\rho = Q\mathcal{L}P\rho$$

Now we multiply from the left by  $G_Q(0, t)$

$$\underbrace{G_Q(0, t)Q\dot{\rho} - G_Q(0, t)Q\mathcal{L}Q\rho}_{\frac{d}{dt} [G_Q(0, t)Q\rho]} = G_Q(0, t)Q\mathcal{L}P\rho$$

$$\frac{d}{dt} [G_Q(0, t)Q\rho]$$

Integrating on both sides we obtain

$$G_Q(0, t)Q\rho - Q\rho(0) = \int_0^t ds G_Q(0, s)Q\mathcal{L}P\rho(s)$$

Finally we multiply by  $G_Q(t,0)$  from the left and solve for  $\rho_f$

$$\rho_f = G_Q(t,0) \rho_f(0) + \int_0^t ds G_Q(t,s) Q_L \rho_f(s) \quad (2.80)$$

If now we plug (2.80) into the first of 2.78 we obtain

$$\dot{\rho}_f(t) = Q_L \rho_f(t) + Q_L G_Q(t,0) \rho_f(0) + \int_0^t ds Q_L G_Q(t,s) Q_L \rho_f(s) \quad (2.81)$$

Eq. 2.81 is already a closed equation in  $\rho_f \Rightarrow$  an equation for the reduced density matrix. We can though specialize slightly the result if we assume

- $\rho(0) = \rho_S(0) \otimes \rho_B \Rightarrow \rho_f(0) = \rho_S(0) \otimes \rho_B - \text{Tr}_B \{ \rho_S(0) \otimes \rho_B \} \otimes \rho_B = 0$
- We can consider  $V = H_T$  as a tunnelling coupling between system and bath.  $\Rightarrow H_T$  does NOT conserve particle number of the bath.

We define  $ihL_T \equiv -[H_T, \cdot]$  and conclude that

$$Q_L \rho_f = \text{Tr}_B \{ [H_T, \text{Tr}_B \{ \rho_f \} \otimes \rho_B] \} \otimes \rho_B = 0 \quad \forall \rho_f$$

Formally one writes  $\boxed{Q_L \rho = 0} \quad (2.82)$

$$\rho_B = e^{-\beta(H_B - \mu N_B)} \quad \text{and} \quad [H_B, N_B] = 0 \Rightarrow [\rho_B, H_B] = 0$$

$$\Rightarrow ihL_B \rho_f = [H_B, \text{Tr}_B \{ \rho_f \} \otimes \rho_B] = \text{Tr}_B \{ \rho_f \} \otimes [H_B, \rho_B] = 0$$

On the other hand one also notices that

$$\begin{aligned}
 i\hbar \rho \mathcal{L}_B \rho &= \text{Tr}_B \{ [H_B, \rho] \} \otimes \rho_B = \\
 &= \sum_{N_B, \alpha} \langle N_B, \alpha | H_B \rho | N_B, \alpha \rangle \otimes \rho_B - \langle N_B, \alpha | \rho H_B | N_B, \alpha \rangle \otimes \rho_B = 0
 \end{aligned}$$

$\Rightarrow$  we can formally conclude  $\boxed{[\mathcal{L}_B, \rho] = \mathcal{L}_B \rho = 0}$  (2.83)

It follows immediately that  $\boxed{[\mathcal{L}_B, Q] = 0}$

• Eventually we observe also that  $[H_S, \rho_B] = 0$ . At the level of the superoperator we can conclude that

$$\boxed{[\rho, \mathcal{L}_S] = [Q, \mathcal{L}_S] = 0} \quad (2.84)$$

proof of (2.84)

$$\begin{aligned}
 i\hbar \rho \mathcal{L}_S \rho &= \text{Tr}_B \{ [H_S, \rho] \} \otimes \rho_B = \sum_{N_B, \alpha} \langle N_B, \alpha | H_S \rho - \rho H_S | N_B, \alpha \rangle \otimes \rho_B \\
 &= [H_S \text{Tr}_B \{ \rho \} - \text{Tr}_B \{ \rho \} H_S] \otimes \rho_B = [H_S, \text{Tr}_B \{ \rho \} \otimes \rho_B] \\
 &= i\hbar \mathcal{L}_S \rho
 \end{aligned}$$

$$[Q, \mathcal{L}_S] = [1 - \rho, \mathcal{L}_S] = [1, \mathcal{L}_S] - [\rho, \mathcal{L}_S] = 0.$$

Now we can combine all previous observations to simplify (2.81) term by term.

