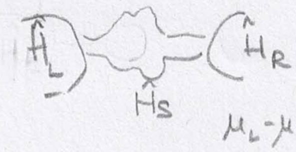
CHAPTER 5 : NONEQUILIBRIUM TRANSPORT

5.1 Statement of the problem (cf. Ch. 2)

Wanted : Average current at finite bias voltages

$$\hat{H}_{TOT} = \hat{H}_L + \hat{H}_S + \hat{H}_R + \hat{H}_{T}$$

$$I(t) = \langle \hat{I} \rangle_t = \mathrm{Tr}\{ \hat{\rho}_{tot}(t)\, \hat{I} \} = \mathrm{Tr}\{ \hat{\rho}_{tot}(0)\, \hat{I}_H(t) \} \quad (5.1)$$



Total density operator is no longer obtained from Kubo formula at finite bias

Needed : nonequilibrium density operators $\hat{\rho}_{tot}(t)$, $\hat{\rho} = \mathrm{Tr}_B \{ \hat{\rho}_{tot} \}$

According to Ch. 2 , given an initial density operator $\hat{\rho}_{tot}(0)$,

$$\hat{\rho}_{tot}(t) = \hat{U}(t,t_0)\, \hat{\rho}_{tot}(t_0)\, \mathcal{U}^{+}(t,t_0) \quad (5.2)$$

where $\hat{U}(t,t_0)$ is the evolution operator associated to $\hat{H}_{tot}$.

Alternatively, upon taking the time derivative of (5.2) and using $i\hbar \frac{\partial \hat{\mathcal{U}}}{\partial t} = \hat{H}_{tot}\, \hat{\mathcal{U}}$, $\hat{\rho}_{tot}$ obeys

$$\boxed{\frac{\partial}{\partial t} \hat{\rho}_{tot}(t) = -\frac{i}{\hbar} [\hat{H}_{tot}, \hat{\rho}_{tot}(t)] = \mathcal{L}_{tot}\, \hat{\rho}_{tot}(t)} \quad (5.3)$$

Liouville - von Neumann equation , where $\mathcal{L}_{tot}$ is the Liouville superoperator

$$\mathcal{L}_{tot}[\,\circ\,] = -\frac{i}{\hbar} [\hat{H}_{TOT}, \,\bullet\,]$$

From (5.3) it then follows for the reduced density operator

$$\boxed{\frac{\partial}{\partial t}\hat{\rho}(t) = \mathrm{Tr}_B\left\{\mathcal{L}_{tot}\,\hat{\rho}_{tot}(t)\right\}} \qquad (5.4)$$

As already discussed in Ch.2, the trace over the bath (reservoirs) degrees of freedom introduces <u>irreversibility</u> and decoherence. At long times a stationary situation is reached. For a time-independent $\hat{\mathcal{H}}_{tot}$ $(\forall\, t > t_0)$ it holds

$$\lim_{t\to\infty}\frac{\partial}{\partial t}\hat{\rho}(t) = 0$$

We shall look for stationary quantities (but transient is possible as well with (5.4))

$$I = \lim_{t\to\infty} I(t) = \lim_{\lambda\to 0}\lambda\,\tilde{I}(\lambda) \qquad (5.5a)$$

central value theorem

$$\rho^{st} = \lim_{t\to\infty}\hat{\rho}(t) = \lim_{\lambda\to 0}\lambda\,\tilde{\rho}(\lambda) \qquad (5.5b)$$

5.2. Liouville space

In what follows we shall work in the Liouville space. Here, $\hat{\varrho}$ is a vector and the Liouvillian $\mathcal{L}_{tot}$ is an operator. One can consequently make the following mapping

	Hilbert space	Liouville space
Schrödinger		
state	$\|\psi\rangle$	$\hat{\varrho}$
dynamics	$\partial_t \|\psi\rangle = -\frac{i}{\hbar} \hat{H} \|\psi\rangle$	$\dot{\hat{\varrho}} = -\frac{i}{\hbar} [\hat{H}, \hat{\varrho}] = \mathcal{L} \hat{\varrho}$
evolution	$\mathcal{U}(t,0) = e^{-i\hat{H}t/\hbar}$	$G(t,0) = e^{\mathcal{L}t}$

Interaction picture

composite system $\hat{H} = \hat{H}_0 + \hat{H}_T$

free evolution $\hat{\mathcal{U}}_0(t,0) = e^{-i\hat{H}_0 t/\hbar}$ $\qquad$ $G_0(t,0) = e^{\mathcal{L}_0 t}$

interaction picture $\hat{A}_I(t) = \mathcal{U}_0^+(t,0) A \hat{\mathcal{U}}_0(t,0)$ $\qquad$ $\mathcal{L}_I(t) = G_0(0,t) \mathcal{L} G_0(t,0)$

$|\psi_I(t)\rangle\rangle = \hat{U}_0^+(t,0) |\psi(t)\rangle\rangle$ $\qquad$ $\hat{\varrho}_I(t) = G_0(0,t) \varrho(t)$

Heisenberg picture

$\hat{C}_\nu(t) = \hat{\mathcal{U}}^+(t,0) \hat{C}_\nu \hat{\mathcal{U}}(t,0)$ $\qquad$ $C_\nu(t) = e^{\mathcal{L}t} C_\nu = G(t,0) C_\nu$

$\dot{\hat{C}}_\nu(t) = +\frac{i}{\hbar} [\hat{H}, \hat{C}_\nu(t)]$ $\qquad$ $\dot{C}_\nu(t) = \mathcal{L} C_\nu(t)$

$\Rightarrow$ noninteracting $\hat{H}$: $\dot{C}_\nu(t) = -\frac{i}{\hbar} \varepsilon_\nu C_\nu(t) \Rightarrow C_\nu(t) = e^{-\frac{i}{\hbar}\varepsilon_\nu t} C_\nu = G(t,0) C_\nu$

5.3. Projector operator formalism

We want a formalism enabling us to evaluate $\hat{\rho}(t)$ including

i) finite bias

ii) e-e interactions

iii) transients

iv) time-dependent perturbations   E.g. ac-electric fields

when needed.

