where the second one is taken with a - sign due to the $Q = 1 - \mathcal{P}$ that originates the central $\mathcal{P}$. All together

$$\mathcal{P}\dot{\rho}_I(t) = \int_0^t ds\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s)\mathcal{P}\rho_I(s) +$$

$$+ \int_0^t ds \int_s^t ds' \int_{s'}^t ds''\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s'')\mathcal{L}^I(s')\mathcal{L}^I(s)\mathcal{P}\rho_I(s)$$

$$- \int_0^t ds \int_s^t ds' \int_{s'}^t ds''\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s'')\mathcal{P}\mathcal{L}^I(s')\mathcal{L}^I(s)\mathcal{P}\rho_I(s) \,. \tag{4.20}$$

In order to recover (4.16) we have still to reorder the integrals according to the general rule:

$$\int_0^t ds \int_s^t ds'\, F(s', s) = \int_0^t ds \int_0^s ds'\, F(s, s') \tag{2.64}$$

First we apply (2.64) to the pair of integrations in ds and ds'. Then we exchange $\int ds'$ with $\int ds''$ and apply again (2.64) between ds and ds''. The renaming $s' = \tau$ $s'' = \tau_1$ $s = \tau_2$ concludes the proof. The result being:

$$\begin{aligned}\mathcal{P}\dot{\rho}_I(t) = & \int_0^t d\tau\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(\tau)\mathcal{P}\rho_I(\tau) \\ & + \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(\tau_2)\mathcal{L}^I(\tau_1)\mathcal{L}^I(\tau)\mathcal{P}\rho_I(\tau) \\ & - \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau\, \mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(\tau_2)\mathcal{P}\mathcal{L}^I(\tau_1)\mathcal{L}^I(\tau)\mathcal{P}\rho_I(\tau)\end{aligned} \tag{4.21}$$

■

The form obtained in the Nakajima-Zwanzig formalism is better suited to the identification of the Kernel K^{I}. If we define:

$$K^{I}(t,\tau) := K^{I(2)}(t,\tau) + \int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2 \; K^{I(4)}(t,\tau_2,\tau_1,\tau) \qquad (4.22)$$

with the further definitions

$$K^{I(2)}(t,\tau)\, \hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_{res}\{\mathcal{P}\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau)\mathcal{P}\rho_{I}(\tau)\} =$$

$$= \mathrm{Tr}_{res}\{\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau)\,\hat{\rho}_{red,I}(\tau)\otimes\hat{\rho}_{res}\}$$

$$K^{I(4)}(t,\tau_2,\tau_1,\tau)\,\hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_{res}\{(\mathcal{P}\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau_2)\mathcal{L}^{I}(\tau_1)\mathcal{L}^{I}(\tau)\mathcal{P} -$$

$$- \mathcal{P}\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau_2)\mathcal{P}\mathcal{L}^{I}(\tau_1)\mathcal{L}^{I}(\tau)\mathcal{P})\,\rho_{I}(\tau)\}$$

$$= \mathrm{Tr}_{res}\{\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau_2)\mathcal{L}^{I}(\tau_1)\mathcal{L}^{I}(\tau)\,\hat{\rho}_{red,I}\,\hat{\rho}_{res}\} +$$

$$- \mathrm{Tr}_{res}\{\mathcal{L}^{I}(t)\mathcal{L}^{I}(\tau_2)\,\mathrm{Tr}_{res}\{\mathcal{L}^{I}(\tau_1)\mathcal{L}^{I}(\tau)\,\hat{\rho}_{red,I}\,\hat{\rho}_{res}\}\otimes\hat{\rho}_{res}\} \qquad (4.23)$$

we obtain the compact form

$$\dot{\hat{\rho}}_{red,I}(t) = \int_{0}^{t} d\tau \; K^{I}(t,\tau)\,\hat{\rho}_{red,I}(\tau)$$

