The equations (3.17) and (3.18) represent two alternative expressions for the current. We want now prove their equivalence. More precisely the statement is:

$$\sum_\alpha \mathrm{Tr}\{ \hat{I}_{\alpha,I}\, Q \hat{\rho}_I \} = e\, \mathrm{Tr}\{ \hat{N}_s \wp \dot{\rho}_I \} \qquad (3.19)$$

<u>proof</u>

$$\sum_\alpha \mathrm{Tr}\{ \hat{I}_{\alpha,I}\, Q \hat{\rho}_I \} = \sum_\alpha \mathrm{Tr}\{ e \tfrac{i}{\hbar} [\hat{N}_\alpha, \hat{H}_{T,I}]\, Q \hat{\rho}_I \} =$$

$$\overset{(1)}{=} \sum_\alpha \mathrm{Tr}\{ e \tfrac{i}{\hbar} [\hat{N}_\alpha, \hat{H}_I]\, Q \hat{\rho}_I \} \overset{(2)}{=} \mathrm{Tr}\{ e \tfrac{i}{\hbar} [\textstyle\sum_\alpha \hat{N}_\alpha, \hat{H}_I]\, Q \hat{\rho}_I \} =$$

$$\overset{(3)}{=} \mathrm{Tr}\{ e \tfrac{i}{\hbar} [\hat{N} - \hat{N}_s, \hat{H}_I]\, Q \hat{\rho}_I \} \overset{(4)}{=} \mathrm{Tr}\{ - e \tfrac{i}{\hbar} [\hat{N}_s, \hat{H}_I]\, Q \hat{\rho}_I \} =$$

$$\overset{(5)}{=} \mathrm{Tr}\{ - e \tfrac{i}{\hbar} [\hat{N}_s, \hat{H}_{T,I}]\, Q \hat{\rho}_I \} \overset{(6)}{=} \mathrm{Tr}\{ e \tfrac{i}{\hbar} [H_{T,I}, \hat{N}_s Q \hat{\rho}_I] \} - \mathrm{Tr}\{ e \hat{N}_s \tfrac{i}{\hbar} [H_{T,I}, Q \rho_I] \}$$

$$\overset{(7)}{=} \mathrm{Tr}\{ e \hat{N}_s \left(-\tfrac{i}{\hbar}\right) [\hat{H}_{T,I}, Q \rho_I] \} \overset{(8)}{=} e\, \mathrm{Tr}\{ \hat{N}_s \mathcal{L} Q \hat{\rho}_I \} =$$

$$\overset{(9)}{=} e\, \mathrm{Tr}\{ \wp \hat{N}_s \mathcal{L} Q \hat{\rho}_I \} \overset{(10)}{=} e\, \mathrm{Tr}\{ \hat{N}_s \wp \mathcal{L} Q \hat{\rho}_I \} \overset{(11)}{=} e\, \mathrm{Tr}\{ \hat{N}_s \wp \dot{\rho}_I \}.$$

The chain of equalities are justified by:

(1) $[\hat{N}_\alpha, \hat{H}_s] = [\hat{N}_\alpha, \hat{H}_{res}] = 0$

(2) linearity of $\mathrm{Tr}\{\ \}$ and $[\cdot,\cdot]$

(3) $\hat{N} = \hat{N}_s + \sum_\alpha \hat{N}_\alpha$

(4) $[\hat{N}, \hat{H}] = 0$

(5) $[\hat{N}_s, \hat{H}_s] = [\hat{N}_s, \hat{H}_{res}] = 0$

(6) $[A, BC] = B[A,C] + [A,B]C$

(7) $\mathrm{Tr}\{[A,B]\} = 0$

(8) $\mathcal{L}\hat{A} \equiv -\frac{i}{\hbar}[H_{T,I}, \rho]$

(9) $\mathrm{Tr}\{\hat{A}\} = \mathrm{Tr}\{\wp \hat{A}\}$

(10) $\mathrm{Tr}_{res}\{\hat{O}_s \hat{O}\} = \hat{O}_s\, \mathrm{Tr}_{res}\{\hat{O}\}$

(11) Eq. (2.58)

Eqs. (3.17), (3.18), (3.19) make the final link between the general theory of the reduced density matrix and the transport problem. What still needs to be analyzed is now the structure of the many-body Hamiltonian.

3.4 The many-body approach to Q-transport

In systems with low conductance $G \lesssim G_Q$ it is natural the separation between SYSTEM and BATH connected by weak tunnelling links. This leads to the total Hamiltonian

$$\hat{H}_{TOT} = \hat{H}_{res} + \hat{H}_S + \hat{H}_T + \hat{H}_{ext} \qquad (3.20)$$

that we analyze here in greater detail. With respect of previous formulations in the course we added $\hat{H}_{ext}$ in (3.20) to take into account the effects of external perturbations like for example an external gate voltage applied on the system or the electrostatic coupling to the metallic contacts. In both cases H_{ext} can be absorbed in $\hat{H}_S$ and we will not give it any further importance. In second quantization, convenient to study many-body physics:

$$\hat{H}_{res} = \sum_{\alpha \vec{k} \sigma} \varepsilon_{\alpha \vec{k}} \, c^{+}_{\alpha \vec{k} \sigma} c_{\alpha \vec{k} \sigma} \qquad (3.21)$$

where $\alpha = L, R$ and $c^{+}_{\alpha \vec{k} \sigma}$ creates an electron with energy $\varepsilon_{\alpha \vec{k}}$. $\vec{k}$ is the quasi-momentum (Bloch states) and σ is the spin degree of freedom. For simplicity we assume the leads (equiv contacts, equiv. reservoirs) as reservoirs of non-interacting electrons.

