Charge and energy transport in time-dependently driven electron systems

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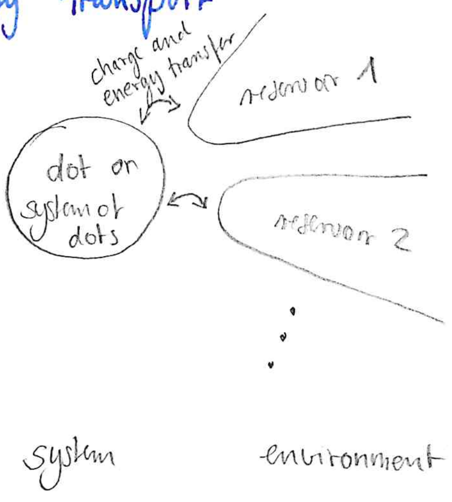
0. Introductory remarks

- energy transport (main topic of the college)
- charge transport
  - → constitutes a relevant means to transform heat to electrical work
    or to use electrical work for cooling
- what is the interest in time-dependently driven systems?
  * heat engines relying on cycles
  * absorb, store, release energy
  * possibly break Onsager relations (which require time-reversal symmetry)
  * no energy conservation anymore
  * use energy-transport as a tool to do spectroscopy on time-dependent systems
    (or vice versa: use time-dependent current source to sample energy-dependent properties of a device)

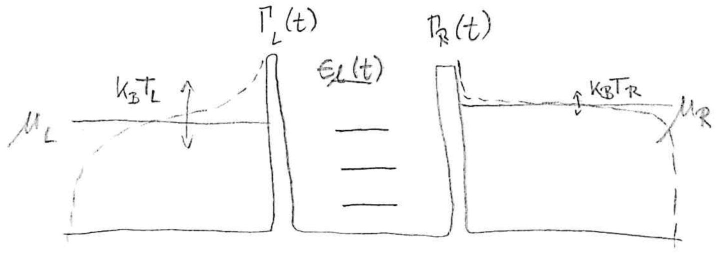
- electron system → example <u>quantum dot devices</u>

Take quantum dots as an example (simple and fundamental), which can be used in the context of heat engines or - more generally - charge / heat / energy transport



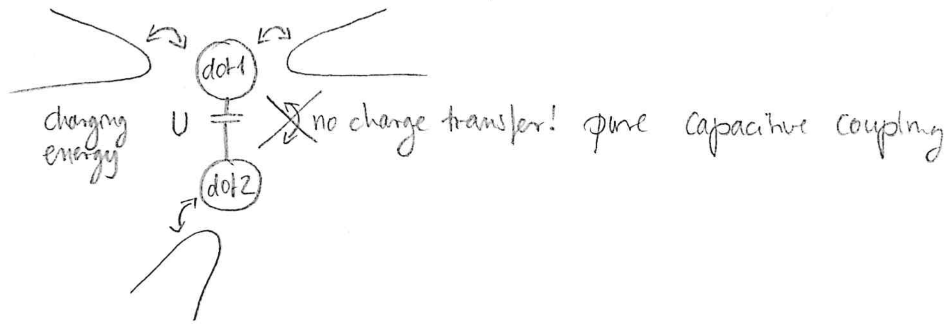
* discrete levels - constitute single-electron control and an ideal spectrum for thermoelectrics

  See also: Hicks & Dresselhaus '1993
  Mahan & Sofo '1996



* control over coupling/decoupling from/to electronic (heat) baths.
* control via gates - do electric work by moving up/down electrons in energy space

* Coulomb (capacitive) coupling to other device parts as a means to transfer energy (without charge)



* quantization and quantum open system effects can be observed in quantum dot systems (via their transport properties) and can be <u>exploited</u> (e.g. in heat engines)