The Kernel in convolution form is obtained, though, only in the Schrödinger picture. Formally the Kernel in convolution form is obtained remembering

$$\dot{\hat{\rho}}_{red,I}(t) = U_0^{+}(t,0)\,\dot{\hat{\rho}}_{red}(t)\,U_0(t,0) + U_0^{+}(t,0)\,\frac{i}{\hbar}[\hat{H}_0,\hat{\rho}_{red}(t)]\,U_0(t,0) \qquad (4.24)$$

and

is obtained from the relation

$$K(t-\tau)\left[\hat{\rho}_{red}(\tau)\right] = U_0(t,0)\, K^{I(2)}(t,\tau)\left[\,U_0^{+}(\tau,0)\,\hat{\rho}_{red}(\tau)\,U_0(\tau,0)\right] U_0^{+}(t,0)$$

$$+\, U_0(t,0)\int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2\; K^{I(4)}(t,\tau_2,\tau_1,\tau)\left[\,U_0^{+}(\tau,0)\,\hat{\rho}_{red}\,U_0(\tau,0)\right] U_0^{+}(t,0)$$

(the convolution form remains to be checked for the fourth order). (4.25)

4.1.2 The role of coherences

If the central system lives in an N-dimensional Hilbert-space, the corresponding RDM has dimension $N\times N$ while the superoperator K has dimension N^4, which means a drastic numerical and analytical effort also for systems with small N. To simplify the analysis one should look at possible approximations. These are in particular related to the presence of coherences, i.e. off-diagonal elements of the RDM. In general:

> When two states a and a' of the system differ by a quantum number associated to a variable conserved in the total system (i.e. including reservoirs) a coherence can be excluded.

Examples:
- the total charge $\Rightarrow$ the reduced density matrix is block diagonal in the charge. (with normal leads in the # of electrons).
- The projection of the spin along a given quantization axis when the leads are unpolarized or parallel polarized.

Moreover, as we already observed in the Bloch-Redfield treatment a SECULAR APPROXIMATION is often applied whereby coherences between states non-degenerated in energy are neglected.

However, this approximation can only be performed on terms of the GME containing the highest order in the perturbation expansion. The non-secular contributions produce corrections of the order of the linewidth $\hbar\Gamma \sim t^2$.

Let's discuss a method to account for these contributions and obtain a new GME of secular form:

$$\hat{\rho}_{red}^{stat} := \begin{pmatrix} \hat{\rho}_s \\ \hat{\rho}_n \end{pmatrix} \begin{matrix} \longleftarrow \text{ secular contribution} \\ \longleftarrow \text{ non-secular contribution} \end{matrix} \qquad (4.26)$$

$\hat{\rho}_n$ contains $\rho_{aa'}$ such that $|E_a - E_{a'}| > \hbar\Gamma$. All other elements can be found in $\hat{\rho}_s$. including populations $(a = a')$.

We write the eq. for the stationary $\hat{\rho}$:

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} (K_0)_{ss} + K_{ss}^{(2)} + K_{ss}^{(4)} & K_{sn}^{(2)} + K_{sn}^{(4)} \\ K_{ns}^{(2)} + K_{ns}^{(4)} & (K_0)_{nn} + K_{nn}^{(2)} + K_{nn}^{(4)} \end{pmatrix} \begin{pmatrix} \hat{\rho}_s \\ \hat{\rho}_n \end{pmatrix}$$

where (4.27)

$$(K_0)_{bb'}^{aa'} = \frac{i}{\hbar} \delta_{ab} \delta_{a'b'} (E_{a'} - e_a) \qquad (4.28)$$

It follows:

$$\hat{\rho}_n = \left((K_0)_{nn} + K_{nn}^{(2)} + K_{nn}^{(4)} \right)^{-1} \left(K_{ns}^{(2)} + K_{ns}^{(4)} \right) \hat{\rho}_s \qquad (4.29)$$

Which contains all orders in Γ due to the inversion operation.
We further proceed:

$$\left((K_0)_{nn} + K_{nn}^{(2)} + K_{nn}^{(4)} \right)^{-1} = (K_0)_{nn}^{-1} \left[1 + (K_0)_{nn}^{-1} \left(K_{nn}^{(2)} + K_{nn}^{(4)} \right) \right]^{-1}$$