For what concerns the system

$$\hat{H}_S = \sum_{i\sigma} \varepsilon_{i\sigma} d^{\dagger}_{i\sigma} d_{i\sigma} + \sum_{\substack{ijkl \\ \sigma\tau}} V_{ijkl}\, d^{\dagger}_{i\sigma} d^{\dagger}_{j\tau} d_{k\tau} d_{l\sigma} \qquad (3.22)$$

which is the most generic interacting Hamiltonian for the system if $|i\sigma\rangle$ is a complete single particle basis. The fact that the sum over the spin components reduces to 2 (σ, and τ) depends on the nature of the Coulomb interaction that preserves spin. Other approximations can derive from the nature of the single particle orbitals. e.g. if they are extremely localized one obtains

$$\sum_{\substack{ijkl \\ \sigma\tau}} V_{ijkl}\, d^{\dagger}_{i\sigma} d^{\dagger}_{j\tau} d_{k\tau} d_{l\sigma} \cong \frac{1}{2} \sum_i V_{iiii} \left(d^{\dagger}_{i\uparrow} d_{i\uparrow} d_{i\downarrow} d_{i\downarrow} \right) \qquad (3.23)$$

the so called Hubbard approximation. If the indices i,j,k,l refer instead to an angular (or quasi-angular) momentum

$$\sum_{\substack{ijkl \\ \sigma\tau}} V_{ijkl}\, d^{\dagger}_{i\sigma} d^{\dagger}_{j\tau} d_{k\tau} d_{l\sigma} \cong \sum_{ijk} V_{i+k,j-k,j,i}\, d^{\dagger}_{i+k\sigma} d^{\dagger}_{j-k\tau} d_{j\tau} d_{i\sigma}$$

and so forth. Finally

$$\hat{H}_T = \sum_{\alpha} \hat{H}_{T,\alpha} = \sum_{\alpha} \sum_{\vec{k} i\sigma} t^{*}_{\alpha\vec{k}i\sigma}\, c^{\dagger}_{\alpha\vec{k}\sigma} d_{i\sigma} + \text{h.c.} \qquad (3.24)$$

where the crucial point is the determination of the tunnelling amplitudes $t^{*}_{\alpha\vec{k}i\sigma}$.

3.4.1 The tunnelling Hamiltonian

The idea of a second quantization description of tunnelling is due to Bardeen [J. Bardeen, Tunnelling from a many-body point of view, Phys. Rev. Lett., 6, 57 (1960)]. We will follow here the spirit of his derivation, adapting it to a tunnelling nanostructure. In order to obtain the second quantization operator $\hat{O}$ one starts from the first quantization one $\hat{o}$. In the case of tunnelling it is convenient to start from the single-electron Hamiltonian:

$$\hat{h} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{r}) \qquad (3.25)$$

where $\hat{V}(\hat{r})$ is the electrostatic potential in the lead, tunnelling region and in the system. Because the Schrödinger equation related to this problem might be quite difficult to solve, it is more convenient to divide the potential in two component, the "extended contact" and the "extended system" components:

