Chapter 4: Diagrammatic approaches

4.1 Iterative method and the Hilbert space description

Using the same iterative procedure analyzed in Ch. 2 it is possible to obtain a master equation to a given perturbative order and from there to extract the evolution kernel $K^{(2n)}(t-t')$. We notice that $\tilde{K}^{(2n)}(0)$ gives the stationary solution of the GME via the equation

$$\left[\mathcal{L}_s + \sum_{n=1}^{N} \tilde{K}^{(2n)}(0)\right] \mathcal{P}\rho(\infty) = 0 \qquad (4.1)$$

and, in particular that $K^{(2n)}_{\text{Markov}} = \tilde{K}^{(2n)}(0) \Rightarrow$ the Markov approximation does not influence the calculation of the stationary solution, but only the time evolution of ρ to approach it.

<u>proof</u>:

$$\tilde{K}^{(2n)}(\lambda = 0) = \lim_{\lambda \to 0} \int_0^\infty d\tau \; K^{(2n)}(\tau)\, e^{-\lambda\tau} = \int_0^\infty d\tau \; K^{(2n)}(\tau)$$

The GME in the Markov approximation reads:

$$\dot{\hat{\rho}}_{red} = \mathcal{L}_s \hat{\rho}_{red} + \underbrace{\int_0^\infty dt' \sum_{n=1}^{N} K^{(2n)}(t')}_{\sum_{n=0}^{N} K^{(2n)}_{\text{Markov}}} \hat{\rho}_{red}(t)$$

$\blacksquare$

The calculation of (4.1) projected on the eigenbasis of H_s is the main task of this chapter.

$$\lim_{t\to\infty} \dot{\hat{\rho}}_{red}(t)_{bb'} = 0 = -\frac{i}{\hbar} \sum_{aa'} \delta_{ab}\delta_{a'b'} (E_a - E_{a'})\, \rho^{stat}_{aa'} + \sum_{aa'} \sum_{n=1}^{N} \tilde{K}^{(2n)\,aa'}_{bb'}\, \rho^{stat}_{aa'} \qquad (4.2)$$

where, given the eigenbasis $\{|a\rangle\}$

$$\hat{\rho}^{stat}_{red} = \sum_{aa'} \rho^{stat}_{aa'} |a\rangle\langle a'| \qquad (4.3)$$

and

$$\tilde{K}^{(2n)\,aa'}_{bb'} := \langle b| \tilde{K}^{(2n)}(0)[\,|a\rangle\langle a'|\,]\,|b'\rangle \qquad (4.4)$$

In (4.4) we have used square brackets to indicate that the kernel superoperator must <u>first</u> act on the density operator $\hat{\rho}^{stat}_{red}$ and then the resulting matrix elements are taken. The diagrammatic representation of $K^{2n\,aa'}_{bb'}$ is very helpful for a classification of the different tunnelling processes considered in the system dynamics.

4.1.1 GME up to 4th order

The iterative approach to the GME derivation moves from the Liouville - von Neumann in interaction picture

$$\dot{\hat{\rho}}_I(t) = \mathcal{L}_{T,I}(t)\,\rho_I(t) \qquad (4.5)$$

which, integrated, and reinserted into itself gives

$$\dot{\hat{\rho}}_I(t) = \mathcal{L}_{T,I}(t)\,\hat{\rho}_I(0) + \int_0^t d\tau\, \mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_I(\tau) \qquad (4.6)$$

Since we are interested to 4th order perturbation theory, we repeat the procedure to obtain:

$$\hat{\rho}_I(t) = \hat{\rho}_I(0) + \int_0^t d\tau\, \mathcal{L}_{T,I}(\tau)\,\hat{\rho}_I(0) +$$

$$+ \int_0^t d\tau_1 \int_0^{\tau_1} d\tau\, \mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_I(\tau) \qquad (4.7)$$

and, eventually by inserting (4.7) in (4.6)

$$\dot{\hat{\rho}}_I(t) = \mathcal{L}_{T,I}(t)\,\hat{\rho}_I(0) + \int_0^t d\tau\; \mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_I(0)$$

$$+ \int_0^t d\tau\; \mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau)\int_0^\tau d\tau_1\; \mathcal{L}_{T,I}(\tau_1)\,\hat{\rho}_I(0) \qquad (4.8)$$

$$+ \int_0^t d\tau_2\; \mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau_2)\int_0^{\tau_2} d\tau_1\int_0^{\tau_1} d\tau\; \mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_I(\tau)$$