But $\left| \Gamma / (K_0)_{nn} \right| \ll 1 \Rightarrow$ we can expand:

$$\left[1 + (K_0)_{nn}^{-1} \left(K_{nn}^{(2)} + K_{nn}^{(4)} \right) \right]^{-1} \simeq 1 - (K_0)_{nn}^{-1} \left(K_{nn}^{(2)} + K_{nn}^{(4)} \right)$$

$$\Rightarrow \hat{\rho}_n \simeq (K_0)_{nn}^{-1} \left[1 - (K_0)_{nn}^{-1} \left(K_{nn}^{(2)} + K_{nn}^{(4)} \right) \right] \left(K_{ns}^{(2)} + K_{ns}^{(4)} \right) \hat{\rho}_s$$

$$= (K_0)_{nn}^{-1} K_{ns}^{(2)} \hat{\rho}_s + O(\Gamma^2)$$

$\Rightarrow$ neglecting all contributions beyond Γ^2 one finds from (4.27)

$$0 = \left((K_0)_{ss} + K_{ss}^{(2)} + K_{ss}^{(4)} \right) \hat{\rho}_s + \left(K_{sn}^{(2)} + K_{sn}^{(4)} \right) \hat{\rho}_n$$

$$= \left((K_0)_{ss} + K_{ss}^{(2)} + K_{eff}^{(4)} \right) \hat{\rho}_s \qquad (4.30)$$

where

$$K_{eff}^{(4)} = K_{ss}^{(4)} + K_c = K_{ss}^{(4)} + K_{sn}^{(2)} (K_0)_{nn}^{-1} K_{ns}^{(2)} \qquad (4.31)$$

which contains the correction to the secular density matrix due to coherences between non secular states.

4.1.3 The current Kernel

Analogously to the time-evolution Kernel that we have calculated up to the 4^{th} order in the tunnelling coupling in section 4.1.1. we can also define a current Kernel associated to the expectation value of the current flowing from the lead α:

$$I_\alpha(t) = \mathrm{Tr}\left\{ \hat{I}_\alpha \hat{\rho}(t) \right\} = \mathrm{Tr}_{sys}\left\{ \int_0^t d\tau\, K_{I_\alpha}(t-\tau)\, \hat{\rho}_{red}(\tau) \right\} \quad (4.32)$$

where the second equality must be read at this point simply as an implicit definition of the current Kernel. The derivation of its explicit from proceed as follows. We start with the definition of the current with an average in interaction picture

$$I_\alpha(t) = \mathrm{Tr}\left\{ \hat{I}_{\alpha,I}(t)\, \hat{\rho}_I(t) \right\} = \mathrm{Tr}\left\{ \hat{I}_{\alpha,I}(t)\, Q\, \hat{\rho}_I(t) \right\}$$

where the second equality only depends on the nature of the current operator which does not conserve the particle number on the lead α. The formal expression for $Q\hat{\rho}_I(t)$ is known in the NZ approach: (2.60)

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

with

$$G(t,s) = T_{\leftarrow} \exp \int_s^t ds'\, Q\, \mathcal{L}_I(s')$$

where the factorized initial condition $\rho_I(0) = \rho_{sys}(0) \otimes \rho_{res}$ has been already used.

$$I_\alpha(t) = \mathrm{Tr}\left\{ \hat{I}_{\alpha,I}(t) \int_0^t ds\; G(t,s)\, Q\mathcal{L}_I(s)\, \mathcal{P}\, \rho_I(s) \right\} \quad (4.33)$$

$$\mathrm{Tr}_{sys}\left\{ \int_0^t d\tau\; \mathrm{Tr}_{res} \left\{ \hat{I}_{\alpha,I}(t)\, G(t,\tau)\, Q\, \mathcal{L}_I(\tau)\, \rho^I_{red}(\tau) \otimes \hat{\rho}_{res} \right\} \right.$$

where the Kernel in interaction picture can be read out:

$$K^{I}_{I\alpha}(t,\tau)\,\hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_{res}\left\{ \hat{I}_{\alpha,I}(t)\, G(t,\tau) Q \mathcal{L}_I(\tau)\, \rho^{I}_{red}(\tau)\otimes\hat{\rho}_{res}\right\} \quad (4.34)$$