$$V(\vec{r}) = V_{res}(\vec{r}) + V_S(\vec{r}) \qquad (3.26)$$

where

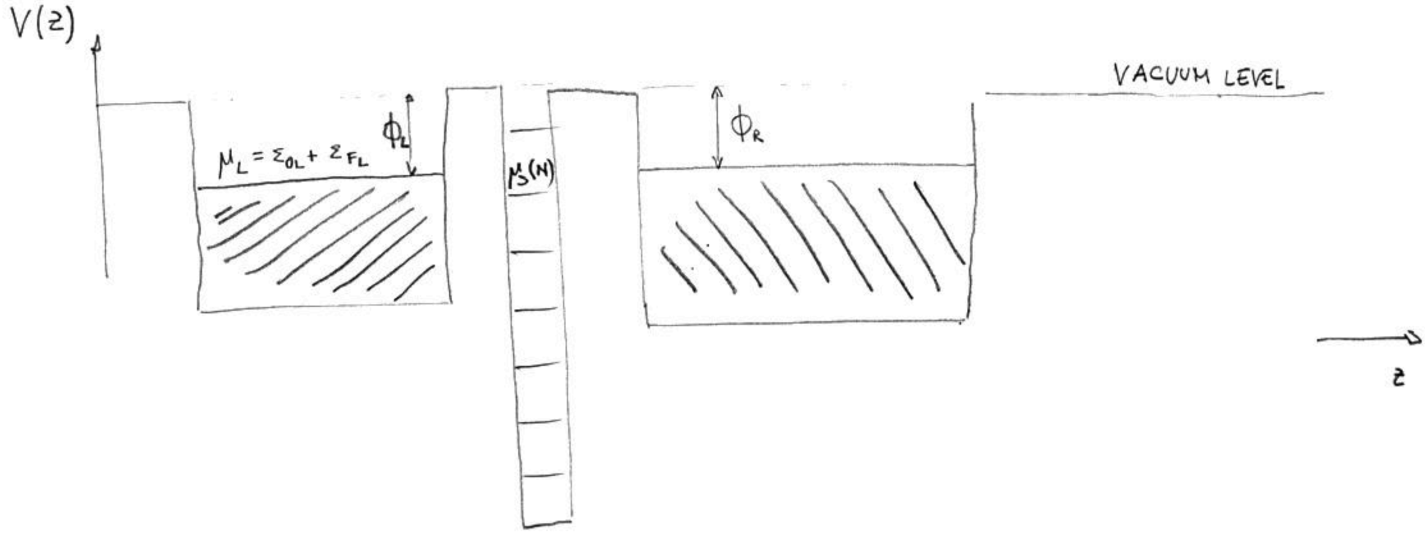
$$V_{res}(\vec{r}) = \begin{cases} V(\vec{r}) & \vec{r} \in R_{res} \\ 0 & \text{otherwise} \end{cases}$$

$$V_S(\vec{r}) = \begin{cases} V(\vec{r}) & \vec{r} \in R_S \\ 0 & \text{otherwise} \end{cases}$$

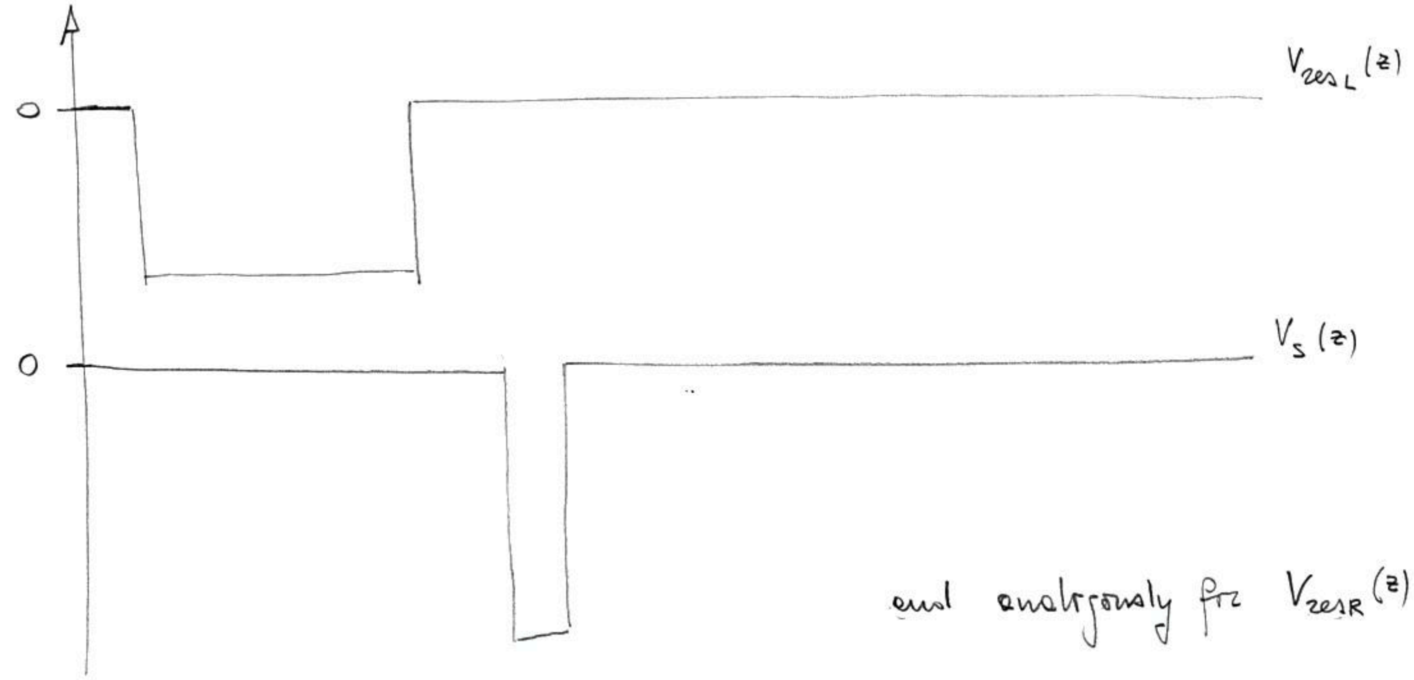
where R_{res} and R_S are regions of space defining the reservoirs and the relevant system.

$R_{res} + R_s$ gives back the entire space. Another way of stating the same concept is to identify $V_{res}(\vec{r})$ with the potential of the reservoir in absence of the system and $V_s(\vec{r})$ as the potential of the system in absence of the reservoir.