A very powerful method in this respect is based on the projector-operator formalism due to Nakajima and Zwanzig (1958). Other approaches rely on coherent state path integrals (based on the Feynman and Vernon influence functional approach (Feynman & Vernon Ann. Phys. 24, 118 (1963), Tu & Zhang PRB 78, 23511 (2008) for a noninteracting DQD, Jin et al. New J. Phys 12, 083013 (2010)

Note: Other methods like the Keldysh field integral approach (cf. Altland and Simons "Condensed matter field theory" Cambridge University Press 2008)

or the non-equilibrium GF (NEGF) formalism

(cf. Haug-Jauho "Quantum kinetics and optics of semiconductors" Springer 2008)

look at different nonequilibrium quantities => Σ, $G^>$, $G^<$, G^K

STEPS

I) Initial preparation

Assume that the interaction between system and bath is switched on at time to. Before that time the bath is in thermal equilibrium

$$\hat{\varrho}_{tot}(t_0) = \hat{\varrho}_S(t_0) \otimes \hat{\varrho}_B \qquad (5.6)$$

where $\hat{\varrho}_B = \hat{\varrho}_{BL} \otimes \hat{\varrho}_{BR}$ and $\hat{\varrho}_{B\alpha} = \frac{1}{Z} e^{-\beta(\hat{H}_\alpha - \mu_\alpha \hat{N}_\alpha)}$ (5.6b)

II) Projection operators

The idea of the Nakajima-Zwanzig technique is to find an exact quantum master equation for the reduced density operator $\hat{\varrho}$ following from (5.3) & (5.4).

To this extent the projectors $\mathcal{P}$ and $\mathcal{Q}$ are introduced

$$\begin{cases} \mathcal{P}\hat{X} \equiv \mathrm{Tr}_B\{\hat{X}\} \otimes \hat{\varrho}_B & (5.7a) \\ \mathcal{Q} = 1 - \mathcal{P} & (5.7b) \end{cases}$$

Further the Liouvillian of system, bath and coupling are defined

$$\mathcal{L}_B[\cdot] = -\frac{i}{\hbar}[\hat{H}_B, \cdot] \quad , \quad \mathcal{L}_S[\cdot] = -\frac{i}{\hbar}[\hat{H}_S, \cdot]$$

$$\mathcal{L}_T[\cdot] = -\frac{i}{\hbar}[\hat{H}_T, \cdot]$$

The projectors fulfill the equations:

a) $\mathcal{P} + \mathcal{Q} = 1$

b) $\mathcal{P}^2 = \mathcal{P}$, $\mathcal{Q}^2 = \mathcal{Q}$

c) $\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$

d) $\mathcal{P}\mathcal{L}_B = 0$

d') $\mathcal{L}_B \mathcal{P} = 0$ <u>if</u> $\mathcal{L}_B \hat{\varrho}_B = 0$ (which is satisfied for (5.6b))

e) $\mathcal{P}\mathcal{L}_S = \mathcal{L}_S \mathcal{P}$ due to $[\hat{H}_S, \hat{\varrho}_B] = 0$

(and hence $\mathcal{Q}\mathcal{L}_S = \mathcal{L}_S \mathcal{Q}$)

f) $\mathcal{P}\mathcal{L}_T^{2n+1}\mathcal{P} = 0$ for $n \in \mathbb{N}$

<u>Proof</u>

All eqs. b) - f) can be proofed from (5.7a) and (5.7b).

b) $$\mathcal{P}^2 \hat{X} = \mathrm{Tr}_B \{ \mathrm{Tr}_B \{ \hat{X} \} \otimes \hat{\varrho}_B \} \otimes \hat{\varrho}_B = \mathrm{Tr}_B \{ \hat{X} \} \otimes \mathrm{Tr}_B \{ \hat{\varrho}_B \} \otimes \hat{\varrho}_B$$

$$= \mathrm{Tr}_B \{ \hat{X} \} \otimes \hat{\varrho}_B = \mathcal{P}\hat{X}$$

$\hat{H}_B |Nj\rangle = \varepsilon_{Nj}$

c) $\mathcal{P}\mathcal{Q} = \mathcal{P}(1 - \mathcal{P}) = \mathcal{P} - \mathcal{P}^2 = 0$

d) $\mathcal{P}\mathcal{L}_B \hat{X} = \mathrm{Tr}_B \{ -\frac{i}{\hbar} [\hat{H}_B, \hat{X}] \} \otimes \varrho_B = \sum_{Nj} \langle Nj | \hat{H}_B \hat{X} - \hat{X} \hat{H}_B | Nj \rangle \otimes \varrho_B \left(-\frac{i}{\hbar}\right) = 0$

e) $\mathcal{P}\mathcal{L}_S \hat{X} = -\frac{i}{\hbar} \sum_{Nj} \langle Nj | \hat{H}_S \hat{X} - \hat{X} \hat{H}_S | Nj \rangle \otimes \varrho_B = (\hat{H}_S \mathrm{Tr}_B \{ \hat{X} \} - \mathrm{Tr}_B \{ \hat{X} \} \hat{H}_S) \otimes \hat{\varrho}_B (-i/\hbar) = \mathcal{L}_S \mathcal{P} \hat{X}$

f) $\mathcal{P}\mathcal{L}_T \mathcal{P} \hat{X} = \mathrm{Tr}_B \{ \mathcal{L}_T (\mathrm{Tr}_B \{ \hat{X} \} \otimes \hat{\varrho}_B) \} = -\frac{i}{\hbar} \underbrace{\mathrm{Tr}_B \{ [\hat{H}_T, \mathrm{Tr}_B \{ \hat{X} \} \times \hat{\varrho}_B] \}}_{=0} \otimes \hat{\varrho}_B$