■ The first term:

$$\begin{aligned} \rho_L \rho_f &= \rho (L_S + L_B + L_T) \rho_f = \rho L_S \rho_f + \cancel{\rho L_B \rho_f} + \cancel{\rho L_T \rho_f} \\ &= L_S \rho_f^2 = L_S \rho_f. \end{aligned}$$

Alternatively one can also keep  $\underbrace{(L_S + L_B)}_{:= L_0} \rho_f$

■ The second term:

$$\rho_L G_Q(t, 0 | Q_f(0)) = \rho_L G_Q(t, 0 | Q(f_S(0) \otimes f_B)) = 0$$

■ The integral

$$\rho_L G_Q(t, s | Q_L \rho_f(s))$$

In general one can prove the relation

$$\rho_L e^{Q_L t} Q_L \rho = \rho_{L_T} e^{(L_S + L_B + Q_L T Q)t} L_T \rho \quad (2.85)$$

proof

$$\begin{aligned} \rho_L e^{Q_L t} Q_L \rho &= \rho_L \sum_{n=0}^{\infty} \frac{1}{n!} (Q_L)^n t^n Q_L \rho = \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \rho_L (Q_L)^n Q_L \rho t^n \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \rho_L Q (Q_L Q)^n Q_L \rho t^n \end{aligned}$$

Now we make the following observations

$$* \rho_L Q = \rho L_S Q + \cancel{\rho L_B Q} + \rho L_T Q = \cancel{L_S \rho Q} + \rho L_T Q = \rho L_T Q = \rho_{L_T}$$

$$* Q_L \rho = Q L_S \rho + \cancel{Q L_B \rho} + Q L_T \rho = \cancel{Q \rho L_S} + Q L_T \rho = Q L_T \rho = L_T \rho$$

$$* Q_L Q = Q L_B Q + Q L_S Q + Q L_T Q = Q (L_B + L_S + Q L_T Q)$$

Since, moreover  $[Q, L_B] = [Q, L_S] = [Q, Q L_T Q] = 0$

$$\Rightarrow [Q(L_B + L_S + Q L_T Q)]^n = Q^n (L_B + L_S + Q L_T Q)^n = Q(L_B + L_S + Q L_T Q)^n$$

Finally

$$\begin{aligned} \rho_L e^{Q L_T t} Q L_T \rho &= \rho L_T Q \sum_n \frac{t^n}{n!} (L_S + L_B + Q L_T Q)^n L_T \rho = \\ &= \rho L_T e^{(L_S + L_B + Q L_T Q)t} L_T \rho \end{aligned}$$

We can now return to the (2.81):

$$\rho_f(t) = L_S \rho_f(t) + \int_0^t \rho L_T e^{(L_S + L_B + Q L_T Q)(t-s)} L_T \rho_f(s) \quad (2.86)$$

The equation above clearly shows how the kernel of the GME has a convolutive form for all orders in the tunnelling coupling. Moreover, it is interesting to identify in (2.86) the "propagator"  $\bar{G}_Q(t, s) \equiv \exp(L_S + L_B + Q L_T Q)(t-s)$ . This propagator satisfies the following perturbative (Dyson) equation

$$\bar{G}_Q(t, s) = G_0(t, s) + \int_s^t dt' G_0(t, t') Q L_T Q \bar{G}_Q(t', s) \quad (2.87)$$

proof:

$$\frac{\partial}{\partial t} \bar{G}_Q(t, s) = (L_S + L_B) \bar{G}_Q(t, s) + Q L_T Q \bar{G}_Q(t, s)$$

$$\text{But } G_0(s, t) = e^{-(L_S + L_B)(t-s)}$$

$$\Rightarrow \frac{\partial}{\partial t} [G_0(s, t) \bar{G}_Q(t, s)] = G_0(s, t) Q L_T Q \bar{G}_Q(t, s)$$

By integration between  $s$  and  $t$  we obtain

$$G_0(s, t) \bar{G}_Q(t, s) - 1 = \int_s^t dt' G_0(s, t') Q L_T Q \bar{G}_Q(t', s)$$

Finally, by multiplying on both sides by  $G_0(t, s)$  we obtain (2.87)

An analogous Dyson equation can also be obtained for the propagator of the factorized part of the density matrix. Eq.