As a simple example consider the one for the STM on thin insulating film: $V(x_{tip}, y_{tip}, z)$



It holds then $V_{res} = V_{resL} + V_{resR}$, $V = V_s + V_{res}$



and analogously for $V_{resR}(z)$

In the tunnelling structures that we are considering we are mainly interested in the tunnelling between bound states for the different structures => in negative energies (the vacuum level is conventionally set to 0.). The wave functions which solve the Schrödinger equation associated to

$$\hat{h}_S = \frac{\hat{p}^2}{2m} + \hat{V}_S \quad , \quad \hat{h}_{res,L} = \frac{\hat{p}^2}{2m} + \hat{V}_{res,L} \quad , \quad \hat{h}_{res,R} = \frac{\hat{p}^2}{2m} + \hat{V}_{res,R} \qquad (3.27)$$

exhibit an exponential decay in the barrier regions, where the potentials $V_S, V_{res,L}, V_{res,R}$ are at the vacuum level. Let us introduce the eigenstates, eigenvalues

$$\hat{h}_S |i\sigma\rangle = \varepsilon_{i\sigma} |i\sigma\rangle \qquad \hat{h}_{res,\alpha} |\alpha\vec{k}\sigma\rangle = \varepsilon_{\alpha\vec{k}\sigma} |\alpha\vec{k}\sigma\rangle$$

$$t_{\alpha\vec{k}i\sigma} = \langle \alpha\vec{k}\sigma | \hat{h} | i\sigma \rangle = \langle \alpha\vec{k}\sigma | \frac{\hat{p}^2}{2m} + \hat{V}_S + \hat{V}_{res,L} + \hat{V}_{res,R} | i\sigma \rangle$$

$$= \sum_{\tau} \int d\vec{r} \; \varphi^*_{\alpha\vec{k}\sigma}(\vec{r}\tau) \, \hat{h}(\vec{r}) \, \psi_{i\sigma}(\vec{r}\tau) \qquad (3.28)$$

Due to the localized nature of the wave function $\psi_{i\sigma}(\vec{r}\tau)$ the product of $\varphi^*_{\alpha\vec{k}\sigma}(\vec{r})\psi_{i\sigma}(\vec{r}\tau)$ is moved towards the system and $\hat{h}$ can be substitute by $\hat{h}_S$ => obtaining

$$t_{\alpha\vec{k}i\sigma} = \left[\sum_{\tau} \int d\vec{r} \; \varphi_{\alpha\vec{k}\sigma}(\vec{r}\tau) \psi_{i\sigma}(\vec{r}\tau) \right] \varepsilon_{i\sigma} . \qquad (3.29)$$

i.e. one has to calculate <u>overlap integrals</u>.

Note: Very often the energy dependence of $t_{\alpha\vec{k}i\sigma}$ is neglected which brings to a very simple form for the tunnelling Hamiltonian

$$\hat{H}_{T,\alpha} = t \sum_{\vec{k}i\sigma} c^{+}_{\alpha\vec{k}\sigma} d_{i\sigma} + h.c. \qquad (3.30)$$

3.4.2 The field operator description

Especially when dealing with complex interacting systems, whose Hamiltonian can be diagonalized in the quasi-continuum description of their degrees of freedom (i.e. interacting SWCNTs as Luttinger liquids), a field operator description of the tunnelling Hamiltonian and of the associated current operator can be usefull. We introduce the field operators

$$\begin{aligned} \hat{\Phi}^{+}_{\alpha\sigma}(\vec{r}) &= \sum_{\vec{k}\tau} \langle \alpha\vec{k}\tau | \vec{r}\sigma \rangle c^{+}_{\alpha\vec{k}\tau} \\ \hat{\psi}^{+}_{\sigma}(\vec{r}) &= \sum_{i\tau} \langle i\tau | \vec{r}\sigma \rangle d^{+}_{i\tau} \end{aligned} \qquad (3.31)$$

and, correspondingly

$$\begin{aligned} c^{+}_{\alpha\vec{k}\sigma} &= \sum_{\tau} \int \frac{d\vec{r}}{V} \langle \vec{r}\tau | \alpha\vec{k}\sigma \rangle \Phi^{+}_{\alpha\tau}(\vec{r}) \\ d^{+}_{i\sigma} &= \sum_{\tau} \int \frac{d\vec{r}}{V} \langle \vec{r}\tau | i\sigma \rangle \psi^{+}_{\tau}(\vec{r}) \end{aligned} \qquad (3.31b)$$

It follows

$$\hat{H}_{T,\alpha} = \sum_{i\vec{k}\sigma} t^{*}_{\alpha\vec{k}i\sigma} \int \frac{d\vec{r}}{V} \int \frac{d\vec{r}'}{V} \langle \vec{r}\sigma | \alpha\vec{k}\sigma \rangle \langle i\sigma | \vec{r}'\sigma \rangle \Phi^{+}_{\alpha\sigma}(\vec{r}) \psi_{\sigma}(\vec{r}') + h.c. =$$