The trace over the leads yields an eq. for $\hat{\rho}_{red,I}$ from which terms with an odd number of $\mathcal{L}_{T,I}$ drop due to conservation of both particle numbers of $\hat{H}_B$. Moreover we can use the relation $\hat{\rho}_I(\tau) = \mathrm{Tr}_B\,\hat{\rho}_I(\tau)\otimes\hat{\rho}_B + O(\hat{H}_T)$ to obtain

$$\dot{\hat{\rho}}_{red,I} = \int_0^t d\tau\; \mathrm{Tr}_B\left\{\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_{red,I}(0)\otimes\rho_B\right\} +$$

$$+ \int_0^t d\tau_2\int_0^{\tau_2} d\tau_1\int_0^{\tau_1} d\tau\; \mathrm{Tr}_B\left\{\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau_2)\,\mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_{red,I}(\tau)\,\rho_B\right\}$$

$$+ O(\hat{H}_T^6). \qquad (4.9)$$

The first contribution in (4.9) contains $\hat{\rho}_{red,I}(0)$ which is not desirable. On the other hand we have from (4.7)

$$\hat{\rho}_{red,I}(0) = \hat{\rho}_{red,I}(t) - \int_0^t d\tau_1\int_0^{\tau_1} d\tau\; \mathrm{Tr}_B\left\{\mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\hat{\rho}_{red,I}(\tau)\otimes\rho_B\right\}$$

$$+ O(H_T^4) \qquad \forall t>0 \qquad (4.10)$$

By inserting (4.10) in (4.9), with $t=\tau$ we obtain

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau)\, \hat{\rho}_{red,I}(\tau) \otimes \hat{\rho}_B \right\} \tag{4.11}$$

$$- \int_0^t d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau) \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(\tau_1)\, \mathcal{L}_{T,I}(\tau_2)\, \hat{\rho}_{red,I}(\tau_2) \otimes \rho_B \right\} \otimes \rho_B \right\}$$

$$+ \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau_2)\, \mathcal{L}_{T,I}(\tau_1)\, \mathcal{L}_{T,I}(\tau)\, \hat{\rho}_{red,I}(\tau) \otimes \rho_B \right\}$$

Since they are mute variables I can exchange $t \leftrightarrow \tau_2$ in the second term and obtain:

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau)\, \hat{\rho}_{red,I}(\tau) \otimes \hat{\rho}_B \right\} + \tag{4.12}$$

(i) $$+ \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau_2)\, \mathcal{L}_{T,I}(\tau_1)\, \mathcal{L}_{T,I}(\tau)\, \hat{\rho}_{red,I}(\tau) \otimes \hat{\rho}_B \right\}$$

(ii) $$- \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t)\, \mathcal{L}_{T,I}(\tau_2)\, \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(\tau_1)\, \mathcal{L}_{T,I}(\tau_2)\, \hat{\rho}_{red,I}(\tau_2) \otimes \rho_B \right\} \otimes \rho_B \right\}$$

(i) represents the most naive 4^{th} order expression. It must though be corrected by (ii). The meaning of the correction becomes clearer once the diagrammatic representation is introduced.

A more elegant derivation of (4.12) can be obtained using the projectors

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

where $$\mathcal{G}_{Q,I}(t,s) = T_{\leftarrow} \exp\left[\int_s^t ds' \; \mathcal{Q}\, \mathcal{L}_{T,I}(s') \right]$$

The second order expansion in $\mathcal{L}_{T,I}$ of the GME is obtained by considering $\mathcal{G}_{Q,I}(t,s) \simeq 1$. The fourth order is obtained by expanding $\mathcal{G}_{Q,I}(t,s)$ up to the second order

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

(4.13)

The equation of motion for the factorized component of $\hat{\rho}$ reads:

$$\begin{aligned}
\mathcal{P}\dot{\hat{\rho}}_I(t) &= \mathcal{P}\mathcal{L}_{T,I}(t) \int_0^t ds \, Q\mathcal{L}_{T,I}(s) \mathcal{P}\hat{\rho}_I(s) + \\
&+ \mathcal{P}\mathcal{L}_{T,I}(t) \int_0^t ds \int_s^t ds' \, Q\mathcal{L}_{T,I}(s') Q\mathcal{L}_{T,I}(s) \mathcal{P}\hat{\rho}_I(s) \qquad (4.14) \\
&+ \mathcal{P}\mathcal{L}_{T,I}(t) \int_0^t ds \int_s^t ds' \int_{s'}^t ds'' \, Q\mathcal{L}_{T,I}(s'') Q\mathcal{L}_{T,I}(s') Q\mathcal{L}_{T,I}(s) \mathcal{P}\hat{\rho}_I(s)
\end{aligned}$$

