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 projectors:

$$\begin{cases} \mathcal{P}: \ \mathcal{P}\rho = \mathrm{Tr}_B\{\rho\} \otimes \rho_B \\ \mathcal{Q} = 1 - \mathcal{P} \end{cases} \qquad (2.76)$$

where ρ_B is a reference bath state. Typically one assumes ρ_B to be the thermal equilibrium state of the bath.
Notice that the following equations hold:

$$\begin{cases} \mathcal{P}^2 = \mathcal{P} \\ \mathcal{Q}^2 = \mathcal{Q} \end{cases} \qquad (2.77)$$

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

proof of (2.77)

$$\mathcal{P}^2\rho = \mathrm{Tr}_B\{\mathrm{Tr}_B\{\rho\}\otimes\rho_B\}\otimes\rho_B = \mathrm{Tr}_B\{\rho\}\underbrace{\mathrm{Tr}_B\,\rho_B}_{=1}\otimes\rho_B = \mathcal{P}\rho$$

$$Q^2 = (1-\mathcal{P})(1-\mathcal{P}) = 1 - 2\mathcal{P} + \mathcal{P}^2 = 1-\mathcal{P} = Q.$$

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

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

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

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

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

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

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

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

Integrating on both sides we obtain

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

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

$$Q\rho = G_Q(t,0)\,Q\rho(0) + \int_0^t ds\; G_Q(t,s)\,Q\mathcal{L}\mathcal{P}\rho(s) \qquad (2.80)$$

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

$$\mathcal{P}\dot\rho(t) = \mathcal{P}\mathcal{L}\mathcal{P}\rho(t) + \mathcal{P}\mathcal{L}\,G_Q(t,0)\,Q\rho(0) + \int_0^t ds\; \mathcal{P}\mathcal{L}\,G_Q(t,s)\,Q\mathcal{L}\mathcal{P}\rho(s) \qquad (2.81)$$

Eq. 2.81 is already a closed equation in $\mathcal{P}\rho$ => an equation for the reduced density matrix. We can though specialize slightly the result if we assume

- $\rho(0) = \rho_S(0)\otimes\rho_B \;\; \Rightarrow \;\; Q\rho(0) = \rho_S(0)\otimes\rho_B - \mathrm{Tr}_B\{\rho_S(0)\otimes\rho_B\}\otimes\rho_B = 0$

- We can consider $V = H_T$ as a tunnelling coupling between system and bath. => H_T does NOT conserves particle number of the bath.

We define $i\hbar\mathcal{L}_T \equiv [H_T, \cdot\,]$ and conclude that

$$\mathcal{P}\mathcal{L}_T\mathcal{P}\rho = \mathrm{Tr}_B\{[H_T, \mathrm{Tr}_B\{\rho\}\otimes\rho_B]\}\otimes\rho_B = 0 \quad \forall\rho.$$

Formally one writes $\boxed{\mathcal{P}\mathcal{L}_T\mathcal{P} = 0}$ (2.82)

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

$$\Rightarrow i\hbar\mathcal{L}_B\mathcal{P}\rho = [H_B, \mathrm{Tr}_B\{\rho\}\otimes\rho_B] = \mathrm{Tr}_B\{\rho\}\otimes[H_B, \rho_B] = 0$$

On the other hand one also notices that

$$i\hbar\,\mathcal{P}\mathcal{L}_B\rho = \mathrm{Tr}_B\{[H_B,\rho]\}\otimes\rho_B =$$

$$= \sum_{N_B\,\alpha} \langle N_B,\alpha|H_B\,\rho|N_B,\alpha\rangle\otimes\rho_B - \langle N_B,\alpha|\rho\,H_B|N_B,\alpha\rangle\otimes\rho_B = 0$$

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

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

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

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

proof of (2.84)

$$i\hbar\,\mathcal{P}\mathcal{L}_S\rho = \mathrm{Tr}_B\{[H_S,\rho]\}\otimes\rho_B = \sum_{N_B,\alpha}\langle N_B,\alpha|H_S\rho-\rho H_S|N_B,\alpha\rangle\otimes\rho_B$$

$$= \left[H_S\,\mathrm{Tr}_B\{\rho\} - \mathrm{Tr}_B\{\rho\}H_S\right]\otimes\rho_B = \left[H_S,\mathrm{Tr}_B\{\rho\}\otimes\rho_B\right]$$

$$= i\hbar\,\mathcal{L}_S\mathcal{P}\rho$$

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

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

- The first term:

$$\mathcal{P}\mathcal{L}\mathcal{P}\rho = \mathcal{P}(\mathcal{L}_S + \mathcal{L}_B + \mathcal{L}_T)\mathcal{P}\rho = \mathcal{P}\mathcal{L}_S\mathcal{P}\rho + \cancel{\mathcal{P}\mathcal{L}_B\mathcal{P}\rho} + \cancel{\mathcal{P}\mathcal{L}_T\mathcal{P}\rho}$$

$$= \mathcal{L}_S\mathcal{P}^2\rho = \mathcal{L}_S\mathcal{P}\rho .$$

Alternatively one can also keep $\underbrace{(\mathcal{L}_S + \mathcal{L}_B)}_{:=\mathcal{L}_0}\mathcal{P}\rho$