since $\hat{H}_T$ does not conserve particles from B

Note on condition d')

d') $\mathcal{L}_B \rho \hat{X} = \mathcal{L}_B \, Tr\{\hat{X}\} \otimes \rho_B = -\frac{i}{\hbar}[H_B, Tr_B\{X\}\hat{\rho}_B] = Tr\{X\} \mathcal{L}_B \rho_B$

in general,

$$\mathcal{L}_B \rho_B = -\frac{i}{\hbar}[\hat{H}_B, \hat{\rho}_B] = \dot{\hat{\rho}}_B$$

for our initial condition

$$\begin{cases} \hat{\rho}_B = \hat{\rho}_{BL} \otimes \hat{\rho}_{BR} & (5.6b) \\ \hat{\rho}_{B\alpha} = \frac{1}{Z_\alpha} e^{-\beta(H_\alpha - \mu_\alpha N_\alpha)} & (5.6c) \end{cases}$$

$\hookrightarrow$ $\mathcal{L}_B \hat{\rho}_B = 0$ since $[\hat{H}_B, \hat{\rho}_B] = [\hat{H}_L + \hat{H}_R, \rho_{BL} \otimes \rho_{BR}] = 0$

Superconductors For the case of a SNS junction the condition (5.6b) does not hold true since the L and R superconductors do not factorize. Rather, the eigenstates of $\hat{H}_B = \hat{H}_{BL} + \hat{H}_{BR}$ are a coherent superposition of states $|N_L\{i_L\}, N_R\{i_R\}\rangle$ such that $N_L + N_R = N$

If $\mu_L = \mu_R = \mu_0$ though, one can still write $\hat{\rho}_B = \frac{1}{Z_B} e^{-\beta(\hat{H}_B - \hat{\mu}_0 \hat{N})}$ (5.6d)

and thus $\mathcal{L}_B \hat{\rho}_B = 0$ applies.

If $\mu_L \neq \mu_R$ however, the L+R system is out of equilibrium and hence the form (5.6d) does not hold true.

III) Quantum master equation

Let us now apply $\mathcal{P}$ or $\mathcal{Q}$ on both sides of (5.3)

$$\begin{cases} \mathcal{P}\dot{\hat{\rho}}_{tot} = \mathcal{P}\mathcal{L}_{tot}\hat{\rho}_{tot} \underset{(a)}{=} \mathcal{P}\mathcal{L}_{tot}\mathcal{P}\hat{\rho}_{tot} + \mathcal{P}\mathcal{L}_{tot}\mathcal{Q}\hat{\rho}_{tot} & (5.8a) \\ \mathcal{Q}\dot{\hat{\rho}}_{tot} = \mathcal{Q}\mathcal{L}_{tot}\hat{\rho}_{tot}^{(t)} \underset{(a)}{=} \mathcal{Q}\mathcal{L}_{tot}\mathcal{P}\hat{\rho}_{tot} + \mathcal{Q}\mathcal{L}_{tot}\mathcal{Q}\hat{\rho}_{tot} & (5.8b) \end{cases}$$

The second equation is formally solved by introducing the operator

$$G_{\mathcal{Q}}(t-t_0) = e^{\mathcal{Q}\mathcal{L}_{tot}(t-t_0)}$$

In fact $(t_0=0)$

$$\frac{d}{dt}\left[G_{\mathcal{Q}}(-t)\,\mathcal{Q}\hat{\rho}_{tot}(t)\right] = \frac{d}{dt}G_{\mathcal{Q}}(-t)\,\mathcal{Q}\hat{\rho}_{tot} + G_{\mathcal{Q}}(-t)\,\mathcal{Q}\dot{\hat{\rho}}_{tot}$$

$$= -G_{\mathcal{Q}}(-t)\,\mathcal{Q}\mathcal{L}_{tot}\mathcal{Q}\,\hat{\rho}_{tot} + G_{\mathcal{Q}}(-t)\,\mathcal{Q}\dot{\hat{\rho}}_{tot}$$

$$\underset{(5.8b)}{=} G_{\mathcal{Q}}(-t)\,\mathcal{Q}\mathcal{L}_{tot}\mathcal{P}\hat{\rho}_{tot}$$

This equation can be formally integrated, yielding

$$\mathcal{Q}\hat{\rho}_{tot}(t) = G_{\mathcal{Q}}(t)\,\mathcal{Q}\hat{\rho}_{tot}(0) + G_{\mathcal{Q}}(t)\int_0^t ds\, G_{\mathcal{Q}}(-s)\,\hat{\mathcal{Q}}\mathcal{L}_{tot}\mathcal{P}\hat{\rho}_{tot}(s)$$

Inserting the result in (5.8a) yields the eq. for $\mathcal{P}\hat{\rho}_{tot}$:

$$\mathcal{P}\dot{\hat{\rho}}_{tot}(t) = \mathcal{P}\mathcal{L}_{tot}\mathcal{P}\hat{\rho}_{tot} + \int_0^t ds\,\mathcal{P}\mathcal{L}_{tot}\,G_{\mathcal{Q}}(t-s)\,\mathcal{Q}\mathcal{L}_{tot}\mathcal{P}\rho_{tot}(s)$$

It is convenient to use the relation

$$\boxed{\begin{aligned} P\mathcal{L}_{tot}\, G_Q(t)\, Q\, \mathcal{L}_{tot} P &= P\mathcal{L}_T\, e^{(\mathcal{L}_S+\mathcal{L}_B+Q\mathcal{L}_T Q)t}\, \mathcal{L}_T P \\ &\equiv P\mathcal{L}_T\, \bar{G}_Q(t)\, \mathcal{L}_T P \quad (5.9) \end{aligned}}$$

<u>Proof:</u>

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

$$\underset{\substack{\uparrow \\ Q=Q^2=Q^n,\ n>1}}{=} \sum_{n=0}^{\infty} \frac{1}{n!} t^n P\mathcal{L}_{tot} Q (Q\mathcal{L}_{tot} Q)^n Q\mathcal{L}_{tot} P$$