By exploiting now the formal relation $\mathcal{P}\mathcal{L}_{T,I}^{(2n+1)}\mathcal{P} = 0$ independently from what follows or comes before; let's consider the two integrands ($Q = 1 - \mathcal{P}$)

$$(I) \quad \mathcal{P}\mathcal{L}_{T,I}(t)(1-\mathcal{P})\mathcal{L}_{T,I}(s')(1-\mathcal{P})\mathcal{L}_{T,I}(s)\mathcal{P}$$

(4.15)

$$(II) \quad \mathcal{P}\mathcal{L}_{T,I}(t)(1-\mathcal{P})\mathcal{L}_{T,I}(s'')(1-\mathcal{P})\mathcal{L}_{T,I}(s')(1-\mathcal{P})\mathcal{L}_{T,I}(s)\mathcal{P}$$

(I) in (4.15) contains always a component $\mathcal{P}\mathcal{L}_{T,I}^{(2n+1)}\mathcal{P}$ with $n \in \mathbb{N}$ $\Rightarrow$ (I) = 0. (II) yields instead 2 non-vanishing contributions

$$\mathcal{P}\mathcal{L}_{T,I}(t)\mathcal{L}_{T,I}(s'')\mathcal{L}_{T,I}(s')\mathcal{L}_{T,I}(s)\mathcal{P}$$

(4.15b)

$$-\mathcal{P}\mathcal{L}_{T,I}(t)\mathcal{L}_{T,I}(s'')\mathcal{P}\mathcal{L}_{T,I}(s')\mathcal{L}_{T,I}(s)\mathcal{P}$$

All together:

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

$$+ \int_0^t ds \int_s^t ds' \int_{s'}^t ds''\, \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(s'')\,\mathcal{L}_{T,I}(s')\,\mathcal{L}_{T,I}(s)\,\mathcal{P}\hat{\rho}_I(s)$$

$$- \int_0^t ds \int_s^t ds' \int_{s'}^t ds''\, \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(s'')\,\mathcal{P}\mathcal{L}_{T,I}(s')\,\mathcal{L}_{T,I}(s)\,\mathcal{P}\hat{\rho}_I(s) \tag{4.16}$$

In order to recover (4.12) we have to reorder the integrals according to the general rule

$$\int_0^t ds \int_s^t ds'\, F(s',s) = \int_0^t ds \int_0^s ds'\, F(s,s') \tag{4.17}$$

We apply (4.17) between ds and ds', we exchange $\int ds'$ and $\int ds''$ and apply (4.17) between ds and ds''. The renaming $s' = \tau$ $s'' = \tau_1$ $s = \tau_2$ concludes the proof. The result being

$$\mathcal{P}\dot{\hat{\rho}}_I(t) = \int_0^t d\tau\, \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau)\,\mathcal{P}\hat{\rho}_I(\tau) +$$

$$+ \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau\, \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau_2)\,\mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\mathcal{P}\hat{\rho}_I(\tau)$$

$$- \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau\, \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(\tau_2)\,\mathcal{P}\mathcal{L}_{T,I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\mathcal{P}\hat{\rho}_I(\tau)$$

The 4^{th} order kernel thus reads (from 4.16) (4.18)

$$K_I^{(4)}(t,\tau) = \int_\tau^t ds' \int_{s'}^t ds'' \Big[\mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(s'')\,\mathcal{L}_{T,I}(s')\,\mathcal{L}_{T,I}(\tau)\,\mathcal{P}$$
$$- \mathcal{P}\mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(s'')\,\mathcal{P}\mathcal{L}_{T,I}(s')\,\mathcal{L}_{T,I}(\tau)\,\mathcal{P}\Big]$$

One should notice though that the convolutive form can only be obtained in the Schrödinger picture:

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

$$= \mathcal{G}_0(t,0)\, K_I^{(2n)}(t,\tau)\, \mathcal{G}_0(0,\tau)\, \hat{\rho}_{red}(\tau) \qquad (4.19)$$

4.1.2 The role of coherences

If the central system lives in a N-dimensional Hilbert space, the corresponding RDM has dimension $N \times N$ while the superoperator $K^{(2n)}$ has dimension $N^2 \times N^2$ which means a considerable numerical and analytical effort even for systems with relatively small N. To simplify the analysis one should look for possible approximations.