- The second term:

$$\mathcal{P}\mathcal{L}\, G_Q(t,0)\mathcal{Q}\rho(0) = \mathcal{P}\mathcal{L}\, G_Q(t,0)\,\mathcal{Q}\left(\rho_S(0)\otimes\rho_B\right) = 0$$

- The integrand

$$\mathcal{P}\,\mathcal{L}\, G_Q(t,s)\mathcal{Q}\mathcal{L}\mathcal{P}\rho(s)$$

In general one can prove the relation

$$\mathcal{P}\mathcal{L}\, e^{\mathcal{Q}\mathcal{L}t}\,\mathcal{Q}\mathcal{L}\mathcal{P} = \mathcal{P}\mathcal{L}_T\, e^{(\mathcal{L}_S + \mathcal{L}_B + \mathcal{Q}\mathcal{L}_T\mathcal{Q})t}\,\mathcal{L}_T\mathcal{P} \qquad (2.85)$$

proof

$$\mathcal{P}\mathcal{L}\, e^{\mathcal{Q}\mathcal{L}t}\,\mathcal{Q}\mathcal{L}\mathcal{P} = \mathcal{P}\mathcal{L}\sum_{n=0}^{\infty}\frac{1}{n!}(\mathcal{Q}\mathcal{L})^n t^n\,\mathcal{Q}\mathcal{L}\mathcal{P} =$$

$$= \sum_{n=0}^{\infty}\frac{1}{n!}\,\mathcal{P}\mathcal{L}(\mathcal{Q}\mathcal{L})^n\mathcal{Q}\mathcal{L}\mathcal{P}\, t^n$$

$$= \sum_{n=0}^{\infty}\frac{1}{n!}\,\mathcal{P}\mathcal{L}\mathcal{Q}(\mathcal{Q}\mathcal{L}\mathcal{Q})^n\,\mathcal{Q}\mathcal{L}\mathcal{P}\, t^n$$

Now we make the following observations

* $\mathcal{P}\mathcal{L}\mathcal{Q} = \mathcal{P}\mathcal{L}_S\mathcal{Q} + \cancel{\mathcal{P}\mathcal{L}_B\mathcal{Q}} + \mathcal{P}\mathcal{L}_T\mathcal{Q} = \cancel{\mathcal{L}_S\mathcal{P}\mathcal{Q}} + \mathcal{P}\mathcal{L}_T\mathcal{Q} = \mathcal{P}\mathcal{L}_T\mathcal{Q} = \mathcal{P}\mathcal{L}_T$
* $\mathcal{Q}\mathcal{L}\mathcal{P} = \mathcal{Q}\mathcal{L}_S\mathcal{P} + \cancel{\mathcal{Q}\mathcal{L}_B\mathcal{P}} + \mathcal{Q}\mathcal{L}_T\mathcal{P} = \cancel{\mathcal{Q}\mathcal{P}\mathcal{L}_S} + \mathcal{Q}\mathcal{L}_T\mathcal{P} = \mathcal{Q}\mathcal{L}_T\mathcal{P} = \mathcal{L}_T\mathcal{P}$
* $\mathcal{Q}\mathcal{L}\mathcal{Q} = \mathcal{Q}\mathcal{L}_B\mathcal{Q} + \mathcal{Q}\mathcal{L}_S\mathcal{Q} + \mathcal{Q}\mathcal{L}_T\mathcal{Q} = \mathcal{Q}\left(\mathcal{L}_B + \mathcal{L}_S + \mathcal{Q}\mathcal{L}_T\mathcal{Q}\right)$

Since, moreover $[Q, \mathcal{L}_B] = [Q, \mathcal{L}_S] = [Q, Q\mathcal{L}_T Q] = 0$

$$\Rightarrow \left[Q(\mathcal{L}_B + \mathcal{L}_S + Q\mathcal{L}_T Q)\right]^n = Q^n (\mathcal{L}_B + \mathcal{L}_S + Q\mathcal{L}_T Q)^n = Q(\mathcal{L}_B + \mathcal{L}_S + Q\mathcal{L}_T Q)^n$$