If now we want to calculate the Kernel up to 4^{th} order in the tunnelling coupling we proceed as for the time evolution Kernel:

$$G(t,\tau) = 1 + \int_{\tau}^{t} d\tau_1\, Q\mathcal{L}_I(\tau_1) + \int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2\, Q\mathcal{L}_I(\tau_2)\, Q\mathcal{L}_I(\tau_1)$$

$$+ O(H_T^3)$$

The odd orders in the expansion of $G(t,\tau)$ do not contribute to the current Kernel due to the Wick's theorem or, in other words since $\mathcal{P}\, \hat{I}_{\alpha I}(t) \prod_{i=1}^{2n} \mathcal{L}_I(\tau_i)\, \mathcal{P} = 0$.

$$K^{I}_{I\alpha}(t,\tau)\,\hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_{res}\left\{\mathcal{P}\,\hat{I}_{\alpha,I}(t)\, Q\mathcal{L}_I(\tau)\,\mathcal{P}\,\rho_I(\tau)\right\} \quad (4.34)$$

$$+ \mathrm{Tr}_{res}\left\{\mathcal{P}\,\hat{I}_{\alpha,I}(t)\int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2\, Q\mathcal{L}_I(\tau_2)\, Q\mathcal{L}_I(\tau_1)\, Q\mathcal{L}_I(\tau)\,\mathcal{P}\,\rho_I(\tau)\right\}$$

And, by inserting once again $Q = 1-\mathcal{P}$

$$K^{I}_{I\alpha}(t,\tau)\,\hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_{res}\left\{ I_{\alpha,I}(t)\,\mathcal{L}_I(\tau)\,\rho^{I}_{red}(\tau)\otimes\hat{\rho}_{res}\right\} +$$

$$+ \int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2\, \mathrm{Tr}_{res}\left\{\hat{I}_{\alpha,I}(t)\,\mathcal{L}_I(\tau_2)\,\mathcal{L}_I(\tau_1)\,\mathcal{L}_I(\tau)\,\rho^{I}_{red}(\tau)\otimes\rho_{res}\right\} + \quad (4.35)$$

$$- \int_{\tau}^{t} d\tau_1 \int_{\tau_1}^{t} d\tau_2\, \mathrm{Tr}_{res}\left\{\hat{I}_{\alpha,I}(t)\,\mathcal{L}_I(\tau_2)\, \mathrm{Tr}_{res}\left\{\mathcal{L}_I(\tau_1)\,\mathcal{L}_I(\tau)\,\rho^{I}_{red}(\tau)\otimes\hat{\rho}_{res}\right\}\otimes\hat{\rho}_{res}\right\}$$

Finally, following the same rules used for the time evolution kernel, one can exchange the integration limits and obtain:

$$I_\alpha(t) = \mathrm{Tr}_{sys} \int_0^t d\tau \, \mathrm{Tr}_{res} \left\{ \hat{I}_{\alpha,I}(t) \mathcal{L}_I(\tau) \hat{\rho}^I_{red}(\tau) \otimes \hat{\rho}_{res} \right\} +$$

$$+ \mathrm{Tr}_{sys} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \, \mathrm{Tr}_{res} \left\{ \hat{I}_{\alpha,I}(t) \mathcal{L}_I(\tau_2) \mathcal{L}_I(\tau_1) \mathcal{L}_I(\tau) \hat{\rho}^I_{red}(\tau) \otimes \hat{\rho}_{res} \right\}$$

$$- \mathrm{Tr}_{sys} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \, \mathrm{Tr}_{res} \left\{ \hat{I}_{\alpha,I}(t) \mathcal{L}_I(\tau_2) \, \mathrm{Tr}_{res} \left\{ \mathcal{L}_I(\tau_1) \mathcal{L}_I(\tau) \hat{\rho}^I_{red}(\tau) \otimes \hat{\rho}_{res} \right\} \otimes \hat{\rho}_{res} \right\} \quad (4.36)$$