But

i) $$P\mathcal{L}_{tot} Q = P\mathcal{L}_S Q + P\mathcal{L}_B Q + P\mathcal{L}_T Q = P\mathcal{L}_T Q \qquad (g)$$

and

$$Q\mathcal{L}_{tot} P = (1-P)\mathcal{L}_{tot} P = \mathcal{L}_{tot} P - P\mathcal{L}_{tot} P = \mathcal{L}_{tot} P - \mathcal{L}_S P \underset{\substack{\uparrow \\ \mathcal{L}_B P = 0 \\ (5d')}}{=} \mathcal{L}_T P \quad (h)$$

Further

ii) $$\begin{aligned} Q\mathcal{L}_{tot} Q &= Q\mathcal{L}_B Q + Q\mathcal{L}_S Q + Q\mathcal{L}_T Q \\ &= Q\mathcal{L}_B + Q\mathcal{L}_S + Q\mathcal{L}_T Q = \mathcal{L}_B + Q\mathcal{L}_S + Q\mathcal{L}_T Q \\ &= Q(\mathcal{L}_B + \mathcal{L}_S + Q\mathcal{L}_T Q) \end{aligned}$$

Hence, using $\mathcal{P}\mathcal{L}_{tot}\mathcal{Q} = \mathcal{P}\mathcal{L}_T\mathcal{Q}$ (g) and

h') $\mathcal{P}\mathcal{L}_{tot}\mathcal{P} = \mathcal{P}(\mathcal{L}_S + \mathcal{L}_T + \mathcal{L}_B)\mathcal{P} = \mathcal{L}_S\mathcal{P}$

we used (5d') $\mathcal{L}_B\mathcal{P}=0$

h) $\mathcal{Q}\mathcal{L}_{tot}\mathcal{P} = (1-\mathcal{P})\mathcal{L}_{tot}\mathcal{P} = \mathcal{L}_{tot}\mathcal{P} - \mathcal{L}_S\mathcal{P} = \mathcal{L}_T\mathcal{P}$

one gets the Nakajima-Zwanzig eq.

$$\boxed{\mathcal{P}\dot{\hat{\rho}}_{tot}(t) = \mathcal{L}_S\mathcal{P}\rho_{tot}(t) + \int_0^t ds\, \mathcal{K}_{\mathcal{P}}(t-s)\mathcal{P}\rho_{tot}(s)} \quad (5.1$$

where the kernel superoperator is

$$\boxed{\mathcal{K}_{\mathcal{P}}(t) = \mathcal{P}\mathcal{L}_T\bar{G}_Q(t)\mathcal{L}_T\mathcal{P}} \quad (5.11)$$

This equation is exact and it enables us to soon obtain also an exact equation for the reduced operator $\hat\rho(t) = Tr_B\{\mathcal{P}\hat\rho_{tot}(t)\}$ by applying Tr_B to both sides:

$$\boxed{\dot{\hat\rho}(t) = \mathcal{L}_S\hat\rho(t) + \int_0^t ds\, \mathcal{K}(t-s)\hat\rho(s)} \quad (5.12)$$

where

$$\mathcal{K}(t-s)\hat\rho(s) = Tr_B\{\mathcal{K}_{\mathcal{P}}(t-s)\mathcal{P}\hat\rho_{tot}(s)\}$$

$$= Tr_B\{\mathcal{P}\mathcal{L}_T\bar{G}_Q(t-s)\mathcal{L}_T\mathcal{P}\,\hat\rho(s)\otimes\hat\rho_B\}$$

$$\boxed{\mathcal{K}(t-s)\hat\rho(s) = Tr_B\{\mathcal{L}_T\bar{G}_Q(t-s)\mathcal{L}_T\,\hat\rho_{red}(s)\otimes\hat\rho_B\}} \quad (5.13)$$

Note: INTERACTION PICTURE

It is possible to derive the QME also in interaction picture

Here it holds

$$\hat{\varrho}_{tot,I}(t) = G_0(-t)\,\hat{\varrho}_{tot}(t)$$

$$\mathcal{L}_{T,I}(t) = G_0(-t)\,\mathcal{L}_T\,G_0(t)$$

with $\mathcal{P}+\mathcal{Q}=1$

$$\mathcal{P}\hat{\varrho}_{tot,I}(t) + \mathcal{Q}\hat{\varrho}_{tot,I}(t) = G_0(-t)\left(\mathcal{P}\hat{\varrho}_{tot} + \mathcal{Q}\hat{\varrho}_{tot}\right)$$

$$\Rightarrow \mathcal{P}\hat{\varrho}_{tot,I}(t) = G_0(-t)\,\mathcal{P}\hat{\varrho}_{tot}$$

Differential equation

$$\frac{d}{dt}\mathcal{P}\hat{\varrho}_{tot,I} = \frac{d}{dt}G_0(-t)\,\mathcal{P}\hat{\varrho}_{tot} + G_0(-t)\frac{d}{dt}\mathcal{P}\hat{\varrho}_{tot}$$

$$= -G_0(-t)\mathcal{L}_0\mathcal{P}\hat{\varrho}_{tot} + G_0(-t)\frac{d}{d}\mathcal{P}\hat{\varrho}_{tot}$$

$$\underset{\substack{\uparrow\\(5.10)}}{=} -G_0(-t)\,\mathcal{L}_S\mathcal{P}\hat{\varrho}_{tot} + G_0(-t)\,\mathcal{L}_S\mathcal{P}\varrho_{tot} + G_0(-t)\int_0^t ds\,\mathcal{K}_P(t-s)\mathcal{P}\hat{\varrho}_{tot}(s)$$

$$= \int_0^t ds\left(G_0(-t)\,\mathcal{P}\mathcal{L}_T\,\bar{G}_Q(t-s)\overset{\downarrow}{}\mathcal{L}_T\mathcal{P}\hat{\varrho}_{tot}(s)\right)$$

$$\uparrow\ \mathbb{1} = G_0(s)\,G_0(-s)$$

$$= \int_0^t ds\left(G_0(-t)\,\mathcal{P}\,\mathcal{L}_T\,\bar{G}_Q(t-s)\,G_0(+s)\;\mathcal{L}_{T,I}(s)\;\mathcal{P}\hat{\varrho}_{tot,I}(s)\right)$$

$$\equiv \int_0^t ds\;\mathcal{K}_{P,I}(t,s)\,\mathcal{P}\hat{\varrho}_{tot,I}(s)$$