Finally

$$\mathcal{P}\mathcal{L}\, e^{Q\mathcal{L}t} Q\mathcal{L}\mathcal{P} = \mathcal{P}\mathcal{L}_T Q \sum_n \frac{t^n}{n!} (\mathcal{L}_S + \mathcal{L}_B + Q\mathcal{L}_T Q)^n \mathcal{L}_T \mathcal{P} =$$

$$= \mathcal{P}\mathcal{L}_T\, e^{(\mathcal{L}_S + \mathcal{L}_B + Q\mathcal{L}_T Q)t} \mathcal{L}_T \mathcal{P}$$

■

We can now return to the (2.81):

$$\mathcal{P}\dot{\rho}(t) = \mathcal{L}_S \mathcal{P}\rho(t) + \int_0^t \mathcal{P}\mathcal{L}_T\, e^{(\mathcal{L}_S + \mathcal{L}_B + Q\mathcal{L}_T Q)(t-s)} \mathcal{L}_T \mathcal{P}\rho(s) \qquad (2.86)$$

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

$$\bar{G}_Q(t,s) = G_0(t,s) + \int_s^t dt'\, G_0(t,t') Q\mathcal{L}_T Q\, \bar{G}_Q(t',s) \qquad (2.87)$$

proof:

$$\frac{\partial}{\partial t} \bar{G}_Q(t,s) = (\mathcal{L}_S + \mathcal{L}_B)\bar{G}_Q(t,s) + Q\mathcal{L}_T Q\, \bar{G}_Q(t,s)$$

But $G_0(s,t) = e^{-(\mathcal{L}_S + \mathcal{L}_B)(t-s)}$

$$\Rightarrow \frac{\partial}{\partial t}\left[G_0(s,t)\bar{G}_Q(t,s)\right] = G_0(s,t) Q\mathcal{L}_T Q\, \bar{G}_Q(t,s)$$

By integration between s and t we obtain

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

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 ($\mathcal{L}_B\mathcal{P} = 0$!)

$$\mathcal{P}\dot{\rho}(t) - \mathcal{L}_0\,\mathcal{P}\rho(t) = \int_0^t ds\; \mathcal{P}\mathcal{L}_T\,\bar{G}_Q(t,s)\,\mathcal{L}_T\mathcal{P}\rho(s)$$

We use again the free propagator $G_0(0,t) = e^{-\mathcal{L}_0 t}$ to obtain

$$\frac{d}{dt}\left[G_0(0,t)\,\mathcal{P}\rho(t)\right] = G_0(0,t)\int_0^t ds\; \mathcal{P}\mathcal{L}_T\,\bar{G}_Q(t,s)\,\mathcal{L}_T\mathcal{P}\rho(s)$$

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

$$\mathcal{P}\rho(t) = G_0(t,0)\,\mathcal{P}\rho(0) + \int_0^t ds'\; G_0(t,s')\int_0^{s'} ds\; \mathcal{P}\mathcal{L}_T\,\bar{G}_Q(s',s)\,\mathcal{L}_T\mathcal{P}\rho(s)$$

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

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

And obtain:

$$\begin{cases} G_P(t,0) = G_0(t,0) + \int_0^t ds'\int_0^{s'} ds\; G_0(t,s')\,\mathcal{P}\mathcal{L}_T\,\bar{G}_Q(s',s)\,\mathcal{L}_T\mathcal{P}\,G_P(s,0) \\ \bar{G}_Q(s',s) = G_0(s',s) + \int_s^{s'} ds''\; G_0(s',s'')\,Q\mathcal{L}_T Q\,\bar{G}_Q(s'',s) \end{cases} \qquad (2.89)$$

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

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

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

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

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

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

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

$$\lim_{t\to\infty} \mathcal{P} \rho(t) = \lim_{t\to\infty} G_P(t,0)\, \rho(0)$$

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

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

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

proof:

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

$$\|$$

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

■

In our specific case we have thus:

$$\mathcal{P}\rho(\infty) = \lim_{\lambda\to 0^+} \lambda \tilde{G}_P(\lambda)\, \rho(0) = \lim_{\lambda\to 0^+} \lambda \left[\lambda - \mathcal{L}_0 - \tilde{\Sigma}_P(\lambda)\right]^{-1} \mathcal{P}\rho(0)$$