It is convenient to introduce the tunnelling function

$$T^{(0)*}_{\alpha\sigma}(\vec{r},\vec{r}') = \frac{1}{V^2}\sum_{i\vec{k}} t^*_{\alpha\vec{k}i\sigma} \langle \vec{r}\sigma | \alpha\vec{k}\sigma\rangle\langle i\sigma | \vec{r}'\sigma\rangle \qquad (3.32)$$

In view o what discussed in the subsection 3.4.1 it is easy to demonstrate that $T^{(0)}_{\alpha\sigma}(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')\, T_{\alpha\sigma}(\vec{r})$ thus obtaining

$$\hat{H}_{T,\alpha} = \sum_\sigma \int d\vec{r}\; T^*_{\alpha\sigma}(\vec{r})\, \Phi^+_{\alpha\sigma}(\vec{r})\, \psi_{i\sigma}(\vec{r}) + h.c. \qquad (3.33)$$

The tunnelling function describes in which region of space the tunnelling takes place. Also the tunnelling current can be expressed in terms of field operators and tunnelling function.

$$\hat{N}_\alpha = \sum_{\vec{k}\sigma} c^+_{\alpha\vec{k}\sigma} c_{\alpha\vec{k}\sigma} = \sum_\sigma \int d\vec{r}\; \Phi^+_{\alpha\sigma}(\vec{r})\, \Phi_{\alpha\sigma}(\vec{r}) \qquad (3.34)$$

It follows from (3.9)

$$\hat{I}_\alpha = -\frac{ie}{\hbar}\left[\hat{H}_{T\alpha}, \hat{N}_\alpha\right] =$$

$$= -\frac{ie}{\hbar}\sum_{\sigma\sigma'}\int d\vec{r}\int d\vec{r}'\; T^*_{\alpha\sigma}(\vec{r})\left[\hat{\Phi}^+_{\alpha\sigma}(\vec{r})\hat{\psi}_\sigma(\vec{r}),\; \hat{\Phi}^+_{\alpha\sigma'}(\vec{r}')\hat{\Phi}_{\alpha\sigma'}(\vec{r}')\right] + h.c.$$

$$= -\frac{ie}{\hbar}\sum_\sigma \int d\vec{r}\left[-T^*_{\alpha\sigma}(\vec{r})\,\hat{\Phi}^+_{\alpha\sigma}(\vec{r})\hat{\psi}_\sigma(\vec{r}) + T_{\alpha\sigma}(\vec{r})\,\psi^+_\sigma(\vec{r})\Phi_{\alpha\sigma}(\vec{r})\right]$$

where we have used the canonical anticommutation rules

$$\{\Phi_{\alpha\sigma}(\vec{r}),\, \Phi^+_{\alpha\sigma'}(\vec{r}')\} = \delta_{\sigma\sigma'}\,\delta(\vec{r}-\vec{r}')$$

Chapter 4 Iterative diagrammatic approach to tunnelling structures

4.1 Generalized Master Equation for the Reduced Density Matrix

In this chapter we use the iterative procedure developed in ch. 2.3 to obtain a generalized master equation (GME) for the RDM which is exact to a given order in the tunnelling Hamiltonian. In the interaction picture it has the form, cf (2.21)

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t dt' \; K(t,t') \, \hat{\rho}_{red,I}(t') \qquad (2.21) \; (4.1)$$

where the superoperator K is a power series in the tunnelling Hamiltonian. Because we shall mostly be interested in stationary properties, e.g. the stationary current, we need to know the stationary RDM. In the Schrödinger picture we have, cf (2.36),

$$\hat{\rho}^{\,stat}_{red} = \lim_{t \to \infty} \hat{\rho}_{red}(t) \;, \quad \dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}\left[\hat{H}_S , \hat{\rho}_{red}\right] + \int_0^t dt' \, K(t,t')\left[\hat{\rho}_{red}(t')\right] \qquad (4.1b)$$

and (if no time-dependent perturbations are applied such that $K(t,t') = K(t-t')$)

$$0 = \lim_{t \to \infty} \dot{\hat{\rho}}_{red}(t) = -\frac{i}{\hbar}\left[\hat{H}_S , \hat{\rho}^{\,stat}_{red}\right] + \lim_{z \to 0} z\, \tilde{K}(z)\, \tilde{\hat{\rho}}_{red}(z)$$

$$= -\frac{i}{\hbar}\left[\hat{H}_S , \hat{\rho}^{\,stat}_{red}\right] + \tilde{K}(z=0)\, \hat{\rho}^{\,stat}_{red} \qquad (4.2)$$

The first term accounts for the coherent dynamics of the isolated system; the second in contrast describes all processes due to tunnelling. Moreover $\tilde{K}(z) := \int_0^\infty d\tau \, e^{-z\tau} K(\tau)$ is the Laplace transform of the kernel superoperator.

