2.5 Alternative approaches to the derivation of the GME

2.5.1 The projector operator approach (Nakajima-Zwanzig 1958)

The starting point is the Liouville-von Neumann equation in interaction picture (1.25):

$$\dot{\hat{\rho}}_I(t) = -\frac{i}{\hbar}\left[\hat{V}_I(t), \hat{\rho}_I(t)\right]$$

Now we make the formal replacement $V \to \alpha V$ where the α dimensionless constant is just usefull to count the order of the perturbation and can be set to $\alpha = 1$ in the end of the derivation. Eq. (1.25) can be formally written in the form:

$$\dot{\rho} = \alpha\, \mathcal{L}(t) \rho(t) \qquad (2.54)$$

where we dropped the I indeces for simplicity. Besides the superoperator $\mathcal{L}(t)$ we also introduce the following projectors:

$$\mathcal{P} \quad \text{and} \quad \mathcal{Q} = 1 - \mathcal{P}$$

$$\mathcal{P}\rho = \mathrm{Tr}_B\{\rho\} \otimes \rho_B \qquad (2.55)$$

where ρ_B is a reference state in the bath. Notice that $\mathcal{P}$ is indeed a projector (super)operator since $\mathcal{P}^2 = \mathcal{P}$ (2.56)

In fact:

$$\mathcal{P}^2\rho = \mathrm{Tr}_B\left\{\mathrm{Tr}_B\{\rho\} \otimes \rho_B\right\} \otimes \rho_B = \left[\mathrm{Tr}_B\{\rho\} \overbrace{\mathrm{Tr}_B\{\rho_B\}}^{=1}\right] \otimes \rho_B = \mathcal{P}\rho .$$

It follows that $\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$. Moreover $\mathcal{P}$ is independent of time. Thus, I can rewrite (1.25) as the set of coupled equations

$$\begin{cases} \frac{\partial}{\partial t} \mathcal{P}\rho = \alpha \mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) + \alpha \mathcal{P}\mathcal{L}(t) \mathcal{Q}\rho(t) \\ \frac{\partial}{\partial t} \mathcal{Q}\rho = \alpha \mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho(t) + \alpha \mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho(t) \end{cases} \qquad (2.57)$$

If we assume $V = \sum_i F_i Q_i$ and $Tr_B\{F_i \rho_B\} = 0$ we can conclude immediately that $\mathcal{P}\mathcal{L}(t)\mathcal{P} = 0$ (2.58)

proof
$$\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho = Tr_B\{[V, Tr_B\{\rho\} \otimes \rho_B]\} \otimes \rho_B =$$

$$= \sum_i \left(Q_i Tr_B\{\rho\} \, Tr_B\{F_i \rho_B\} - Tr_B\{\rho\} Q_i \, Tr_B\{\rho_B F_i\} \right) \otimes \rho_B$$

$$= \sum_i [Q_i, Tr_B\{\rho\}] \underbrace{Tr_B\{F_i \rho_B\}}_{=0} \otimes \rho_B = 0 .$$

This observation yields the new set of equations

$$\begin{cases} \frac{\partial}{\partial t} \mathcal{P}\rho = \alpha \mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho(t) \\ \frac{\partial}{\partial t} \mathcal{Q}\rho = \alpha \mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho(t) + \alpha \mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho(t) \end{cases} \qquad (2.58)$$

The second equation can be formally resolved by introducing the propagator:

$$\mathcal{G}(t,s) = T_{\leftarrow} \exp\left[\alpha \int_s^t ds' \, \mathcal{Q}\mathcal{L}(s') \right] \qquad (2.59)$$ solution of the homogeneous equation

$$\frac{\partial}{\partial t} \mathcal{G}(t,s) = \mathcal{Q}\mathcal{L}(t)\mathcal{G}(t,s)$$ with b.c. $\mathcal{G}(t,t) = 1$.