If we multiply both sides by $[\lambda - \mathcal{L}_0 - \tilde{\Sigma}_P(\lambda)]$ we obtain the equation satisfied by $\rho(\infty)$

$$\boxed{\left[\mathcal{L}_S + \tilde{\Sigma}_P(0)\right] \mathcal{P}\rho(\infty) = 0} \qquad (2.94)$$

where we have used again the fact that $\mathcal{L}_B \mathcal{P} = 0$. If we consider the general formulation (in Schrödinger picture)

$$\mathcal{P}\dot{\rho} = \mathcal{L}_S \mathcal{P}\rho + \int_0^t ds\, k(t-s)\, \mathcal{P}\rho(s)$$

we can again go into the Laplace space and obtain

$$\lambda \mathcal{P}\tilde{\rho}(\lambda) - \rho_0 = \mathcal{L}_S \mathcal{P}\tilde{\rho}(\lambda) + \tilde{K}(\lambda)\mathcal{P}\tilde{\rho}(\lambda)$$

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

$$\lim_{\lambda\to 0^+} \lambda^2 \mathcal{P}\tilde{\rho}(\lambda) - \lambda\rho_0 = \lim_{\lambda\to 0^+} \left[\mathcal{L}_S + \tilde{K}(\lambda)\right] \lambda \mathcal{P}\tilde{\rho}(\lambda)$$

or

$$0 = \left[\mathcal{L}_S + \tilde{K}(0)\right] \mathcal{P}\rho(\infty) \qquad (2.95)$$

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

$$\tilde{K}(0) = \tilde{\Sigma}_P(0) \qquad (2.96)$$

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

$$\tilde{\Sigma}_P(0) = \lim_{\lambda\to 0^+} \mathcal{P}\mathcal{L}_T \sum_{n=0}^{\infty} \left(\tilde{G}_0(\lambda) Q \mathcal{L}_T Q\right)^n \tilde{G}_0(\lambda)\, \mathcal{L}_T \mathcal{P}$$

$$\stackrel{*}{=} \lim_{\lambda\to 0^+} \mathcal{P}\mathcal{L}_T \sum_{n=0}^{\infty} \left(\tilde{G}_0(\lambda) Q \mathcal{L}_T Q \tilde{G}_0(\lambda) Q \mathcal{L}_T Q\right)^n \tilde{G}_0(\lambda)\, \mathcal{L}_T \mathcal{P}$$

$$= \lim_{\lambda\to 0^+} \mathcal{P}\mathcal{L}_T \left[\lambda - \mathcal{L}_0 - Q\mathcal{L}_T Q \tilde{G}_0(\lambda) Q \mathcal{L}_T Q\right]^{-1} \mathcal{L}_T \mathcal{P}$$

(*) This equality follows from the observation that only an even number of tunnelling Liouvilleans give a non vanishing contribution when sandwitched between $\mathcal{P}$ operators.

$$\tilde{K}^{(2)}(0) = \lim_{\lambda\to 0^+} \mathcal{P}\mathcal{L}_T \frac{1}{\lambda - \mathcal{L}_0} \mathcal{L}_T \mathcal{P} \qquad (2.97)$$

$$\tilde{K}^{(4)}(0) = \lim_{\lambda\to 0^+} \mathcal{P}\mathcal{L}_T \frac{1}{\lambda - \mathcal{L}_0} Q\mathcal{L}_T Q \frac{1}{\lambda - \mathcal{L}_0} Q\mathcal{L}_T Q \frac{1}{\lambda - \mathcal{L}_0} \mathcal{L}_T \mathcal{P}$$

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 extend it is instructive to make the following mapping between Hilbert space and Liouville space:

	Hilbert space	Liouville space
Eq. of motion	$\vert\dot{\psi}\rangle = -\frac{i}{\hbar} H \vert\psi\rangle$	$\dot{\rho} = \mathcal{L}\rho$
Evolutors	$U(t,0) = e^{-i/\hbar H t}$	$\mathcal{G}(t,0) = e^{\mathcal{L}t}$
	$U_0(t,0) = e^{-i/\hbar H_0 t}$	$\mathcal{G}_0(t,0) = e^{\mathcal{L}_0 t}$
Interaction picture	$\vert\psi_I\rangle = U_0^\dagger(t,0)\vert\psi\rangle$	$\rho_I(t) = \mathcal{G}_0(0,t)\,\rho(t)$
	$A_I = U_0^\dagger(t,0) A_S U_0(t,0)$	$A_I(t) = \mathcal{G}_0(0,t)\, A\, \mathcal{G}_0(t,0)$