1. Quantum dot devices - Model and dynamics

1.1. Model for the quantum dot system

Describe the system by a Hamiltonian (operator)

$$H_{tot} = H + H_{res} + H_{tun}$$

$$= H + \sum_{\alpha} \left(H_{res,\alpha} + H_{tun,\alpha} \right)$$

↑ sum over all reservoirs

* reservoirs are large and effectively non-interacting:

$$H_{res,\alpha} = \sum_{k,\sigma} \varepsilon_{\alpha k \sigma} c^{\dagger}_{\alpha k \sigma} c_{\alpha k \sigma}$$

the occupation of these reservoirs is determined by a Fermi function

$$f_{\alpha}(E) = \frac{1}{1+e^{(E-\mu_{\alpha})/k_B T_{\alpha}}}$$

with electrochemical potential μ_{α} and temperature T_{α}

their density matrix is the one of a grandcanonical ensemble:

$$\rho_{\alpha} = \frac{1}{Z_{\alpha}} e^{-(H_{res,\alpha} - \mu_{\alpha} \hat{N}_{\alpha})/k_B T_{\alpha}}$$

with partition function Z_{α}

and $\hat{N}_{\alpha} = \sum_{k,\sigma} c^{\dagger}_{\alpha k \sigma} c_{\alpha k \sigma}$

* the system couples to these reservoirs via tunneling of particles:

$$H_{tun,\alpha} = H^{+}_{tun,\alpha} + H^{-}_{tun,\alpha}$$

with $$H^{+}_{tun,\alpha} = \sum_{k,\sigma,\ell} t^{\alpha *}_{k\sigma\ell}\, d^{+}_{\ell\sigma}\, c_{\alpha k\sigma}$$

$$H^{-}_{tun,\alpha} = \sum_{k,\sigma,\ell} t^{\alpha}_{k\sigma\ell}\, c^{+}_{\alpha k\sigma}\, d_{\ell\sigma}$$

here we took tunneling to be spin-conserving

some orbital of the quantum dot system

this sets the "coupling strength" $\Gamma \sim \nu |t|^2$ between system + bath

reservoir density of states

* quantum dot system:

$$H = \sum_{s} E_s |s\rangle\langle s|$$

with eigenenergies and eigenstates of the (isolated) system:

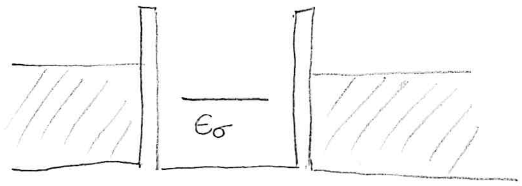
$$H|s\rangle = E_s|s\rangle$$

eigenstates are in general <u>not</u> given by single-particle states (Slater determinant) due to strong onsite interaction

for example: onsite Coulomb interaction, spin-spin interaction ...

1.2. Example systems of this course

A: Single-level quantum dot (single impurity Anderson model (SIAM))



$$H = \sum_\sigma \epsilon_\sigma d_\sigma^\dagger d_\sigma + U \hat{n}_\uparrow \hat{n}_\downarrow$$

with $\hat{n}_\sigma = d_\sigma^\dagger d_\sigma$

Eigenstates + Eigenenergies.

$$|s\rangle \in \{ |0\rangle, |\uparrow\rangle, |\downarrow\rangle, |d\rangle \}$$

$$E_s \in \{ 0, \epsilon_\uparrow, \epsilon_\downarrow, \epsilon_\uparrow + \epsilon_\downarrow + U \}$$

B: double dot

$$H = \sum_{\alpha = L,R} \epsilon_\alpha \hat{n}_\alpha + U \hat{n}_L \hat{n}_R + U' \sum_\alpha \hat{n}_{\alpha\uparrow} \hat{n}_{\alpha\downarrow}$$
$$- \frac{t_c}{2} \sum_{\sigma = \uparrow,\downarrow} \left(d_{L\sigma}^\dagger d_{R\sigma} + h.c. \right)$$

with $\hat{n}_\alpha = \sum_\sigma \hat{n}_{\alpha\sigma}$

$\hat{n}_{\alpha\sigma} = d_{\alpha\sigma}^\dagger d_{\alpha\sigma}$

We now assume that U' is the largest energy scale and exclude states of local double occupation.