Notice: For the derivation of limit $t \to \infty$ above we have used the following relations

① $$f(t) = \int_0^t dt'\, g(t-t')\, h(t')$$

$$\tilde{f}(z) = \tilde{g}(z)\, \tilde{h}(z)$$

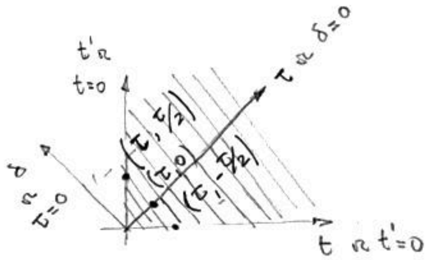
proof

$$\tilde{f}(z) = \int_0^\infty dt\, e^{-zt} f(t) = \int_0^\infty dt\, e^{-zt} \int_0^t dt'\, g(t-t')\, h(t')$$ but, on the other end

$$\tilde{g}(z)\, \tilde{h}(z) = \int_0^\infty dt \int_0^\infty dt'\, e^{-z(t+t')}\, g(t)\, h(t')$$

$$\tau = t'+t$$

$$\delta = \frac{t'-t}{2}$$



$$= \int_0^\infty d\tau \int_{-\tau/2}^{\tau/2} d\delta\, e^{-z\tau}\, g\left(\tfrac{\tau}{2} - \delta\right) h\left(\tfrac{\tau}{2} + \delta\right)$$

$$\delta' = \delta + \frac{\tau}{2}$$

$$= \int_0^\infty d\tau \int_0^\tau d\delta'\, e^{-z\tau}\, g(\tau - \delta')\, h(\delta') .$$

② $$\lim_{t \to \infty} f(t) = \lim_{z \to 0} z \tilde{f}(z)$$

proof

$$f(\infty) - f(0) = \lim_{z \to 0} \int_0^\infty dt\, e^{-zt} \frac{d}{dt} f(t) = \lim_{z \to 0} \left[\int_0^\infty \frac{d}{dt}\left(e^{-zt} f(t) \right) dt + z \int_0^\infty e^{-zt} f(t)\, dt \right.$$

$$= -f(0) + \lim_{z \to 0} z \tilde{f}(z) .$$

Notice: The stationary solution for a generalized master equation solves the equation

$$0 = -\frac{i}{\hbar}\left[\hat{H}_s, \hat{\rho}_{red}^{stat}\right] + \tilde{K}(z=0)\,\hat{\rho}_{red}^{stat}$$

But

$$\hat{K}(z=0) = \int_0^\infty d\tau\; K(\tau).$$ The GME in the Markov approximation reads:

$$\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}\left[\hat{H}_s, \hat{\rho}_{red}\right] + \underbrace{\int_0^\infty dt''\, K(t'')}_{=\hat{K}(z=0)}\,\hat{\rho}_{red}(t)$$

Thus, the stationary solution is identical in the Markov or exact form of the Master equation, given the absence of time dependent perturbations.

$$\rho_{red,\,Markov}^{stat} = \rho_{red,\,exact}^{stat} \qquad (4.3)$$

Let us now take eq. (4.2) and project it on the many-body eigenstates of $\hat{H}_s$:

$$\lim_{t\to\infty}\left(\dot{\hat{\rho}}_{red}(t)\right)_{bb'} = 0_{bb'} = -\frac{i}{\hbar}\sum_{aa'}\delta_{ab}\,\delta_{a'b'}\left(E_a - E_{a'}\right)\rho_{aa'}^{stat} + \sum_{aa'} K_{bb'}^{aa'}\,\rho_{aa'}^{stat} \qquad (4.4)$$

with, in the eigenbasis $\{|a\rangle\}$,

$$\rho_{red}^{stat} = \sum_{aa'}\rho_{aa'}\,|a\rangle\langle a'| \qquad (4.5)$$

and

$$\boxed{K_{bb'}^{aa'} := \langle b|\, K\left[\,|a\rangle\langle a'|\,\right]|b'\rangle} \qquad (4.6)$$

In (4.6) we have used square brackets to indicate that the kernel superoperator must first act on the density operator ρ_{red}^{stat} and then the resulting matrix elements are taken. The diagrammatic representation of $K_{bb'}^{aa'}$ is the main task of this chapter. This representation will be very helpful for a classification of the different tunnelling processes considered in the dynamics of the system.

4.1.1 GME up to fourth order

Using the standard notation for system-bath problems

$$H = \underbrace{\hat{H}_{res} + \hat{H}_S}_{\hat{H}_0} + \underbrace{\hat{H}_T}_{\hat{V}} \qquad (1.18)\ (3.6)$$

and operators in interaction picture

$$\hat{V}_I(t) = \hat{U}_0^+(t)\,\hat{V}\,\hat{U}_0(t) \overset{\text{time-indep. perturbation}}{=} e^{i/\hbar \hat{H}_0 t}\,\hat{V}\,e^{-i/\hbar \hat{H}_0 t} \qquad (1.20)$$

$$\hat{\rho}_I(t) = \hat{U}_0^+(t)\,\hat{\rho}(t)\,\hat{U}_0(t) \qquad (1.24)$$

as well as the Liouville eq. in the interaction picture

$$i\hbar \frac{\partial}{\partial t}\hat{\rho}_I(t) = [\hat{V}_I(t), \hat{\rho}_I(t)] \qquad (1.25)$$