Hence upon taking the trace

$$\frac{d}{dt}\hat{\varrho}_I(t) = \int_0^t ds\,\mathrm{Tr}_B\left\{\mathcal{K}_{P,I}(t,s)\,\hat{\varrho}_I(s)\otimes\hat{\varrho}_B\right\}$$

IV DYSON EQ. FOR $\bar{G}_Q(t)$

Recall

$$\bar{G}_Q(t) = e^{(\mathcal{L}_S+\mathcal{L}_B+Q\mathcal{L}_TQ)t} = e^{(\mathcal{L}_0+Q\mathcal{L}_TQ)t}$$

We look for the time evolution of $\bar{G}_Q$:

$$\frac{d}{dt}\bar{G}_Q(t) = \mathcal{L}_0\bar{G}_Q(t) + Q\mathcal{L}_TQ\,\bar{G}_Q(t)$$

- Introduce the propagator $G_0(t) = e^{\mathcal{L}_0 t}$ for the uncoupled system

$$\hookrightarrow \frac{d}{dt}\left[G_0(-t)\,\bar{G}_Q(t)\right] = \frac{d}{dt}G_0(-t)\,\bar{G}_Q(t) + G_0(-t)\frac{d}{dt}\bar{G}_Q(t)$$

$$= -\mathcal{L}_0G_0(-t)\,\bar{G}_Q(t) + G_0(-t)\,(\mathcal{L}_0+Q\mathcal{L}_TQ)\,\bar{G}_Q(t)$$

$$= G_0(-t)\,Q\mathcal{L}_TQ\,\bar{G}_Q(t)$$

- Integrating over time

$$G_0(-t)\,\bar{G}_Q(t) = \mathbb{1} + \int_0^t ds\; G_0(-s)\,Q\mathcal{L}_TQ\,\bar{G}_Q(s)$$

and hence

$$\boxed{\bar{G}_Q(t) = G_0(t) + \int_0^t ds\; G_0(t-s)\,\underbrace{Q\mathcal{L}_TQ}_{\Sigma_Q}\,\bar{G}_Q(s)} \quad (5.14)$$

Σ_Q self-energy associated to $\bar{G}_Q$

In Laplace space we get the Dyson equation

$$\begin{cases}\tilde{G}_Q(\lambda) = \tilde{G}_0(\lambda) + \tilde{G}_0(\lambda)\,\Sigma_Q\,\tilde{G}_Q(\lambda) & (5.15) \\ \Sigma_Q = Q\mathcal{L}_TQ & (5.15b)\end{cases}$$

← "vacuum fluctuations" $\Rightarrow$ $\boxed{\tilde{G}_Q(\lambda) = \frac{\tilde{G}_0(\lambda)}{1-\Sigma_Q\tilde{G}_0(\lambda)}}$ (5

Importantly, (5.14) and (5.15) allow a systematic expansion of $\bar{G}_Q(t)$ or $\tilde{G}(\lambda)$ in powers of the tunneling Liouvillian $\mathcal{L}_T$.

E.g. in Laplace space $\quad \tilde{G}_Q(\lambda) = \tilde{G}_0(\lambda) \sum_{m=0}^{\infty} \left(\Sigma_Q \tilde{G}_0(\lambda) \right)^m \quad$ (5.16b)

$$\hookrightarrow \quad \tilde{G}_Q(\lambda) = \tilde{G}_0(\lambda) + \tilde{G}_0(\lambda) \Sigma_Q \tilde{G}_0(\lambda) + \cdots \qquad (5.17)$$

NOTE: EQUATION FOR THE PROPAGATOR $G_P(t)$

In a similar way as done for $\bar{G}_Q(t)$ we can look at the evolution of the propagator $G_P(t)$ defined as

$$P\rho_{tot}(t) = G_P(t-s)\, P\rho_{tot}(s) \qquad (5.18)$$

Specifically,

$$\frac{d}{dt}\left[G_0(-t) \underbrace{P\rho_{tot}(t)}_{G_P(t)} \right] = -\mathcal{L}_0 G_0(-t)\, G_P(t) + G_0(-t) \frac{d}{dt} G_P(t)$$

$$= -\mathcal{L}_0 G_0(-t)\, G_P(t) + G_0(-t) \Big[\underbrace{\mathcal{L}_0 G_P(t)}_{\text{NZ with } \mathcal{L}_S P\rho_{tot} = \mathcal{L}_0 P\rho_{tot}} + \int_0^t ds\, \mathcal{K}_P(t-s)\, G_P(s) \Big]$$

$$= \int_0^t ds\, \mathcal{K}_P(t-s)\, G_P(s)$$

$$\Rightarrow \boxed{G_P(t) = G_0(t) \underbrace{\left[G_0(0) G_P(0) \right]}_{1} + G_0(t) \int_0^t ds' \int_0^{s'} ds\, \mathcal{K}_P(s'-s)\, G_P(s)} \qquad (5.18)$$

V ∞-ORDER PERTURBATION THEORY

An advantage of the NZ approach is that, with the help of the Dyson eq. for $\bar{G}_Q$, it also enables a systematic expansion of the kernels $\mathcal{K}_P$ and $\mathcal{K}$ in even powers of $\mathcal{L}_T$.