Eigenstates: $|S\rangle \in \{ |0\rangle, |b,\uparrow\rangle, |b,\downarrow\rangle, |a,\uparrow\rangle, |a,\downarrow\rangle,$
$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \}$

with (molecular) bonding and antibonding states:

$$|b/a,\sigma\rangle = \frac{1}{\sqrt{2}} \left[\sqrt{1 \pm \frac{\epsilon}{\sqrt{\epsilon^2+t_c^2}}}\, |R,\sigma\rangle \pm \sqrt{1 \mp \frac{\epsilon}{\sqrt{\epsilon^2+t_c^2}}}\, |L,\sigma\rangle \right]$$

local single-dot states (here no eigenstates anymore)

with $\epsilon = \epsilon_L - \epsilon_R$

Eigenenergies: $E_S \in \{ 0, \epsilon_b, \epsilon_a, \epsilon_L + \epsilon_R + U \}$

with $\epsilon_{b/a} = E \mp \frac{1}{2} \sqrt{\epsilon^2 + t_c^2}$

and $E = \frac{1}{2} (\epsilon_L + \epsilon_R)$

these states are obtained from diagonalizing this <u>local</u> Hamiltonian!

1.3. Master equation for quantum dot dynamics

We are interested in the time-evolution of the dot-system states (in the presence of weakly coupled reservoirs) and measurable transport quantities / observables like charge and energy or heat currents flowing through the driven dot system.

Here, we will use a Master equation approach, which is particularly useful for the description of

- strongly interacting [→ prevents using a noninteracting approach]
- small [allows to easily diagonalize the local system (see examples)]
- weakly coupled [justifies an approximation based on perturbation theory in system-bath coupling]

systems.

We start with a short overview over the equations that will be used for the study of the examples. (1st order in the tunnel coupling).

Reduced density matrix of the system:

$$\mathrm{Tr}_{res}\{\rho^{tot}\} = \rho$$

Diagonal elements of ρ are the occupation probabilities of the dot-system energy eigenstates: $\mathbf{P} = \{P_s\}$ (vector)

It's time evolution fulfills a Master equation

$$\boxed{\frac{d}{dt} P_s(t) = \sum_{s'} W_{ss'} P_{s'}(t)}$$

with the transition matrix (Kernel) introducing <u>dissipation</u> due to tunneling processes to the reservoirs:

$$W_{ss'} = \sum_{\alpha} W^{\alpha}_{ss'} \qquad \text{[tunneling wrt different reservoirs]}$$

with the Stückelberg condition (imposed by probability conservation)

$$W_{ss} = - \sum_{ss'} W_{s's}$$

Rewrite the Master equation in a different (well-known) form:

$$\boxed{\frac{d}{dt} P_s(t) = \sum_{s'} \Big[\underset{\uparrow \\ \text{gain}}{W_{ss'} P_{s'}} - \underset{\uparrow \\ \text{loss}}{W_{s's} P_s} \Big]}$$

with $\sum_s P_s(t) = 1$ and $\sum_s \dot{P}_s = 0$ (conserved probabilities)

* For the <u>stationary state</u> (absence of driving), we have

$$\dot{P} = 0 \qquad \boxed{0 = \sum_{s'} W_{ss'} P_{s'}}$$

* For slow, continuous driving, for example with a driving frequency $\Omega = 2\pi/\tau$, it can be useful to expand the Master equation in orders of the driving frequency:

$$\boxed{\dot{P}_s^{(K-1)}(t) = \sum_{s'} W_{ss'} P_{s'}^{(K)}(t)}$$

$K > 0$: delayed response of the system to the time-dependent modulation

To calculate the resulting probabilities and their dynamics, we need an explicit form for W

→ given by <u>Fermi's golden rule</u>.