and the Liouville superoperator

$$\mathcal{L}^I(t)\,\hat{X}^I := -\frac{i}{\hbar}[V_I(t), \hat{X}^I] \qquad (4.7)$$

the Liouville equation (1.25) becomes

$$\dot{\hat{\rho}}^I = \mathcal{L}^I(t)\,\hat{\rho}^I(t) \qquad (2.54)$$

Integrating over time and reinserting in the Liouville eq. yields

$$\dot{\hat{\rho}}_I(t) = \mathcal{L}^I(t)\,\hat{\rho}_I(0) + \int_0^t d\tau\ \mathcal{L}^I(t)\,\mathcal{L}^I(\tau)\,\hat{\rho}_I(\tau) \qquad (4.9)\ (1.27)$$

As we are interested in an eq. to fourth order in the tunnelling, we do not stop at this stage but repeat the iteration. We transform (1.27) to an integral eq.

$$\hat{\rho}_I(t) = \hat{\rho}_I(0) + \int_0^t d\tau\ \mathcal{L}^I(\tau)\,\hat{\rho}_I(0) + \int_0^t d\tau_1 \int_0^{\tau_1} d\tau\ \mathcal{L}^I(\tau_1)\,\mathcal{L}^I(\tau)\,\hat{\rho}_I(\tau) \qquad (4.10)$$

which is once more inserted in (1.27) yielding

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

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

$$+ \int_0^t d\tau_2\ \mathcal{L}^I(t)\,\mathcal{L}^I(\tau_2)\int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau\ \mathcal{L}^I(\tau_1)\,\mathcal{L}^I(\tau)\,\hat{\rho}_I(\tau) \qquad (4.11)$$

We can now perform the trace over the leads to obtain an equation for $\hat{\rho}_{red,I}$

In order to perform the trace we also assume (cf. 2.9)

$$\hat{\rho}(0) = \hat{\rho}_S(0) \otimes \hat{\rho}_{res}(0) = \hat{\rho}_I(0) \qquad (4.12)$$

with the leads in thermal equilibrium

$$\hat{\rho}_{res}(0) = \prod_{\alpha=L,R} \frac{e^{-\beta\left(\hat{H}_{res,\alpha} - \mu_\alpha \hat{N}\right)}}{Z_{res,\alpha}} \qquad (4.13)$$

As a consequence, when evaluating Tr_{res} in (4.11) terms containing an odd number of lead operators (which are contained linearly in $\mathcal{L}^I$) vanish. One thus obtains in fourth order:

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t d\tau \; \mathrm{Tr}_{res}\{\mathcal{L}^I(t)\mathcal{L}^I(\tau)\,\hat{\rho}_s(0)\,\hat{\rho}_{res}\} \; +$$

$$+ \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; \mathrm{Tr}_{res}\{\mathcal{L}^I(t)\mathcal{L}^I(\tau_2)\mathcal{L}^I(\tau_1)\mathcal{L}^I(\tau)\,\hat{\rho}_{red\,I}(\tau)\,\rho_{res}\}$$

$$+ \; O(\mathcal{L}^6) \qquad (4.14)$$

where we observed that from $(1.24) \leftrightarrow (4.7)$ and $(2.9) \leftrightarrow (4.12)$ it follows

$$\hat{\rho}_I(t) = \hat{\rho}_{red,I}(t)\,\hat{\rho}_{res} + O(\hat{V}) \qquad (4.15)$$

The first contribution in (4.14) contains $\hat{\rho}_I(0)$ instead of $\hat{\rho}_I(\tau)$. This is not desirable. However we have from (4.10)

$$\mathrm{Tr}_{res}\,\hat{\rho}_I(0) = \hat{\rho}_s(0) = \hat{\rho}_{red,I}(t) - \int_0^t d\tau_1 \int_0^{\tau_1} d\tau \,\mathrm{Tr}_{res}\{\mathcal{L}^I(\tau_1)\mathcal{L}^I(\tau)\,\hat{\rho}_{red,I}(t)\otimes\rho_{res}\}\forall t \qquad (4.16)$$

$$+ \; O(V^4)$$

By inserting (4.16) in (4.14) with $t = \tau$

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t d\tau \; \mathrm{Tr}_{res}\{\mathcal{L}^I(t)\mathcal{L}^I(\tau)\;\hat{\rho}_{red}(\tau)\otimes\hat{\rho}_{res}\}$$

$$- \int_0^t d\tau \; \mathrm{Tr}_{res}\{\mathcal{L}^I(t)\mathcal{L}^I(\tau)\int_0^{\tau} d\tau_1 \int_0^{\tau_1} d\tau_2 \; \mathrm{Tr}_{res}\{\mathcal{L}^I(\tau_1)\mathcal{L}^I(\tau_2)\,\hat{\rho}_{red,I}(\tau_2)\otimes\rho_{res}\}\otimes\hat{\rho}_{res}\}$$