The "vectors" of the Liouville space are the density operators. The operators are represented by all superoperators acting on the density operators, like for example the tunnelling Liouvillean $\mathcal{L}_T = [H_T, \bullet]$. The propagator in interaction picture $\mathcal{G}_I(t,0) = \mathcal{G}_0(0,t)\mathcal{G}(t,0)$, thus, from (2.89) we obtain:

$$\mathcal{G}_{P,I}(t,0) = \mathcal{G}_0(0,t)\,\mathcal{G}_0(t,0) + \int_0^t ds' \int_0^{s'} ds\; \mathcal{G}_0(0,t)\,\mathcal{G}_0(t,s')\,\mathcal{P}\mathcal{L}_T\,\bar{\mathcal{G}}_Q(s',s)\,\mathcal{L}_T\,\mathcal{P}\mathcal{G}_P(s,0)$$

$$= 1 + \int_0^t ds' \int_0^{s'} ds\; \mathcal{P}\,\mathcal{G}_0(0,s')\,\mathcal{L}_T\,\mathcal{G}_0(s',0)\,\bar{\mathcal{G}}_0(0,s')\,\bar{\mathcal{G}}_Q(s',s)\,\mathcal{G}_0(s,0)\;\mathcal{G}_0(0,s)\,\mathcal{L}_T\,\mathcal{G}_0(s,0)\,\mathcal{P}\,\mathcal{G}_{P,I}(s,0)$$

$$= 1 + \int_0^t ds' \int_0^{s'} ds\; \mathcal{P}\,\mathcal{L}_{T,I}(s')\,\mathcal{G}_0(0,s')\,\bar{\mathcal{G}}_Q(s',s)\,\mathcal{G}_0(s,0)\,\mathcal{L}_{T,I}(s)\,\mathcal{P}\,\mathcal{G}_{P,I}(s,0)$$

On the other side

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

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

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

Summarizing

$$\begin{cases} G_{P,I}(t,0) = 1 + \int_0^t ds' \int_0^{s'} ds\; \mathcal{P}\mathcal{L}_{T,I}(s')\,\bar{G}_{Q,I}(s',s)\,\mathcal{L}_{T,I}(s)\,\mathcal{P}G_{P,I}(s,0 \\ \bar{G}_{Q,I}(s',s) = 1 + \int_s^{s'} ds''\; Q\,\mathcal{L}_{T,I}(s'')\,Q\,\bar{G}_{Q,I}(s'',s) \end{cases} \tag{2.98}$$

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

$$\frac{d}{dt} G_{P,I}(t) = \int_0^t dt'\; \mathcal{P}\,\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(t')\,\mathcal{P}\,G_{P,I}(t',0)$$

or in other terms, by applying the super-operator above to $\mathcal{P}\rho_I(0) =$
$= \rho(0)$.

$$\frac{d}{dt}\,\mathcal{P}\rho_I(t) = \int_0^t dt'\; \mathcal{P}\,\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(t')\,\mathcal{P}\,\rho_I(t') \tag{2.99}$$

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

2.5.2 The T-matrix approach

The idea consists in assuming a Hamiltonian of the form

$$H(t) = \underbrace{H_S + H_B}_{= H_0} + H_{S-B}\, e^{\eta t} \qquad (2.100)$$

where $0 < \eta \ll 1$. Thus the interaction start adiabatically at $t = -\infty$ and it is turned on completely at $t = 0$. For a large time interval around $t = 0$ the total Hamiltonian contains thus H_S, H_B and H_{S-B}.
Now, let us consider 2 different eigenstates of H_0, $|i\rangle$ and $|f\rangle$ with associated energies E_i and E_f. Let us further assume that at time t_0 the System and Bath combination are in the initial state vector $|i\rangle$

What is the probability that $S+R$ is in the state vector $|f\rangle$ at time t?

$$\rho(t_0) = |i\rangle\langle i| \quad \Rightarrow \quad \rho(t) = U(t,t_0)\,|i\rangle\langle i|\,U^{+}(t,t_0) \qquad (2.101)$$

Thus, the probability reads

$$P_{fi}(t,t_0) = \mathrm{Tr}\{|f\rangle\langle f|\,\rho(t)\} = |\langle f|\,U(t,t_0)\,|i\rangle|^2 \qquad (2.102)$$

Since $H_0|i,f\rangle = E_{i,f}|i,f\rangle$ and $U_0(t_1,t_2) = U_0(t_1-t_2) = \exp\left[\left(-\frac{i}{\hbar}H_0(t_1-t_2)\right)\right]$

we can also write (the phases formally disappear!)

$$P_{fi}(t,t_0) = |\langle f|\,U_0^{+}(t,0)\,U(t,t_0)\,|i\rangle|^2 = |\langle f|\,U_I(t,t_0)\,U_0^{+}(t_0,0)\,|i\rangle|^2 = |\langle f|\,U_I(t,t_0)\,|i\rangle|^2$$

where $t = 0$ is conventionally taken as the time at which all representation coincide.