4.2 Diagrammatic analysis

In the following we discuss a graphical (= diagrammatic) language which enables to visualize all contributions to the kernels $K^{(2)}$, $K^{(4)}$, K_c and K_{I_α} and extract from the diagrams the corresponding analytical expressions. To start, we separate the tunnelling operator in a in-tunnelling (+) and out-tunnelling (-) part:

$$\frac{1}{\hbar} \hat{H}^I_T(\tau_i) = \hat{A}^+_i + \hat{A}^-_i \quad (4.37)$$

with $\displaystyle \hat{A}^+_i := \sum_{l\sigma} \hat{D}^+_{i,l\sigma} \hat{C}^-_{i,l\sigma} = \sum_{l\sigma} \left(\hbar^{-1} \hat{d}^+_{l\sigma}(\tau_i) \right) \left(\sum_{\alpha\vec{k}} t_{\alpha\vec{k}l\sigma} \, \hat{c}_{\alpha\vec{k}\sigma}(\tau_i) \right)$

and $\displaystyle \hat{A}^-_i := \sum_{l\sigma} \hat{C}^+_{i,l\sigma} \hat{D}^-_{i,l\sigma} = \sum_{l\sigma} \left(\sum_{\alpha\vec{k}} t^*_{\alpha\vec{k}l\sigma} \, \hat{c}^+_{\alpha\vec{k}\sigma}(\tau_i) \right) \left(\hbar^{-1} d_{l\sigma}(\tau_i) \right)$

where l labels a single particle basis for the system. Notice that, via the tunnelling amplitude $t_{\alpha\vec{k}l\sigma}$ some information on the microscopic system state $l\sigma$ propagated to the lead. Moreover, the operator $\hat{C}^\pm_{i,l\sigma}$ is the one relevant for transport since its correlator decay in time, contrary

to the one for the free electron operator $c_{\alpha \vec{k} \sigma}$ which oscillates.
Since fermions of the lead and the system anticommute, it holds

$$\hat{C}^{\pm}_{i,l\sigma} \hat{D}^{\mp}_{i,l'\sigma'} = - \hat{D}^{\mp}_{i,l'\sigma'} \hat{C}^{\pm}_{i,l\sigma} \qquad (4.38)$$

Out of the definitions (4.37) it follows that the Kernel component $K^{I(2)}$ and $K^{I(4)}$ (4.23) can be written

$$K^{I(2)}(t,\tau)\, \hat{\rho}_{red,I}(\tau) = - \sum_{p_0 p_3 \in \{+,-\}} \mathrm{Tr}_{res}\left\{ \left[\hat{A}_3^{p_3}, \left[\hat{A}_0^{p_0}, \rho^{I}_{red}(\tau) \otimes \hat{\rho}_{res} \right]\right]\right\} \qquad (4.39)$$

$$K^{I(4)}(t,\tau_2,\tau_1,t)\, \hat{\rho}_{red,I}(\tau) = \sum_{p_0 p_1 p_2 p_3 \in \{+,-\}} \cdot$$

$$\Big(\mathrm{Tr}_{res}\left\{ \left[\hat{A}_3^{p_3} \left[\hat{A}_2^{p_2}, \left[\hat{A}_1^{p_1}, \left[\hat{A}_0^{p_0}, \hat{\rho}^{I}_{red,}(\tau) \otimes \hat{\rho}_{res} \right]\right]\right]\right]\right\} \qquad (4.39b)$$

$$- \mathrm{Tr}_{res}\left\{ \left[\hat{A}_3^{p_3}, \left[\hat{A}_2^{p_2}, \mathrm{Tr}_{res}\left\{ \left[\hat{A}_1^{p_1}, \left[\hat{A}_0^{p_0}, \hat{\rho}^{I}_{red}(\tau) \otimes \hat{\rho}_{res} \right]\right]\right\} \otimes \hat{\rho}_{res} \right]\right]\right\} \Big)$$

where $\tau_0 = \tau$ and $\tau_3 = t$.

As we shall see, the evaluation of the commutators is a lengthy but standard task which is achieved by invoking Wick's theorem and the cyclic invariance of the trace.

One obtains: $\begin{cases} 8 \text{ contributions in } 2^{nd} \text{ order} \\ 128 \text{ contributions in } 4^{th} \text{ order} \end{cases}$

Note: the number of contributions given above already takes into account the constraints on the $\sum_{p_i}$ given by the Wick's theorem.