The solution $$\mathcal{Q}\rho(t) = \mathcal{G}(t,0)\mathcal{Q}\rho(0) + \alpha \int_0^t ds \, \mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho(s) \qquad (2.60)$$

Now we assume $\rho(0) = \rho_{sys}(0) \otimes \rho_B \Rightarrow \mathcal{Q}\rho(0) = 0$ and the equation for the factorized component of ρ, reads

$$\boxed{\frac{\partial}{\partial t} \mathcal{P}\rho = \alpha^2 \mathcal{P}\mathcal{L}(t) \int_0^t ds \, \mathcal{G}(t,s) \, \mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho(s)} \qquad (2.61)$$

proof of eq. (2.60). I will not enter a rigorous proof of (2.60) but

i) Verify that it is a solution

ii) Show a plausible "constructive" algorithm.

i)

$$\frac{d}{dt}\left[G(t,0)\,Q\rho(0) + \alpha \int_0^t ds\; G(t,s)\, Q\mathcal{L}(s)\, \mathcal{P}\rho(s) \right] =$$

$$= \frac{d}{dt}\left\{ T_{\leftarrow} \exp\left[\alpha \int_0^t ds'\, Q\mathcal{L}(s')\right] Q\rho(0) + \alpha \int_0^t ds\; T_{\leftarrow}\exp\left[\alpha\int_s^t ds'\, Q\mathcal{L}(s')\right] Q\mathcal{L}(s)\,\mathcal{P}\rho(s)\right\}$$

$$= \alpha Q\mathcal{L}(t)\; T_{\leftarrow}\exp\left[\alpha\int_0^t ds'\, Q\mathcal{L}(s')\right] Q\rho(0) + \alpha\; \overset{1}{\cancel{T_{\leftarrow}\exp\left[\alpha\int_t^t ds'\, Q\mathcal{L}(s')\right]}}\; Q\mathcal{L}(t)\,\mathcal{P}\rho(t)$$

$$+ \alpha \int_0^t ds\, \alpha Q\mathcal{L}(t)\; T_{\leftarrow}\exp\left[\alpha\int_s^t ds'\, Q\mathcal{L}(s')\right] Q\mathcal{L}(s)\,\mathcal{P}\rho(s)$$

$$= \alpha Q\mathcal{L}(t)\left[G(t,0)\,Q\rho(0) + \alpha\int_0^t ds\; G(t,s)\, Q\mathcal{L}(s)\,\mathcal{P}\rho(s)\right] + \alpha Q\mathcal{L}(t)\,\mathcal{P}\rho(t)$$

■

ii) The constructive algorithm to obtain (2.60) starts with the formal integration of the second of (2.58)

$$Q\rho(t) = Q\rho(0) + \alpha\int_0^t ds\; Q\mathcal{L}(s)\,\mathcal{P}\rho(s) + \int_0^t ds\; \alpha Q\mathcal{L}(s)\, Q\rho(s) \qquad (2.62)$$

and continues with inserting (2.62) into itself. For simplicity we make the following identifications

$$\begin{aligned} Q\rho(t) &:= y(t) \qquad (2.62b)\\ Q\mathcal{L}(t)\,\mathcal{P}\rho(t) &:= a(t)\\ Q\mathcal{L}(t) &:= b(t) \end{aligned}$$

(2.62) becomes

$$y(t) = y(0) + \alpha\int_0^t a(s)\,ds + \alpha\int_0^t b(s)\,y(s)\,ds \qquad (2.62b)$$

Iteration gives.