We concentrate here on the role of coherences, i.e. off-diagonal element 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 baths) the associated coherence can be excluded.

Examples:

- The particle number => the RDM is block diagonal in the particle number (the only exception is the one of superconducting leads treated in mean field)
- 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 derivation of the Pauli master equation the <u>secular approximation</u> neglects coherences between states with different energies.

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 $\hbar\Gamma \sim t^2 D$, with D the density of states in the bath.

In order to account for those contributions we first separate $\hat{\rho}^{stat}_{red}$:

$$\hat{\rho}^{stat}_{red} := \begin{pmatrix} \hat{\rho}_s \\ \hat{\rho}_n \end{pmatrix} \begin{matrix} \longleftarrow \text{secular contribution} \\ \longleftarrow \text{non-secular contributions} \end{matrix} \qquad (4.20)$$

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

The equation for the stationary $\hat{\rho}$ assumes the form

$$\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} (K_0)_{ss} + K^{(2)}_{ss} + K^{(4)}_{ss} & K^{(2)}_{sn} + K^{(4)}_{sn} \\ K^{(2)}_{ns} + K^{(4)}_{ns} & (K_0)_{nn} + K^{(2)}_{nn} + K^{(4)}_{nn} \end{pmatrix} \begin{pmatrix} \hat{\rho}_s \\ \hat{\rho}_n \end{pmatrix} \qquad (4.21)$$

where

$$(K_0)^{aa'}_{bb'} = \frac{i}{\hbar} \delta_{ab} \delta_{a'b'} (E_{a'} - E_a) = (\mathcal{L}_s)^{aa'}_{bb'}$$

It follows

$$\hat{\rho}_n = - \left((K_0)_{nn} + K^{(2)}_{nn} + K^{(4)}_{nn} \right)^{-1} \left(K^{(2)}_{ns} + K^{(4)}_{ns} \right) \hat{\rho}_s \qquad (4.22)$$

We further proceed

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

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

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

which allows us to conclude

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

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

$\Rightarrow$ neglecting contributions beyond Γ^2 one finds, from (4.21)

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

$$= \left[(K_0)_{ss} + K^{(2)}_{ss} + K^{(4)}_{eff}\right]\hat{\rho}_s \qquad (4.23)$$

where

$$K^{(4)}_{eff} = K^{(4)}_{ss} + K_C = K^{(4)}_{ss} - K^{(2)}_{sn}(K_0)^{-1}_{nn}K^{(2)}_{ns} \qquad (4.24)$$

which contain the correction to the secular density matrix due to coherences between non-secular terms.

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:

$$I_\alpha(t) = \mathrm{Tr}\left\{ \hat{I}_\alpha \, \hat{\rho}(t) \right\} = \mathrm{Tr}_{S+B}\left\{ \int_0^t d\tau \, K_{I_\alpha}(t-\tau) \, \hat{\rho}(\tau) \right\} \quad (4.25)$$

where the second equality must be read at this point simply as an implicit definition of the current Kernel. The derivation of its explicit form 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: (3.18)

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

with

$$G_{Q,I}(t,s) = T_{\leftarrow} \exp \int_s^t ds' \, Q \, \mathcal{L}_{T,I}(s')$$

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

$$I_\alpha(t) = \mathrm{Tr}\left\{ \hat{I}_{\alpha,I}(t) \int_0^t ds \; G(t,s) \, Q \, \mathcal{L}_{T,I}(s) \, P \rho_I(s) \right\} \quad (4.26)$$

$$\mathrm{Tr}_{sys}\left\{ \int_0^t d\tau \; \mathrm{Tr}_B \left\{ \hat{I}_{\alpha,I}(t) \, G_{Q,I}(t,\tau) \, Q \, \mathcal{L}_{T,I}(\tau) \, \rho_{red,I}(\tau) \otimes \hat{\rho}_{B} \right\} \right\}$$

where the Kernel in interaction picture can be read out:

$$K^{I}_{I\alpha}(t,\tau)\,\hat{\rho}^{I}_{red}(\tau) = \mathrm{Tr}_B\left\{ \hat{I}_{\alpha,I}(t)\; \underset{Q,I}{G}(t,\tau)\, Q\mathcal{L}_{T,I}(\tau)\; \rho^{I}_{red}(\tau)\otimes\hat{\rho}_B \right\} \quad (4.27)$$