(2.86) can in fact be rewritten as ( $d_B \rho = 0!$ )

$$\dot{\rho}(t) - L_0 \rho(t) = \int_0^t ds \rho L_T \bar{G}_Q(t, s) L_T \rho(s)$$

We use again the free propagator  $G_0(0, t) = e^{-L_0 t}$  to obtain

$$\frac{d}{dt} [G_0(0, t) \rho(t)] = G_0(0, t) \int_0^t ds \rho L_T \bar{G}_Q(t, s) L_T \rho(s)$$

and, by integration and multiplication by  $G_0(t, 0)$

$$\rho(t) = G_0(t, 0) \rho(0) + \int_0^t ds' G_0(t, s') \int_0^{s'} ds \rho L_T \bar{G}_Q(s', s) L_T \rho(s)$$

We can finally introduce the propagator  $G_P(t, s)$  for the factorized component of the density matrix as:

$$\rho(t) = G_P(t, s) \rho(s) \quad (2.88)$$

And obtain:

$$\left\{ \begin{aligned} G_P(t, 0) &= G_0(t, 0) + \int_0^t ds' \int_0^{s'} ds G_0(t, s') \rho L_T \bar{G}_Q(s', s) L_T \rho G_P(s, 0) \\ \bar{G}_Q(s', s) &= G_0(s', s) + \int_s^{s'} ds'' G_0(s', s'') Q L_T Q \bar{G}_Q(s'', s) \end{aligned} \right. \quad (2.89)$$

Thanks to their convolution form eq. (2.89) here a simple algebraic form in Laplace space:

$$\begin{cases} \tilde{G}_P(\lambda) = \tilde{G}_0(\lambda) + \tilde{G}_0(\lambda) P \mathcal{L}_T \tilde{G}_Q(\lambda) \mathcal{L}_T P \tilde{G}_P(\lambda) \\ \tilde{G}_Q(\lambda) = \tilde{G}_0(\lambda) + \tilde{G}_0(\lambda) Q \mathcal{L}_T Q \tilde{G}_Q(\lambda) \end{cases} \quad (2.90)$$

We can formally introduce the super-operators  $\tilde{\Sigma}_Q = Q \mathcal{L}_T Q$  and  $\tilde{\Sigma}_P(\lambda) = P \mathcal{L}_T \tilde{G}_Q(\lambda) \mathcal{L}_T P$  and obtain

$$\begin{cases} \tilde{G}_P(\lambda) = [1 - \tilde{G}_0(\lambda) \tilde{\Sigma}_P(\lambda)]^{-1} \tilde{G}_0(\lambda) \\ \tilde{G}_Q(\lambda) = [1 - \tilde{G}_0(\lambda) \tilde{\Sigma}_Q]^{-1} \tilde{G}_0(\lambda) \end{cases} \quad (2.91)$$

$$\tilde{G}_0(\lambda) = \int_0^{\infty} dt e^{(\mathcal{L}_0 - \lambda)t} = \frac{1}{\lambda - \mathcal{L}_0} \quad \text{we thus obtain}$$

$$\begin{cases} \tilde{G}_P(\lambda) = [\lambda - \mathcal{L}_0 - \tilde{\Sigma}_P(\lambda)]^{-1} = [\lambda - \mathcal{L}_0 - P \mathcal{L}_T [\lambda - \mathcal{L}_0 - Q \mathcal{L}_T Q] \mathcal{L}_T P]^{-1} \\ \tilde{G}_Q(\lambda) = [\lambda - \mathcal{L}_0 - Q \mathcal{L}_T Q]^{-1} \end{cases} \quad (2.92)$$

The equations above can be used, for example, to calculate the stationary density matrix up to an arbitrary perturbative order in the coupling between the system and the bath.