Let us consider Eq. (5.10) in Laplace space

$$\lambda P \tilde{\rho}_{tot}(\lambda) = P_{tot}(0) + \mathcal{L}_S P \tilde{\rho}_{tot}(\lambda) + \tilde{\mathcal{K}}_P(\lambda) P \tilde{\rho}_{tot}(\lambda)$$

where

$$\tilde{\mathcal{K}}_P(\lambda) = P \mathcal{L}_T \tilde{G}_Q(\lambda) \mathcal{L}_T P$$

$$\underset{(5.16b)}{=} P \mathcal{L}_T \tilde{G}_0(\lambda) \sum_{m=0}^{\infty} \left(\Sigma_Q \tilde{G}_0(\lambda)\right)^m \mathcal{L}_T P$$

Due to the presence of P at the ends only even powers of the series survive since $\Sigma_Q = Q \mathcal{L}_T Q$ does not conserve the particle number for the bath

$$\Rightarrow \tilde{\mathcal{K}}_P(\lambda) = P \mathcal{L}_T \tilde{G}_0(\lambda) \sum_{p=0}^{\infty} \left(\Sigma_Q \tilde{G}_0(\lambda)\right)^{2p} \mathcal{L}_T P$$

$$\equiv \sum_{m=1}^{\infty} \tilde{\mathcal{K}}_P^{(2m)}(\lambda) \quad (5.19)$$

Similar expansion holds for $\tilde{\mathcal{K}}(\lambda)$.

VI. STATIONARY LIMIT

Given the convolutive form of the QME, the stationary density operator is easily found upon Laplace transformation.

For time-independent Hamiltonians which fulfill the factorization condition $\hat{\rho}_B = \hat{\rho}_{BL} \otimes \hat{\rho}_{BR}$ is

$$\lim_{t\to\infty} \dot{\hat{\rho}}(t) = 0 \qquad \text{i.e.} \quad \rho^{\infty} = \lim_{t\to\infty} \hat{\rho}(t) = \text{const}$$

Further, using the final value theorem $\lim_{t\to\infty} f(t) = \lim_{\lambda\to 0^+} \lambda \tilde{f}(\lambda)$

$$0 = \lim_{t\to\infty} \dot{\hat{\rho}}(t) = \lim_{\lambda\to 0} \left[\lambda \mathcal{L}_S \tilde{\rho}(\lambda) + \lambda \tilde{K}(\lambda) \tilde{\rho}(\lambda) \right]$$

using $\rho^{\infty} = \lim_{\lambda\to 0^+} \lambda \tilde{\rho}(\lambda)$ we get the exact eigenvalue equation

$$\boxed{\left(\mathcal{L}_S + \tilde{K}(0)\right) \rho^{\infty} = 0} \qquad (5.20)$$

The exact form of $\tilde{K}(0)$ is obtained from

$$\tilde{K}(0)\rho^{\infty} = \lim_{\lambda\to 0} \tilde{K}(\lambda)\rho^{\infty} = \mathrm{Tr}_B \{ \mathcal{L}_T \tilde{G}_Q(0) \mathcal{L}_T \rho^{\infty} \otimes \rho_B \} \qquad (5.21)$$

with

$$\tilde{G}_Q(\lambda) = \frac{\tilde{G}_0(\lambda)}{1 - (\tilde{G}_0(\lambda) \Sigma_Q)^2}, \quad \tilde{G}_0(\lambda) = \int_0^{\infty} ds\, e^{-\lambda s} G_0(s) = \frac{1}{\lambda - \mathcal{L}_0}$$

and $\Sigma_Q = Q \mathcal{L}_T Q$ $\Rightarrow$ $\boxed{\tilde{G}_Q = \frac{\tilde{G}_0(\lambda)}{1 - \tilde{G}_0(\lambda) \Sigma_P}}$ with $\Sigma_P = \Sigma_Q G_0 \Sigma_Q$

(5.21b)

We shall deal in detail in the next sections with the implications of the stationary eq. (5.24). Before doing this, we shall look at

a) the second and fourth order kernels $\tilde{K}^{(2)}\rho^{\infty}$, $\tilde{K}^{(4)}\rho^{\infty}$

b) the expression for the average current

Then, we shall turn to a diagrammatic formulation for the stationary RDM ρ^{∞} and the steady state current I

c) in Liouville space

d) in Fock space

We shall conclude by applying our general results to the SIAM.

.4.1 second order QME

We can get acquainted with our results by looking at the lowest order in the expansion of $\bar{G}_Q$:

lowest order $\quad \bar{G}_Q = G_0 \quad \Rightarrow \quad \mathcal{K} = \mathcal{K}^{(2)} = \mathcal{L}_T G_0(t)\mathcal{L}_T$

Hence in the Schrödinger picture

$$\boxed{\dot{\hat{\rho}}(t) = \underbrace{-\frac{i}{\hbar}[\hat{H}_S, \hat{\rho}(t)]}_{\mathcal{L}_S\hat{\rho}} + \int_0^t ds \, \mathrm{Tr}_B \{ \mathcal{L}_T G_0(t-s)\mathcal{L}_T \, \hat{\rho}(s) \otimes \hat{\rho}_B \}} \qquad (5.22)$$

Note: Interaction picture

We can redo our analysis also in the interaction picture

where $\quad \hat{\rho}_{tot,I}(t) = G_0(-t)\,\hat{\rho}_{tot}(t)$

$\quad \mathcal{L}_{T,I}(t) = G_0(-t)\,\mathcal{L}_T\, G_0(t)$

and $\quad \mathcal{P}\hat{\rho}_{tot,I} = G_0(-t)\,\mathcal{P}\hat{\rho}_{tot}$

We find (see next page)

$$\boxed{\dot{\hat{\rho}}_I(t) = \int_0^t ds \, \mathrm{Tr}_B \{ \mathcal{L}_{T,I}(t)\,\mathcal{L}_{T,I}(s)\,\hat{\rho}_I(s) \otimes \hat{\rho}_B \}} \qquad (5.23)$$

Eqs. (5.20) e (5.21) rule the dynamics in the weak coupling limit.