For transitions $|s'\rangle \longrightarrow |s\rangle$ with $N_s = N_{s'}+1$

(and hence $N_{res,\alpha} \rightarrow N_{res,\alpha} - 1$)

$$W^{\alpha+}_{ss'} = \frac{2\pi}{\hbar} \underbrace{\sum_{\chi,\chi'}}_{\text{initial + final reservoir states}} |\langle s\chi|\, H^{+}_{tun,\alpha}\, |s'\chi'\rangle|^2\, \nu_\alpha(\chi')\, \delta\big(\underbrace{E_s + E_\chi}_{\text{energy of final state}} \underbrace{- E_{s'} - E_{\chi'}}_{\text{- energy of initial state}}\big)$$

and equivalently for transitions $|s'\rangle \rightarrow |s\rangle$ with $N_s = N_{s'} - 1$ described by $W^{\alpha-}_{ss'}$.

Leads to

$$\boxed{\begin{aligned} W^{\alpha+}_{ss'} &= \frac{1}{\hbar}\Gamma_\alpha\, |\langle s|\sum_\ell x_\ell\, d^{+}_{\ell\cancel{\sigma}}|s'\rangle|^2\, f_\alpha(E_s - E_{s'}) \\ W^{\alpha-}_{s's} &= \frac{1}{\hbar}\Gamma_\alpha\, |\langle s|\sum_\ell x_\ell\, d^{+}_{\ell}\,|s'\rangle|^2\, \big(1 - f_\alpha(E_s - E_{s'})\big) \end{aligned}}$$

coupling strength — selection rules — Pauli principle + energy conservation

with $\Gamma_\alpha = \cancel{\sum_k} 2\pi \nu_\alpha |t_\alpha|^2$

and assuming $t^{\alpha}_{k\ell\sigma} \sim t_\alpha \cdot x_\ell$

Charge, energy, and heat currents

Similar equations can be found for the relevant transport observables. We have

$$I_\alpha^N = -\frac{d}{dt}\langle \hat{N}_\alpha \rangle$$

particle current out of the reservoirs into the system.

$$\boxed{I_\alpha^N = + \sum_{s,s'} (n_s - n_{s'}) W_{ss'}^\alpha P_{s'}}$$

From this, obtain the charge current as

$$\boxed{I_\alpha = -e\, I_\alpha^N}$$

with the electron charge $-e$

$$I_\alpha^E = -\frac{d}{dt}\langle H_{res,\alpha} \rangle$$

energy current out of the reservoirs, into the system

we assume $H_{res,\alpha}$ not to be explicitly time-dependent

$$\boxed{I_\alpha^E = \sum_{s,s'} (E_s - E_{s'}) W_{ss'}^\alpha P_{s'}}$$

From this, obtain the heat current

$$\boxed{J_\alpha = I_\alpha^E - \mu_\alpha I_\alpha^N}$$

$\hat{=}$ current of excess energy wrt the reservoir's electrochemical potential

$\rightarrow$ is dissipated as heat.

All these currents are time-dependent (via time-dependent parameters entering W and via $P(t)$) if we do not only consider the stationnary state.

1.4. Derivation of the time-dependent Master equation and transport observables - rough overview and selected aspects

We want to calculate objects of the type $\langle \hat{A}(t) \rangle$ where $\hat{A}$ could be a current operator or a projector on a certain dot state (to calculate elements of the reduced density matrix)

$$\langle \hat{A}(t) \rangle = \underset{\uparrow}{\mathrm{Tr}}\, \mathrm{Tr}_{res} \left[\rho^{tot}(t)\, \hat{A} \right]$$

system trace

Schrödinger picture with

$$\partial_t \rho^{tot}(t) = -\frac{i}{\hbar} \left[H_{tot}, \rho^{tot}_{q}(t) \right]$$

$$=: -\frac{i}{\hbar} L_{tot}\, \rho^{tot}(t)$$

At an initial time t_0, we assume reservoirs and system to be decoupled

$$\rho^{tot}(t_0) = \rho_0^{tot} = \rho(t_0) \prod_\alpha \rho_{\alpha,0} \qquad \text{with } \rho_{\alpha,0} = \frac{1}{Z_{\alpha,0}} e^{-(H_{res,\alpha} - \mu_\alpha \hat{N}_\alpha)/k_B T_\alpha}$$

with μ_α, T_α at $t = t_0$

the system has some arbitrary density matrix $\rho(t_0) = \rho_0$ at t_0

time-evolution of the reduced density matrix

Remember that we are not interested in reservoir states ...