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

$$+ \; O(V^6)$$

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

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t d\tau \, Tr_{res} \left\{ \mathcal{L}^I(t) \mathcal{L}^I(\tau) \, \hat{\rho}_{red,I}(\tau) \, \hat{\rho}_{res} \right\}$$

$$\text{(i)} \quad + \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; Tr_{res} \left\{ \mathcal{L}^I(t) \mathcal{L}^I(\tau_2) \mathcal{L}^I(\tau_1) \mathcal{L}^I(\tau) \, \hat{\rho}_{red,I}(\tau) \, \hat{\rho}_{res} \right\}$$

$$\text{(ii)} \quad - \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \int_0^{\tau_1} d\tau \; Tr_{res} \left\{ \mathcal{L}^I(t) \mathcal{L}^I(\tau_2) \, Tr_{res} \left\{ \mathcal{L}^I(\tau_1) \mathcal{L}^I(\tau) \, \hat{\rho}_{red,I}(\tau) \, \hat{\rho}_{res} \right\} \hat{\rho}_{res} \right\} \tag{4.16}$$

The fourth order parts of this equation have the following significance: from (i) all possible fourth order contributions emerge, among them also reducible ones, which basically describe two sequential, but uncorrelated second order events. Those are already accounted for in the 2^{nd} order contribution, and thus need to be excluded, which is achieved by the subtraction (ii). The meaning of the above statement will become clearer once the diagrammatic rules are presented.

Here we want to make a more elegant derivation of (4.16) based on the Nakajima-Zwanzig formalism. The starting point is the equation of motion for the factorized component of the full density matrix

$$\mathcal{P} \dot{\rho}_I(t) = \mathcal{P} \mathcal{L}^I(t) \int_0^t ds \; \mathcal{G}(t,s) \, \mathcal{Q} \mathcal{L}^I(s) \, \mathcal{P} \rho_I(s) \tag{2.61}$$

where $\mathcal{G}(t,s) = T_{\leftarrow} \exp\left[\int_s^t ds' \, \mathcal{Q}\mathcal{L}^I(s') \right]$ is the propagator.

The second order expansion in $\mathcal{L}^I$ of the GME is obtained for $G(t,s) \cong 1$. The fourth order by expanding $G(t,s)$ up to the second order:

$$G(t,s) = 1 + \int_s^t ds' \, Q\mathcal{L}^I(s') + \int_s^t ds' \int_{s'}^t ds'' \, Q\mathcal{L}^I(s'') Q\mathcal{L}^I(s') \tag{4.17}$$

And, inserting back into (2.61)

$$\begin{aligned} \mathcal{P}\dot{\rho}_I(t) = {} & \mathcal{P}\mathcal{L}^I(t) \int_0^t ds \, Q\mathcal{L}^I(s) \mathcal{P}\rho_I(s) + \\ & + \mathcal{P}\mathcal{L}^I(t) \int_0^t ds \int_s^t ds' \, Q\mathcal{L}^I(s') Q\mathcal{L}^I(s) \mathcal{P}\rho_I(s) + \\ & + \mathcal{P}\mathcal{L}^I(t) \int_0^t ds \int_s^t ds' \int_{s'}^t ds'' \, Q\mathcal{L}^I(s'') Q\mathcal{L}^I(s') Q\mathcal{L}^I(s) \mathcal{P}\rho_I(s) \end{aligned} \tag{4.18}$$

Now the proof continues considering that $\mathcal{P}\mathcal{L}^I\mathcal{P} = 0$, no matter what follows. Thus one concentrate on the two integrands. $(Q = 1 - \mathcal{P})$

$$\begin{aligned} &(\mathrm{I}) \qquad \mathcal{P}\mathcal{L}^I(t)(1-\mathcal{P})\mathcal{L}^I(s')(1-\mathcal{P})\mathcal{L}^I(s)\mathcal{P} \\ &(\mathrm{II}) \qquad \mathcal{P}\mathcal{L}^I(t)(1-\mathcal{P})\mathcal{L}^I(s'')(1-\mathcal{P})\mathcal{L}^I(s')(1-\mathcal{P})\mathcal{L}^I(s)\mathcal{P} \end{aligned} \tag{4.19}$$

In the case (I) the string $\mathcal{P}\mathcal{L}^I\mathcal{P}$ is unavoidable except for the case $\mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s')\mathcal{L}^I(s)\mathcal{P}$ which also vanishes since $\mathcal{L} \propto c_k^+$ or c_k and $\mathcal{P}$ contains a trace over the lead degrees of freedom. Analogously, the case (II) gives only 2 non vanishing contributions:

$$\mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s'')\mathcal{L}^I(s')\mathcal{L}^I(s)\mathcal{P} \tag{4.19b}$$

and

$$\mathcal{P}\mathcal{L}^I(t)\mathcal{L}^I(s'')\mathcal{P}\mathcal{L}^I(s')\mathcal{L}^I(s)\mathcal{P}$$

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

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

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

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

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

$$\int_0^t ds \int_s^t ds'\, F(s', s) = \int_0^t ds \int_0^s ds'\, F(s, s') \qquad (2.64)$$

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.