Proof of Eq. (5.23)

We observe that

$$\mathcal{P} G_0(-t) \mathcal{L}_T G_0(t-s) \mathcal{L}_T \mathcal{P} \rho_{tot}(s)$$

$$= \mathcal{P} G_0(-t) \mathcal{L}_T G_0(t) G_0(-s) \mathcal{L}_T G_0(s) G_0(-s) \mathcal{P} \rho_{tot}(s)$$

$$= \mathcal{P} \mathcal{L}_{T,I}(t) \mathcal{L}_T(s) \mathcal{P} \rho_{tot,I}(s) \qquad \text{given that } [\mathcal{P}, \mathcal{L}_0] = 0$$

Thus, given the interaction kernel

$$\mathcal{K}_{\mathcal{P},I}(t,s) = G_0(-t) \mathcal{P} \mathcal{L}_T \bar{G}_Q(t-s) \mathcal{L}_T \mathcal{P} \rho_{tot}(s)$$

we find in lowest order with $\bar{G}_Q(t-s) = G_0(t-s)$

$$\mathcal{K}^{(2)}_{\mathcal{P},I}(t,s) = \mathcal{P} \mathcal{L}_{T,I}(t) \mathcal{L}_{T,s}(s) \mathcal{P} \rho_{tot,I}(s)$$

Upon taking Tr_B Eq. (5.23) follows.

Explicitly, the second order eq. (5.21) can be written as

$$\dot{\hat{\rho}}_{I}(t) = -\frac{1}{\hbar^2}\int_0^t ds \, \mathrm{Tr}_B \left\{ \left[\hat{H}_{T,I}(t), \left[\hat{H}_{T,I}(s), \hat{\rho}_{I}(s) \otimes \hat{\rho}_B \right]\right]\right\}. \qquad (5.24b)$$

This form is also easily obtained from the interaction picture von Neumann-Liouville eq. in the interaction picture for $\hat{\rho}_{tot,I}(t)$ upon iteration:

From (3.4)

$$\dot{\hat{\rho}}_{tot,I}(t) = -\frac{i}{\hbar}\left[\hat{H}_{T,I}(t), \hat{\rho}_{tot,I}(t) \right]$$

and hence

$$\hat{\rho}_{tot,I}(t) = \hat{\rho}_{tot,I}(t_0) - \frac{i}{\hbar}\int_{t_0}^{t} ds \left[\hat{H}_{T,I}(s), \hat{\rho}_{tot,I}(s) \right]$$

Upon reinsertion

$$\dot{\hat{\rho}}_{tot,I}(t) = -\frac{i}{\hbar}\left[H_{T,I}(t), \hat{\rho}_{tot,I}(t_0) \right] - \frac{1}{\hbar^2}\int_{t_0}^{t} ds \left[\hat{H}_{T,I}(t), \left[\hat{H}_{T,I}(s), \hat{\rho}_{tot,I}(s) \right]\right]$$

This yields the exact equation

$$\dot{\hat{\rho}}_I(t) = \mathrm{Tr}_B\left\{ \dot{\hat{\rho}}_{tot,I}(t) \right\} = \underbrace{\mathrm{Tr}_B\left\{ \mathcal{L}_{T,I}(t)\, \rho_{tot,I}(t_0) \right\}}_{=\,0}$$

since $\mathcal{L}_T$ does not conserve particles in B

$$-\frac{i}{\hbar^2}\int_0^t ds \, \mathrm{Tr}_B\left\{ \left[\hat{H}_{T,I}(t), \left[\hat{H}_{T,I}(s), \hat{\rho}_{tot,I}(s) \right]\right]\right\} \leftarrow \text{exact}$$

Second order

Eq. (5.24) follows with $\boxed{\hat{\rho}_{tot,I}(t) = \hat{\rho}_I(t) \otimes \rho_B + O(H_T)}$ cf. next page

Proof of the relation

To lowest order in $\hat{H}_T$:

$$\boxed{\hat{\rho}_{tot,I}(t) = \mathrm{Tr}_{B}\{\hat{\rho}_{tot,I}(t)\} \otimes \rho_B + O(H_T^2)} = \rho\{\hat{\rho}_{tot,I}(t)\}$$

I) start from initial condition

$$\hat{\rho}_{tot}(t_0) = \hat{\rho}(t_0) \otimes \hat{\rho}_B(t_0) = \hat{\rho}_{tot,I}(t_0)$$

with

$$\hat{\rho}_B(t_0) = \hat{\rho}_B \;, \quad \frac{1}{Z_\alpha} e^{-\beta(\hat{H}_{B\alpha} - \mu_\alpha N_\alpha)} = \hat{\rho}_{B\alpha} \;, \qquad \hat{\rho}_B = \hat{\rho}_{BL} \otimes \hat{\rho}_{BR}$$

II) The time evolution of $\hat{\rho}_{tot\,I}(t)$ is governed by $H_{T,I}$

$$\dot{\hat{\rho}}_{tot\,I}(t) = -\frac{i}{\hbar}[\hat{H}_{T,I}(t), \hat{\rho}_{tot,I}(t)]$$

$$\hookrightarrow \hat{\rho}_{tot,I}(t) = \rho_{tot,I}(t_0) - \frac{i}{\hbar}\int_0^t dt' \, [\hat{H}_{T,I}(t'), \hat{\rho}_{tot\,I}(t')]$$

Hence

$$\boxed{\hat{\rho}_{tot\,I}(t) = \hat{\rho}_{tot\,I}(t_0) - \frac{i}{\hbar}\int_0^t dt' \, [\hat{H}_{T,I}(t'), \rho_{tot\,I}(t_0)] + O(H_T^2)} \quad (1)$$

$$\Rightarrow \boxed{\mathrm{Tr}_B\{\hat{\rho}_{tot\,I}(t)\} \otimes \hat{\rho}_B = \hat{\rho}_{tot,I}(t_0) + 0 + O(H_T^2)} \quad (2)$$

$$\underline{(1) + (2)} \Rightarrow \boxed{\hat{\rho}_{tot,I}(t) = \mathrm{Tr}_{B}\{\hat{\rho}_{tot,I}(t)\} \otimes \hat{\rho}_{res} + O(H_T)}$$

The time evolution is still decoupled to first order in H_T

5.4.2 fourth order

In some situations, e.g. in Coulomb blockaded quantum dots, some fourth order processes can become relevant ($\Rightarrow$ cotunneling).