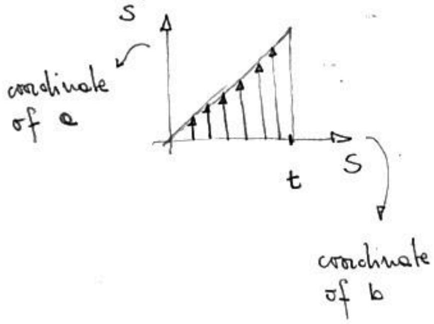
$$y(t) = y(0) + \alpha\int_0^t a(s)ds + \alpha\int_0^t b(s)\left[y(0) + \int_0^s a(s')ds' + \alpha\int_0^s b(s')y(s')ds'\right]ds$$

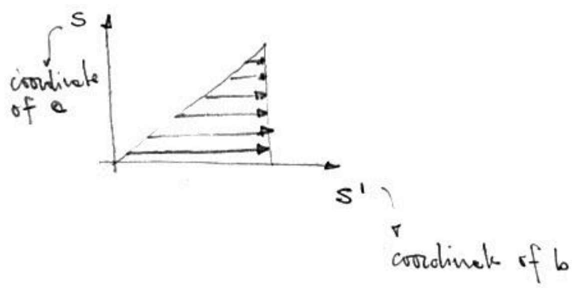
$$= \left[1 + \alpha\int_0^t b(s)ds\right]y(0) + \alpha\int_0^t\left[a(s) + \alpha b(s)\int_0^s a(s')ds'\right]ds +$$

$$+ \alpha^2\int_0^t b(s)\int_0^s b(s')\,y(s')\,ds' \qquad (2.63)$$

$$\boxed{\begin{aligned}&\int_0^t ds\int_0^s ds'\ F(s,s') = \\ &= \int_0^t ds\int_s^t ds'\ F(s',s)\end{aligned}} \qquad (2.64)$$

But $\displaystyle\int_0^t b(s)\int_0^s a(s')\,ds'ds = \int_0^t ds\int_s^t ds'\ b(s')\,a(s)$





It follows that

$$y(t) = \left[1 + \alpha\int_0^t b(s)ds\right]y(0) + \alpha\int_0^t ds\left[1 + \alpha\int_s^t ds'\ b(s')\right]a(s) +$$

$$+ \alpha^2\int_0^t b(s)\int_0^s b(s')\,y(s')ds' = \text{repeating the operation}$$

$$\left[1 + \alpha\int_0^t b(s)ds + \alpha^2\int_0^t b(s)\int_0^s b(s')\,ds'ds\right]y(0) + \alpha\int_0^t ds\left[1+\alpha\int_s^t ds'\,b(s')\right]a(s)$$

$$+ \alpha^3\int_0^t b(s)\underbrace{\int_0^s b(s')\int_0^{s'} b(s'')\,a(s'')\,ds''ds'}_{F''(s)}ds = + \alpha^3\int_0^t b(s)\int_0^s b(s')\int_0^{s'} b(s'')\,y(s'')ds''ds'ds$$

$$(2.65)$$

The but last term can be analyzed as follows

$$\alpha^3\int_0^t b(s)\int_0^s \underbrace{b(s')\int_0^{s'} b(s'')a(s'')\,ds''}_{F(s')}ds'ds = \alpha^3\int_0^t ds\int_s^t ds'\ b(s')\int_0^{s'} b(s'')\,a(s'')\,ds''$$

$$= \alpha^3 \int_0^t ds \int_0^s ds'' \int_s^t ds' \; b(s')\, b(s'')\, a(s'') \qquad (2.66)$$

Now I use again (2.64) for the variable s and s''

$$= \alpha^3 \int_0^t ds \int_s^t ds'' \int_{s''}^t ds' \; b(s')\, b(s'')\, a(s) =$$

in this integral $s' \geq s''$ but the integrand is symmetric under the exchange $s' \leftrightarrow s''$ if we save the ordering.

$$= \alpha^3 \int_0^t ds \; \frac{1}{2} \int_s^t ds'' \int_s^t ds' \; T_{\leftarrow}\left(b(s')\, b(s'') \right) a(s)$$