Intermezzo on interaction picture:

Let us consider the time dependent Hamiltonian:

$$H = H_0 + V(t)$$

We can associate to H the time evolution operator $U(t_2,t_1)$ such that

$$U(t_2,t_1)|\psi(t_1)\rangle = |\psi(t_2)\rangle \qquad (2.103)$$

Now, let us assume t_0 as the time at which all representations are equal. The evolutor in interaction picture is by definition the one that brings $|\psi(t_1)\rangle_I$ into $|\psi(t_2)\rangle_I$. But $|\psi(t_1)\rangle_I = U_0^\dagger(t_1,t_0)|\psi(t_1)\rangle$ and $|\psi(t_2)\rangle_I = U_0^\dagger(t_2,t_0)|\psi(t_2)\rangle$. From (2.73) one obtains

$$U(t_2,t_1)\, U_0(t_1,t_0)\, |\psi(t_1)\rangle_I = U_0(t_2,t_0)|\psi(t_2)\rangle_I$$

or

$$\underbrace{U_0^\dagger(t_2,t_0)\, U(t_2,t_1)\, U_0(t_1,t_0)}_{U_I(t_2,t_1)}\, |\psi(t_1)\rangle_I = |\psi(t_2)\rangle_I \qquad (2.104)$$

For a closed expression of $U_I(t_2,t_1)$ it is enough to notice that:

$$\frac{\partial}{\partial t_2} U_I(t_2,t_1) = U_0^\dagger(t_2,t_0)\, V(t_2)\, U_0(t_2,t_0)\; U_I(t_2,t_1) \quad \text{and} \quad U_I(t_1,t_1) = 1$$

$$\Rightarrow \quad U_I(t_2,t_1) = T_\leftarrow \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t_1}^{t_2} dt'\; U_0^\dagger(t',t_0)\, V(t')\, U_0(t',t_0)\right]$$

By integrating now the equation of motion of U_I (Eq. 1.22) we obtain

$$P_{fi}(t,t_0) = \left| \langle f | T_{\leftarrow} \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} dt' \left(H_{S-B}\, e^{\eta t'}\right)_I(t')\right] | i\rangle \right|^2 \qquad (2.105)$$

Instead of calculating now directly $P_{fi}(t,t_0)$ I concentrate on its RATE OF CHANGE

$$\Gamma_{fi}(t,t_0) = \frac{d}{dt} P_{fi}(t,t_0) \qquad (2.106)$$

The essence of the T-matrix approach to the master equation relies on the evaluation of (2.106) for $t_0 \to -\infty$ and $\eta \to 0^+$, in the order. The statement is that

$$\Gamma_{fi}(t,-\infty) = 2\pi\, \delta(E_i - E_f)\, |\langle f | T(E_i) | i\rangle|^2 \qquad (2.107)$$

where

$$T(E_i) = H_{S-B} + H_{S-B}\,(E_i - H_0 + i0^+)^{-1}\, T(E_i) \qquad (2.107b)$$

is the T-matrix. Let us prove (2.107). First we develop $U_I(t,t_0)$ in series

$$U_I(t,t_0) = T_{\leftarrow} \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{1}{n!} \prod_{i=1}^{n} \int_{t_0}^{t} dt_i \left(H_{S-B}\, e^{\eta t_i}\right)_I(t_i)$$

For $n=0$ $\prod_{i=1}^{0} = 1$, conventionally. $\Rightarrow$ the rate vanishes because it is time independent.

$\boxed{n=1}$ $\Gamma^{(1)}_{fi}(t,t_0) = \frac{d}{dt}\left|\langle f | \left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} dt' \left(H_{S-B}\, e^{\eta t'}\right)_I(t') | i\rangle\right|^2 =$

$$= \left(\frac{d}{dt}F(t)\right)F^*(t) + F(t)\left(\frac{d}{dt}F^*(t)\right) = 2\mathrm{Re}\left[\left(\frac{d}{dt}F(t)\right)F^*(t)\right]$$

$$= \frac{1}{\hbar^2} 2\mathrm{Re}\left\{ \langle f | e^{iH_0 t/\hbar} H_{S-B} e^{\eta t} e^{-iH_0 t/\hbar} | i \rangle \langle i | \int_{t_0}^{t} dt' \, e^{iH_0 t'/\hbar} H_{S-B} e^{\eta t'} e^{-iH_0 t'/\hbar} | f \rangle \right\}$$