Considering the expansion of $\bar{G}_Q(t)$ to the next nonvanishing order,

$$\bar{G}_Q(t) = G_0(t) + \underbrace{\int_0^t ds\, G_0(t-s)\, Q \mathcal{L}_T Q\, G_0(s)}_{\text{vanishes under the trace}}$$

$$+ \int_0^t ds\, G_0(t-s)\, Q\mathcal{L}_T Q \int_0^{s} ds'\, G_0(s-s')\, Q\mathcal{L}_T Q\, G_0(s')$$

This yields to fourth order in H_T

$$\dot{\hat{\rho}}(t) = \mathcal{L}_S \hat{\rho}(t) + \int_0^t ds\, \mathrm{Tr}_B\{\mathcal{L}_T G_0(t-s)\mathcal{L}_T\, \hat{\rho}(s) \otimes \hat{\rho}_B\} +$$

$$+ \int_0^t ds\, \mathrm{Tr}_B\{\mathcal{L}_T \int_0^{t-s} ds_1\, G_0(t-s-s_1)\, Q\mathcal{L}_T Q \int_0^{s_1} ds_2\, G_0(s_1-s_2)\, Q\mathcal{L}_T Q\, G_0(s_2)$$
$$\cdot \mathcal{L}_T\, \hat{\rho}(s) \otimes \rho_B\}$$

Hence

$$\dot{\hat{\rho}}(t) = \mathcal{L}_S \hat{\rho}(t) + \int_0^t ds\, \mathrm{Tr}_B\{\mathcal{L}_T G_0(t-s)\mathcal{L}_T\, \hat{\rho}_S \otimes \hat{\rho}_B\} +$$

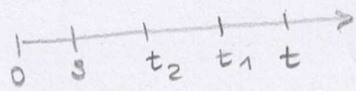
$$+ \int_0^t ds \int_s^t dt_1 \int_s^{t_1} dt_2\, \mathrm{Tr}_B\{\mathcal{L}_T G_0(t-t_1)\, Q\mathcal{L}_T Q\, G_0(t_1-t_2)\, Q\mathcal{L}_T Q\, G_0(t_2-s)\mathcal{L}_T$$
$$\cdot \rho(s) \otimes \rho_B\}$$

$s + s_1 = t_1$ $\qquad$ $s_1 - s_2 = t_1 - s - t_2 = t_1 - t_2$

$ds_1 = dt_1$ $\qquad$ $\Rightarrow t_2 = s + s_2$

For this nested integral it holds (see proof)

$$\int_0^t ds \int_s^t dt_1 \int_s^{t_1} dt_2 \ldots \quad = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} ds \ldots$$



Hence, to fourth order

$$\dot{\hat{\rho}}(t) = \mathcal{L}_S \hat{\rho}(t) + \int_0^t ds \, \mathrm{Tr}_B \left\{ \mathcal{L}_T G_0(t-s) \mathcal{L}_T \hat{\rho}(s) \otimes \hat{\rho}_B \right\} \qquad (5,25)$$

$$+ \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} ds \, \mathrm{Tr}_B \left\{ \mathcal{L}_T G_0(t-t_1) \Sigma_Q G_0(t_1-t_2) \Sigma_Q G_0(t_2-s) \mathcal{L}_T \hat{\rho}(s) \otimes \rho_B \right\}$$

and in <u>interaction picture</u>

$$\frac{d}{dt} \hat{\rho}_I(t) = \int_0^t ds \, \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t) \mathcal{L}_{T,I}(s) \hat{\rho}_I(s) \otimes \hat{\rho}_B \right\}$$

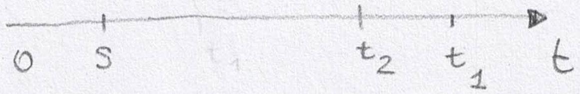
$$+ \int_0^t ds \int_0^{t_1} dt_2 \int_0^{t_2} ds \, \mathrm{Tr}_B \left\{ \mathcal{L}_{T,I}(t) \Sigma_{Q,I}(t_1) \Sigma_{Q,I}(t_2) \mathcal{L}_{T,I}(s) \hat{\rho}_I(s) \otimes \rho_B \right\}$$

with $\quad \Sigma_{Q,I}(t) = Q \mathcal{L}_{T,I}(t) Q \qquad (5.26)$

Analogous expressions are easily derived for the higher orders.

cf. Nested integral

$$\int_0^t ds \int_s^t dt_1 \underbrace{\int_s^{t_1} dt_2 \; \mathcal{P}\mathcal{L}_T G_0(t-t_1)\Sigma_Q \overbrace{G_0(t_1-t_2)\Sigma_Q G_0(t_2-s)\mathcal{L}_T \mathcal{P}\rho_s}^{B(t,\, t_1,\, t_2,\, s)}}_{A(t,\, t_1,\, s)}$$



Use the property of double integrals recursively:

$$\boxed{\int_0^t ds \int_s^t dt_1 \; A(t, t_1, s) = \int_0^t dt_1 \int_0^{t_1} ds \; A(t, t_1, s)}$$

Apply again this property

$$\int_0^{t_1} ds \int_s^{t_1} dt_2 \; B(t, t_1, t_2, s) = \int_0^{t_1} dt_2 \int_0^{t_2} ds \; B(t, t_1, t_2, s)$$

$$\hookrightarrow \quad \int_0^t ds \int_s^t dt_1 \int_s^{t_1} dt_2 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} ds$$