By putting now all together one obtains:

$$y(t) = \left[1 + \alpha \int_0^t b(s)\, ds + \frac{\alpha^2}{2} \int_0^t ds \int_0^t ds' \; T_{\leftarrow}\left(b(s)\, b(s') \right) \right] y(0) +$$

$$+ \alpha \int_0^t ds \left[1 + \alpha \int_s^t ds'\, b(s') + \frac{\alpha^2}{2} \int_s^t ds' \int_s^t ds'' \; T_{\leftarrow}\left(b(s')\, b(s'') \right) \right] a(s)$$

$$+ \alpha^3 \int_0^t b(s) \int_0^s b(s') \int_0^{s'} b(s'')\, y(s'')\, ds''\, ds'\, ds \qquad (2.67)$$

where the first three terms of the propagators $G(t,0)$ and $G(t,s)$ have already been reconstructed. Indefinite iteration reconstruct the exact solution (2.60).

Let us now analyze in more detail (2.61).

$$\frac{\partial}{\partial t} \mathcal{P}\rho = \alpha^2 \int_0^t ds \; \mathcal{P}\mathcal{L}(t)\, \mathcal{G}(t,s)\, \mathcal{Q}\, \mathcal{L}(s)\, \mathcal{P}\rho(s)$$

* The lowest contribution to the dynamics of the factrized component of ρ is of second order in V_{S-B}. (α^2) and reads:

$$\frac{\partial}{\partial t} \mathcal{P}\rho \approx \alpha^2 \int_0^t ds \; \mathcal{P}\mathcal{L}(t)\, \mathcal{Q}\, \mathcal{L}(s)\, \mathcal{P}\rho(s).$$

i.e. $\mathcal{G}(t,s) = 1$ to lowest order in α.

* The evolution of the total density matrix reads:

$$\rho(t) = \mathcal{P}\rho(t) + \mathcal{Q}\rho(t) = \rho_{red}(t) \otimes \rho_B + \Delta\rho$$

if the initial condition is factorized, $\Delta\rho$ assumes the form:

$$\Delta\rho = \alpha\int_0^t ds\; \mathcal{G}(t,s)\,\mathcal{Q}\,\mathcal{L}(s)\,\mathcal{P}\rho(s) = \alpha\int_0^t ds\; \mathcal{G}(t,s)\,\mathcal{L}(s)\,\mathcal{P}\rho(s)$$

$$= -\frac{i\alpha}{\hbar}\int_0^t ds\; [\, V(s), \mathrm{Tr}_B\{\rho\}\otimes\rho_B] + O(\alpha^2) \qquad (2.68) \qquad (\,\mathcal{G}(t,s)\approx 1\,)$$

An expansion to higher order gives

$$\Delta\rho^{(2)} = \alpha\int_0^t ds\; \mathcal{L}(s)\mathcal{P}\rho(s) + \alpha^2\int_0^t ds\int_s^t ds'\; \mathcal{Q}\mathcal{L}(s')\,\mathcal{Q}\mathcal{L}(s)\,\mathcal{P}\rho(s)$$

$$= \alpha\int_0^t ds\; \mathcal{L}(s)\mathcal{P}\rho(s) + \alpha^2\int_0^t ds\int_s^t ds'\; \mathcal{Q}\mathcal{L}(s')\,(1-\cancel{\mathcal{P}})\mathcal{L}(s)\,\mathcal{P}\rho(s)$$

$$= -\frac{i}{\hbar}\alpha\int_0^t ds\; [\, V(s), \rho_{red}^{(s)}\otimes\rho_B] + \alpha^2\int_0^t ds\int_s^t ds'\left(-\frac{1}{\hbar^2}\right)[\, V(s'), [\, V(s), \rho_{red}\otimes\rho_B]]$$

$$+ \frac{1}{\hbar^2}\int_0^t ds\int_s^t ds'\; \mathrm{Tr}_B\{[\, V(s'), [\, V(s), \rho_{red}\otimes\rho_B]]\}\otimes\rho_B . \qquad (2.69)$$

To first order, the interaction with the bath produces only non factorized components. To second order, instead, both are present (in general) and the factorized component must be subtracted.