$$\rho(t) = \mathrm{Tr}_{res} \left\{ \rho^{tot}(t) \right\} = \mathrm{Tr}_{res} \left\{ e^{-iL_{tot} t} \rho_{res,0} \right\} \rho_0$$

$$\equiv \underbrace{\Pi(t,t_0)}_{\text{propagator}}\, \rho_0$$

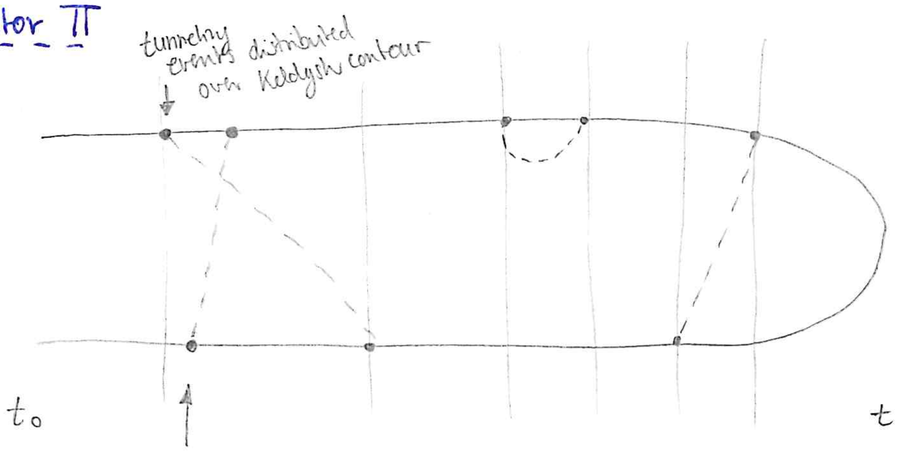
perceiving the coupling between system and reservoirs as a "perturbation", it makes sense to go to the interaction picture

with $H_{res} + H$ uncoupled system

H_{tun} coupling (the "interaction")

$$\rightarrow \langle \hat{A}(t) \rangle = \mathrm{Tr}\, \rho_0\, \mathrm{Tr}_{res} \left\{ \rho_{res,0}\; \underbrace{T_K}_{\text{Keldysh time-ordering}}\, e^{\overbrace{-i \int_K H_{tun}(t')_I}^{\text{time-integral over Keldysh contour}}}\, \hat{A}(t)_I \right\}$$

⇒ propagator Π



The propagator $\Pi(t,t_0)$ fulfills a Dyson equation

$$\boxed{\Pi(t,t_0) = \Pi_0(t,t_0) + \int dt_1 \int dt_2\, \Pi_0(t,t_1)\, W(t_1,t_2)\, \Pi(t_2,t_0)}$$

$W(t_1,t_2)$ is a self energy (sum over all irreducible diagrams) related to the Kernel of the Master equation W, considered before [Here, for weakly coupled systems, we consider only 1-line diagrams $\sim \Gamma$]

From this one can derive:

$$\boxed{\frac{d}{dt} P_s(t) = \sum_{s'} \int_{t_0}^{t} dt'\, W_{ss'}(t,t')\, P_{s'}(t')}$$

Here, we can observe a number of important facts and issues!

(i) in general, $P_s(t)$ depends on all occupation probabilities at all earlier times t'.