$$= \frac{1}{\hbar^2} 2\mathrm{Re}\left\{ \exp\left[\tfrac{i}{\hbar}(E_f - E_i)t + \eta t \right] \langle f | H_{S-B} | i \rangle \langle i | H_{S-B} | f \rangle \int_{t_0}^{t} dt' \exp\left[\frac{i}{\hbar}(E_i - E_f)t' + \eta t' \right] \right\}$$

$$= \frac{1}{\hbar^2} |\langle f | H_{S-B} | i \rangle|^2 \, 2\mathrm{Re}\left\{ \cancel{\exp\left[\frac{i}{\hbar}(E_f - E_i)t + \eta t \right]} \cdot \frac{1}{\frac{i}{\hbar}(E_i - E_f) + \eta} \left(\cancel{\exp\left[\frac{i}{\hbar}(E_i - E_f)t + \eta t \right]} - \right.\right.$$

$$\left.\left. - \cancel{\exp\left[\frac{i}{\hbar}(E_i - E_f)t_0 + \eta t_0 \right]} \right) \right\}$$

$$t_0 \to -\infty$$

$$= \frac{e^{2\eta t}}{\hbar^2} |\langle f | H_{S-B} | i \rangle|^2 \frac{2\eta}{\left(\frac{E_i - E_f}{\hbar}\right)^2 + \eta^2} \overset{\eta \to 0^+}{=} \frac{2\pi}{\hbar^2} |\langle f | H_{S-B} | i \rangle|^2 \delta\left(\frac{E_i - E_f}{\hbar} \right).$$

$$= \frac{2\pi}{\hbar} |\langle f | H_{S-B} | i \rangle|^2 \delta(E_i - E_f) . \quad \checkmark$$

$\boxed{n = 2}$

$$\Gamma_{fi}^{(2)}(t, t_0) = \frac{d}{dt} \left| \langle f | \left(-\frac{1}{\hbar^2}\right) \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left(H_{S-B} e^{\eta t_1} \right)_I (t_1) \left(H_{S-B} e^{\eta t_2} \right)_I (t_2) | i \rangle \right|^2$$

$$= \frac{1}{\hbar^4} 2\mathrm{Re}\left\{ \langle f | e^{iH_0 t/\hbar + \eta t} H_{S-B} e^{-iH_0 t/\hbar} \int_{t_0}^{t} dt_2 \, e^{iH_0 t_2/\hbar + \eta t_2} H_{S-B} e^{-iH_0 t_2/\hbar} | i \rangle \right.$$

$$\left. \langle i | \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \, e^{iH_0 t_1/\hbar + \eta t_1} H_{S-B} e^{-iH_0 t_1/\hbar} e^{iH_0 t_2/\hbar + \eta t_2} H_{S-B} e^{-iH_0 t_2/\hbar} | f \rangle \right\}$$

$$= \frac{1}{\hbar^4} 2\mathrm{Re}\left\{ \exp\left[\frac{i}{\hbar} E_f t + \eta t \right] \langle f | H_{S-B} \cancel{e^{-iH_0 t/\hbar}} \left(\frac{iH_0}{\hbar} + \eta - i\frac{E_i}{\hbar} \right)^{-1} \left(\cancel{\exp\left[\frac{i}{\hbar} H_0 t + \eta t - \frac{i}{\hbar} E_i t \right]} \right) H_{S-B} | i \rangle \right.$$

$$\left. \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \exp\left[\frac{i}{\hbar} E_i t_1 + \eta t_1 \right] \langle i | H_{S-B} \exp\left[-\frac{i}{\hbar} H_0 (t_1 - t_2) \right] H_{S-B} | f \rangle \, e^{\eta t_2 - \frac{i}{\hbar} E_f t_2} \right\}$$

$$= \frac{1}{\hbar^4}\, 2\mathrm{Re}\Big\{ \exp\Big[\frac{i}{\hbar}(E_f - E_i)t + 2\eta t\Big] \langle f|\, H_{S-B} \Big(\frac{i}{\hbar}H_0 + \eta - \frac{i}{\hbar}E_i\Big)^{-1} H_{S-B}\,|i\rangle$$

$$\int_{t_0}^{t} dt_1 \; \exp\Big[\frac{i}{\hbar}E_i t_1 + \eta t_1\Big] \langle i|\, H_{S-B} \Big(\frac{i}{\hbar}H_0 - \frac{i}{\hbar}E_f + \eta\Big)^{-1} \cancel{e^{-\frac{i}{\hbar}H_0 t_1}} \,\cdot$$