* Eq. (2.61) coincide (when written to lowest order) with equation (2.12)

$$\frac{\partial}{\partial t}\mathcal{P}\rho = \alpha^2\int_0^t ds\; \mathcal{P}\mathcal{L}(t)\,\mathcal{Q}\mathcal{L}(s)\,\mathcal{P}\rho(s) = \alpha^2\int_0^t ds\; \mathcal{P}\mathcal{L}(t)\,\mathcal{L}(s)\,\mathcal{P}\rho(s)$$

In other terms and reintroducing the index I for the interaction picture.

$$\mathrm{Tr}_B\{\dot{\rho}_I\}\otimes\rho_B = \left(-\frac{1}{\hbar^2}\right)\alpha^2\int_0^t ds\ \mathrm{Tr}_B\{[V_I(t),[V_I(s),\mathrm{Tr}_B\{\rho_I(s)\}\otimes\rho_B]]\}\otimes\rho_B$$

And due to the generic state ρ_B. By setting $\alpha=1$

$$\dot{\rho}_{I,red} = -\frac{1}{\hbar^2}\int_0^t ds\ \mathrm{Tr}_B\{[V_I(t),[V_I(s),\rho_{I,red}(s)\otimes\rho_B]]\}.$$

2.5.2 The T-matrix approach

The idea consists in assuming a Hamiltonian of the form:

$$H(t) = \underbrace{H_S + H_B}_{=H_0} + \underbrace{H_{S-B}\, e^{\eta t}}_{=V(t)} \qquad (2.70)$$

where $0<\eta\ll 1$. Thus the interaction starts slowly at $t=-\infty$ and adiabatically is turned on until $t=0$. 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 S+B is in $|i\rangle$. What is the probability that S+B is in $|f\rangle$ at time t?

$$\rho(t_0) = |i\rangle\langle i| \quad \Rightarrow \quad \rho(t) = U(t,t_0)|i\rangle\langle i|U^\dagger(t,t_0) \qquad (2.71)$$

hus, the probability reads.

$$P_{fi}(t,t_0) = \mathrm{Tr}\{|f\rangle\langle f|\rho(t)\} = |\langle f|U(t,t_0)|i\rangle|^2 \qquad (2.72)$$

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

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

here $t=0$ is conventionally taken as the time at which all representations are equal.

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

$$U(t_2,t_1)|\psi(t_1)\rangle = |\psi(t_2)\rangle \qquad (2.73)$$

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

$$\underbrace{U_0^+(t_2,t_0)\,U(t_2,t_1)\,U_0(t_1,t_0)}_{U_I(t_2,t_1)}\,|\psi(t_1)\rangle_I = |\psi(t_2)\rangle_I \qquad (2.74)$$

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

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

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

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

$$P_{fi}(t,t_0) = \left| \langle f | T_{\leftarrow} \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} dt' \left(H_{S-B}\, e^{\eta t'}\right)_I(t')\right] | i \rangle \right|^2 \qquad (2.75)$$

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

RATE OF CHANGE

$$\Gamma_{fi}(t,t_0) = \frac{d}{dt} P_{fi}(t,t_0) \qquad (2.76)$$

The essence of the T-matrix approach to the master equation relies on the evaluation of (2.74) for "$t_0 \to -\infty$ and $\eta \to 0^+$", in the order. The statement is that

$$\Gamma_{fi}(t,-\infty) = 2\pi\, \delta(E_i - E_f)\, |\langle f | T(E_i) | i \rangle|^2 \qquad (2.77)$$

where

$$T(E_i) = H_{S-B} + H_{S-B}\left(E_i - H_0 + i0^+\right)^{-1} T(E_i) \qquad (2.77b)$$

is the T-matrix. Let us prove (2.75). 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.