On one hand we have

$$\lim_{t \rightarrow \infty} \rho_P(t) = \lim_{t \rightarrow \infty} G_P(t, 0) \rho(0)$$



Due to the final value theorem it holds, in general that,  
given

$$\tilde{f}(\lambda) = \int_0^{\infty} dt f(t) e^{-\lambda t}$$

$$\lim_{t \rightarrow \infty} f(t) = \lim_{\lambda \rightarrow 0^+} \lambda \tilde{f}(\lambda) \quad (2.93)$$

proof:

$$\lim_{\lambda \rightarrow 0^+} \int_0^{\infty} dt e^{-\lambda t} f'(t) = \lim_{t \rightarrow \infty} f(t) - f(0)$$

||

$$\lim_{\lambda \rightarrow 0^+} \left( e^{-\lambda t} f(t) \Big|_0^{\infty} + \lambda \int_0^{\infty} dt e^{-\lambda t} f(t) \right) = -f(0) + \lim_{\lambda \rightarrow 0^+} \lambda \tilde{f}(\lambda)$$

In our specific case we have thus:

$$\rho_p(\infty) = \lim_{\lambda \rightarrow 0^+} \lambda \tilde{G}_p(\lambda) \rho(0) = \lim_{\lambda \rightarrow 0^+} \lambda [\lambda - \lambda_0 - \tilde{\Sigma}_p(\lambda)]^{-1} \rho_p(0)$$

If we multiply both sides by  $[\lambda - \lambda_0 - \tilde{\Sigma}_p(\lambda)]$  we obtain the equation satisfied by  $\rho(\infty)$

$$\boxed{[\lambda_s + \tilde{\Sigma}_p(0)] \rho_p(\infty) = 0} \quad (2.94)$$

where we have used again the fact that  $\lambda_s \rho = 0$ . If we consider the general formulation (in Schrödinger picture)

$$\rho_p^{\dot{}} = \lambda_s \rho_p + \int_0^t ds k(t-s) \rho_p(s)$$

we can again go into the Laplace space and obtain

$$\lambda \rho \tilde{p}(\lambda) - p_0 = L_S \rho \tilde{p}(\lambda) + \tilde{k}(\lambda) \rho \tilde{p}(\lambda)$$

If one multiplies by  $\lambda$  and takes the limit  $\lambda \rightarrow 0^+$  one obtains

$$\lim_{\lambda \rightarrow 0^+} \lambda^2 \rho \tilde{p}(\lambda) - \lambda p_0 = \lim_{\lambda \rightarrow 0^+} [L_S + \tilde{k}(\lambda)] \lambda \rho \tilde{p}(\lambda)$$

$$0 = [L_S + \tilde{k}(0)] \rho p(\infty) \quad (2.95)$$

The comparison between (2.94) and (2.95) allows one to identify

$$\tilde{k}(0) = \tilde{\Sigma}_P(0) \quad (2.96)$$

By expanding  $\tilde{\Sigma}_P(0)$  in power series of  $L_T$  one obtains

$$\tilde{\Sigma}_P(0) = \lim_{\lambda \rightarrow 0^+} \rho L_T \sum_{n=0}^{\infty} \left( \tilde{G}_0(\lambda) Q L_T Q \right)^n \tilde{G}_0(\lambda) L_T \rho$$

$$= \lim_{\lambda \rightarrow 0^+} \rho L_T \sum_{n=0}^{\infty} \left( \tilde{G}_0(\lambda) Q L_T Q \tilde{G}_0(\lambda) Q L_T Q \right)^n \tilde{G}_0(\lambda) L_T \rho$$

$$= \lim_{\lambda \rightarrow 0^+} \rho L_T \left[ \lambda - L_0 - Q L_T Q \tilde{G}_0(\lambda) Q L_T Q \right]^{-1} L_T \rho$$

(\*) This equality follows from the observation that only an even number of tunnelling Liouvillean give a non vanishing contribution when sandwiched between  $\rho$  operators.

$$\tilde{k}^{(2)}(0) = \lim_{\lambda \rightarrow 0^+} \rho L_T \frac{1}{\lambda - L_0} L_T \rho \quad (2.97)$$

$$\tilde{k}^{(4)}(0) = \lim_{\lambda \rightarrow 0^+} \rho L_T \frac{1}{\lambda - L_0} Q L_T Q \frac{1}{\lambda - L_0} Q L_T Q \frac{1}{\lambda - L_0} L_T \rho$$