$$\cdot \; \exp\Big[\Big(\cancel{\frac{i}{\hbar}H_0} - \frac{i}{\hbar}E_f + \eta\Big) t_1\Big] H_{S-B}\,|f\rangle \Big\} \;=$$

$$= \frac{1}{\hbar^4}\, 2\mathrm{Re}\Big\{ \exp\Big[\cancel{\frac{i}{\hbar}(E_f - E_i)t} + 2\eta t\Big] \langle f|\, H_{S-B} \Big(\frac{i}{\hbar}H_0 + \eta - \frac{i}{\hbar}E_i\Big)^{-1} H_{S-B}\,|i\rangle$$

$$\langle i|\, H_{S-B} \Big(\frac{i}{\hbar}H_0 + \eta - \frac{i}{\hbar}E_f\Big)^{-1} H_{S-B}\,|f\rangle \; \frac{1}{\frac{i}{\hbar}(E_i - E_f) + 2\eta} \; \exp\Big[\cancel{\frac{i}{\hbar}(E_i - E_f)t} + 2\eta t\Big] \Big\}$$

$$= \frac{1}{\hbar^4} \Big|\langle f|\, H_{S-B} \Big(\frac{i}{\hbar}(H_0 - E_i) + 0^+\Big)^{-1} H_{S-B}\,|i\rangle\Big|^2 \; 2\pi\hbar\; \delta(E_i - E_f)$$

$$= \frac{2\pi}{\hbar} \Big|\langle f|\, H_{S-B} \big(E_i - H_0 + i0^+\big)^{-1} H_{S-B}\,|i\rangle\Big|^2 \delta(E_i - E_f) \quad \checkmark$$

In order to extract the matrix elements from the Re function we have used the relation

$$\langle f|\, H_{S-B} \Big(\frac{i}{\hbar}(H_0 - E_i) + \eta\Big)^{-1} H_{S-B}\,|i\rangle = \langle i|\, H_{S-B} \Big(\frac{i}{\hbar}(H_0 - E_f) + \eta\Big)^{-1} H_{S-B}\,|f\rangle^*$$

which can be proven as follows:

$$\langle f|\, H_{S-B} \Big(\frac{i}{\hbar}(H_0 - E_i) + \eta\Big)^{-1} H_{S-B}\,|i\rangle^* = \sum_m \Big(\langle f|\, H_{S-B}\,|m\rangle \frac{1}{\frac{i}{\hbar}(E_m - E_i) + \eta} \langle m|\, H_{S-B}\,|i\rangle\Big)^*$$

$$= \sum_m \langle i|\, H_{S-B}\,|m\rangle \frac{1}{\underset{\pm E_f}{\frac{i}{\hbar}(E_i - E_m)} + \eta} \langle m|\, H_{S-B}\,|f\rangle = \sum_{m'} \langle i|\, H_{S-B}\,|m'\rangle \frac{1}{\frac{i}{\hbar}(E_{m'} - E_f) + \eta} \langle m'|\, H_{S-B}\,|f\rangle$$

$$E_{m'} = E_i + E_f - E_m$$

The connection to the master equation is obtained by choosing both $|i\rangle$ and $|f\rangle$ as product states of $|n\rangle_S \otimes |i\rangle_B$ and $|m\rangle_S \otimes |f\rangle_B$. The rate from $n \to m$ is then construct as

$$\tilde{\Gamma}_{n\to m} = 2\pi \sum_{if} W_i \,|\, {}_B\langle f| \otimes {}_S\langle m| \, T \, |n\rangle_S \otimes |i\rangle_B |^2 \, \delta(E_n + \varepsilon_i - E_m - \varepsilon_f)$$

where E_m (ε_i) are eigenenergies of system (bath) states and W_i is the probability to find the bath in the initial state $|i\rangle_B$.
The factorization assumption is about the S+B at time $t_0 \to -\infty$ and is analogous to the $\rho = \rho_{red} \otimes \rho_B$ of the density operator approaches.
The next step is the identification of $\tilde{\Gamma}_{n\to m}$ with the rates W_{mn} of (2.47). More specifically $\tilde{\Gamma}_{n\to m} = W_{mn}$ when evaluated to lowest order in H_{S-B}. Otherwise it should be considered as a generalization.
Notice that the rate $\tilde{\Gamma}_{n\to m}$ represents the variation of the population per unit time of the state $|m\rangle$ at time t under the assumption that the system was in $|n\rangle$ at time $t_0 \to -\infty$. The rate Γ_{mn} in the BRE represents the rate of transition at EQUAL time. => in principle 2 different concepts. To lowest order in H_T, though, they coincide since multiple interaction events intercalated by free system evolution are neglected.