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:

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

$$+\; O(H_T^3)$$

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

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

$$+\; \mathrm{Tr}_B\left\{\mathcal{P}\,\hat{I}_{\alpha,I}(t)\int_\tau^t d\tau_1\int_{\tau_1}^t d\tau_2\; Q\mathcal{L}_{T,I}(\tau_2)\, Q\mathcal{L}_{T,I}(\tau_1)\, Q\mathcal{L}_{T,I}(\tau)\,\mathcal{P}\,\rho_I(\tau)\right\} \quad (4.28)$$

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

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

$$+ \int_\tau^t d\tau_1\int_{\tau_1}^t d\tau_2\; \mathrm{Tr}_B\left\{\hat{I}_{\alpha,I}(t)\,\mathcal{L}_{T,I}(\tau_2)\,\mathcal{L}_{I}(\tau_1)\,\mathcal{L}_{T,I}(\tau)\,\rho^{I}_{red}(\tau)\otimes\hat{\rho}_B\right\} + \quad (4.29)$$

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

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

$$I_\alpha(t) = Tr_{sys} \int_0^t d\tau \, Tr_B \{ \hat{I}_{\alpha,I}(t) \mathcal{L}_{T,I}(\tau) \hat{\rho}^{I}_{red}(\tau) \otimes \hat{\rho}_B \} + \tag{4.30}$$

$$+ Tr_{sys} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \, Tr_B \{ \hat{I}_{\alpha,I}(t) \mathcal{L}_{T,I}(\tau_2) \mathcal{L}_{T,I}(\tau_1) \mathcal{L}_{T,I}(\tau) \hat{\rho}_{red,I}(\tau) \otimes \hat{\rho}_B \}$$

$$- Tr_{sys} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \, Tr_B \{ \hat{I}_{\alpha,I}(t) \mathcal{L}_{T,I}(\tau_2) Tr_B \mathcal{L}_{T,I}(\tau_1) \mathcal{L}_{T,I}(\tau) \hat{\rho}_{red,I}(\tau) \otimes \hat{\rho}_B \} \otimes \hat{\rho}_B$$

It is thus clear that the propagator kernel of ρ_{red} and the current kernel are closely related. The first is turned into the second by substituting the first Liouville tunnelling superoperator by the current operator $\hat{I}_\alpha(t)$.

Summarizing, in the Schrödinger picture:

$$K^{(2)}(t-\tau) = \mathcal{P} \mathcal{L}_T G_0(t-\tau) \mathcal{L}_T \mathcal{P} \tag{4.31}$$

$$K^{(4)}(t-\tau) = \int_\tau^t ds' \int_{s'}^t ds'' \left[\mathcal{P} \mathcal{L}_T G_0(t-s'') \mathcal{L}_T G_0(s''-s') \mathcal{L}_T G_0(s'-\tau) \mathcal{L}_T \mathcal{P} \right.$$
$$\left. - \mathcal{P} \mathcal{L}_T G_0(t-s'') \mathcal{L}_T \mathcal{P} G_0(s''-s') \mathcal{P} \mathcal{L}_T G_0(s'-\tau) \mathcal{L}_T \mathcal{P} \right]$$

and

$$K^{(2)}_{I_\alpha}(t-\tau) = \mathcal{P} \hat{I}_\alpha G_0(t-\tau) \mathcal{L}_T \mathcal{P}$$

$$K^{(4)}_{I_\alpha}(t-\tau) = \int_\tau^t ds' \int_{s'}^t ds'' \left[\mathcal{P} \hat{I}_\alpha G_0(t-s'') \mathcal{L}_T G_0(s''-s') \mathcal{L}_T G_0(s'-\tau) \mathcal{L}_T \mathcal{P} \right. \tag{4.32}$$
$$\left. - \mathcal{P} \hat{I}_\alpha G_0(t-s'') \mathcal{L}_T \mathcal{P} G_0(s''-s') \mathcal{P} \mathcal{L}_T G_0(s'-\tau) \mathcal{L}_T \mathcal{P} \right]$$

$\mathcal{P}\rho(t)$ is calculated using the first two kernels. $I_\alpha(t) = \int_0^t d\tau \, Tr \left(K^{(2)}_{I_\alpha} + K^{(4)}_{I_\alpha} \right)(t-\tau) \, \mathcal{P}\rho(\tau)$