The direct comparison between the Nakajima-Zwanzig and the iterative method of derivation of the GME will be performed in the interaction picture. To this extent it is instructive to make the following mapping between Hilbert space and Liouville space:

Hilbert space

Liouville space

Eq. of motion  $|\dot{\psi}\rangle = -\frac{i}{\hbar} H |\psi\rangle$

$$\dot{\rho} = \mathcal{L} \rho$$

Evolution  $U(t,0) = e^{-\frac{i}{\hbar} H t}$

$$G(t,0) = e^{\mathcal{L} t}$$

$$U_0(t,0) = e^{-\frac{i}{\hbar} H_0 t}$$

$$G_0(t,0) = e^{\mathcal{L}_0 t}$$

Interaction picture  $|\psi_I\rangle = U_0^\dagger(t,0) |\psi\rangle$

$$\rho_I(t) = G_0(0,t) \rho(t)$$

$$A_I = U_0^\dagger(t,0) A_S U_0(t,0)$$

$$\text{ex. } A_I(t) = G_0(0,t) A G_0(t,0)$$

The "vectors" of the Liouville space are the density operators. The operators are represented by all superoperator acting on the density operator, like for example the tumbling Liouvilleon  $\mathcal{L}_T = [H_T, \cdot]$

The propagator in interaction picture  $G_I(t,0) = G_0(0,t) G(t,0)$ , thus, from (2.89) we obtain:

$$\begin{aligned} G_{P,I}(t,0) &= G_0(0,t) G_0(t,0) + \int_0^t ds' \int_0^{s'} ds G_0(0,t) G_0(t,s') \mathcal{P} \mathcal{L}_T \bar{G}_Q(s',s) \mathcal{L}_T \mathcal{P} G_P(s,0) \\ &= 1 + \int_0^t ds' \int_0^{s'} ds \mathcal{P} G_0(0,s') \mathcal{L}_T G_0(s',0) \bar{G}_Q(0,s') \bar{G}_Q(s',s) G_0(s,0) \\ &\quad G_0(0,s) \mathcal{L}_T G_0(s,0) \mathcal{P} G_{P,I}(s,0) \\ &= 1 + \int_0^t ds' \int_0^{s'} ds \mathcal{P} \mathcal{L}_{T,I}(s') G_0(0,s') \bar{G}_Q(s',s) G_0(s,0) \mathcal{L}_{T,I}(s) \mathcal{P} G_{P,I}(s,0) G_I \end{aligned}$$

On the other side

$$G_0(0, s') \bar{G}_Q(s', s) G_0(s, 0) \equiv \bar{G}_{Q, I}(s', s)$$

$$= 1 + \int_s^{s'} ds'' G_0(0, s'') Q L_T Q G_0(s'', 0) G_0(0, s'') \bar{G}_Q(s'', s) G_0(s, s'')$$

$$= 1 + \int_s^{s'} ds'' Q L_{T, I}(s'') Q \bar{G}_{Q, I}(s'', s)$$

Summarizing

$$\left\{ \begin{aligned} G_{P, I}(t, 0) &= 1 + \int_0^t ds' \int_0^{s'} ds Q L_{T, I}(s') \bar{G}_{Q, I}(s', s) L_{T, I}(s) Q G_{P, I}(s, 0) \\ \bar{G}_{Q, I}(s', s) &= 1 + \int_s^{s'} ds'' Q L_{T, I}(s'') Q \bar{G}_{Q, I}(s'', s) \end{aligned} \right. \quad (2.98)$$

$\bar{G}_{Q, I}(s', s)$  to lowest order is 1. It follows that, to lowest non vanishing order:

$$\frac{d}{dt} G_{P, I}(t) = \int_0^t dt' Q L_{T, I}(t) L_{T, I}(t') Q G_{P, I}(t', 0)$$

or in other terms, by applying the <sup>super-</sup>operator above to  $\rho_{I(0)} = \rho_I(0)$ .

$$\frac{d}{dt} \rho_{I(t)} = \int_0^t dt' Q L_{T, I}(t) L_{T, I}(t') Q \rho_I(t') \quad (2.99)$$

which coincides with eq. (2.29) if we trace on both sides over the both degrees of freedom.