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

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

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

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

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

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

$$t_0 \to -\infty$$

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

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

$\boxed{n = 2}$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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. $\Rightarrow$, 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.

2.5.3 Discussion over the Markov approximation

In the derivation of the BRE we have justified the Markov approximation using the time dependence of the correlator functions. In Sheet 4 you have calculated that, for a bath of non interacting particles:

$$C_{\vec{k}\vec{k}'}(t-t') := \langle c^+_{\vec{k}}(t)\, c_{\vec{k}'}(t')\rangle_B = f(\varepsilon_k-\mu)\, e^{i\,\varepsilon_k/\hbar\,(t-t')}\,\delta_{\vec{k}\vec{k}'}$$

Namely, the correlator itself does NOT decay. This is an approximation due to the fact that we neglected completely electron-electron interaction in the leads. By reintroducing it one would obtain a quasi-particle description with lifetimes $\sim \frac{1}{T^2}$. The point of the Anderson model nevertheless is that the bath operators in the S-B hamiltonian can be taken as

$$F_1 = \tau\sum_k c^+_k \qquad \text{and} \qquad F_2 = \tau\sum_k c_k$$

$\Rightarrow$ the correlator function of the master equation

$$C_{12}(t-t') = \tau^2 \sum_{kk'} \langle c^+_k(t)\, c_{k'}(t')\rangle_B =$$

$$\pi\hbar D\tau^2\, e^{i\frac{\mu}{\hbar}(t-t')}\left[\delta(t-t') - \frac{i}{\hbar\beta\,\sinh\left(\pi\frac{t-t'}{\hbar\beta}\right)}\right]$$

indeed decays in time on a time scale $t_T = \hbar\beta \sim 1/T$. Thus, the lower the temperatures, the longer is "both" the quasi-particle life time and the correlation time of C_{12}. The later dominates the picture. Already anticipating arguments of the next part one would like to know if there are other energy scales relevant for the correlator in a transport set-up out of equilibrium. We refer again to the paradigmatic (even if in some aspects pathological) Anderson impurity model.

The presence of the two leads (two baths at different chemical potential and, or temperature) leads to the definition of

$$F_1 = \tau \sum_{k\chi}' c^+_{\chi k} \quad \text{and} \quad F_2 = \tau \sum_{\chi k} c_{\chi k}$$

$$C_{12}(t-t') = \sum_{\substack{k\chi \\ k'\chi'}}' \langle c^+_{k\chi}(t) c_{k'\chi'}(t') \rangle_B = \sum_{\chi k} \langle c^+_{k\chi}(t) c_{k\chi}(t') \rangle_B$$

$$= \pi\hbar\Delta\tau^2 \left[e^{i\mu_S/\hbar (t-t')} + e^{i\mu_D/\hbar (t-t')} \right] \left[\delta(t-t') - \frac{i}{\hbar\beta \sinh\left(\pi \frac{t-t'}{\hbar\beta}\right)} \right]$$

which, in the limit $T \to 0$ goes into $(t \neq t')$

$$\overset{T\to\infty}{=} 2\pi\hbar\Delta\tau^2 \, e^{i\mu_0/\hbar (t-t')} \frac{\cos\left(\frac{e\Delta V_b}{2\hbar}(t-t')\right)}{t-t'}$$

Thus introducing a new time scale $\frac{\hbar}{e\Delta V_b}$ for the time correlator.

If now we assume uncorrelated transport $\Rightarrow I = \frac{e}{\tau_0}$ where τ_0 is the typical time of variation of the density matrix and the interval between tunneling events. If $I/V \ll e^2/h$ ← conductance quantum

$$\frac{e}{V\tau_0} \ll \frac{e^2}{h} \Rightarrow \quad \tau_0 \gg \frac{eV}{h} \quad \text{and the}$$

Markov approximation is justified.