(ii) in general, W depends on $\underline{\underline{2}}$ times
(A possibly time-dependent Hamiltonian is crucial here)

(iii) macroscopic properties, like μ_α, T_α enter only with their values at t_0!

To discuss these issues (in particular i, ii) we introduce some relevant time scales

τ_{res} : memory time or decay time of the Kernel
for $|t-t'| \gg \tau_{res}$ we have $W(t,t') = 0$

typically given by $1/k_B T$ in our case

τ_{drive} : time scale of a (continuous) driving
For periodically driven systems $\sim \frac{1}{\Omega}$ (but also amplitude of driven parameters can play a role !!)

τ_{tun} : time scale on which occupation probabilities change due to tunneling events $\sim \frac{1}{\Gamma}$ $\left(\frac{1}{W}\right)$

(i) $\frac{d}{dt} P(t) = \int_{t_0}^{t} dt' \, W(t,t') \, P(t')$

expand around the final time t

$$= \int_{t_0}^{t} dt' \, W(t,t') \left[P(t) + (t-t')\dot{P}(t) + \dots \right]$$

These terms can be neglected in the so-called Markov approximation

justified if $\tau_{tun}, \tau_{drive} \gg \tau_{res}$

namely for weakly coupled, slowly driven systems

$\Rightarrow$ in Markov approximation

$$\frac{d}{dt} P \approx \left[\int_{t_0}^{t} dt' \, W(t,t') \right] \cdot P(t)$$

see PRB 74, 085305 (2006) for an extension of this

(ii) $W(t,t')$ does <u>not only</u> depend on a time difference if the Hamiltonian H_{tot} is time-dependent on a time-scale of the Kernel decay time

However, if $\tau_{drive} \gg \tau_{res}$, we can write

$$W(t,t') = W_t(t-t')$$ in lowest order τ_{res}/τ_{drive}

all parameters taken at time t

see PRB 74, 085305 (2006) for an extension of this

$$\Rightarrow \boxed{\frac{d}{dt} P(t) \approx W_t \, P(t)}$$

with $W_t = \int_{t_0}^{t} dt' \, W_t(t-t')$

golden-rule Kernel calculated previously

Zero-frequency Laplace transform of the Kernel

A further expansion of this equation in orders in the driving frequency is justified if $\tau_{drive} \gg \tau_{tun}$

$$\Rightarrow \boxed{\frac{d}{dt} P^{(k-1)}(t) = W_t P^{(k)}(t)}$$

(k) : order in the driving frequency

(iii) How to model time-dependent temperature or electrochemical potential?

→ see e.g. Luttinger, Phys. Rev 135, A 1505 (1964)
Hasegawa & Kato J. Phys. Soc. Jpn 86, 024710 (2017)
"thermo-mechanical model"

idea: start with a time-dependent reservoir Hamiltonian

$$H_{res,\alpha}(t) = c(t) H^{0}_{res,\alpha} + v(t) \hat{N}_\alpha$$

$$\Rightarrow \epsilon_{\alpha k\sigma}(t) = c(t)\, \epsilon^{0}_{\alpha k\sigma} + v(t)$$

time-dependence should be adiabatic → no entropy change:

$$\frac{dS_\alpha}{dt} = -k_B \sum_{k,\sigma} \dot{p}_{\alpha k\sigma} \ln p_{\alpha k\sigma} = 0$$

implying $f_\alpha(\epsilon_{\alpha k\sigma}(t) - \mu_\alpha(t)) \equiv \sigma$ to have $\dot{p}_{\alpha k\sigma} = 0$

$$\Rightarrow \frac{1}{T^0_\alpha}(\epsilon^0_{\alpha k\sigma} - \mu^0_\alpha) = \frac{1}{T_\alpha(t)}(\epsilon_{\alpha k\sigma}(t) - \mu_\alpha(t)) = \frac{1}{T_\alpha(t)}(c(t)\epsilon^0_{\alpha k\sigma} + v(t) - \mu_\alpha(t))$$

fulfilled if
$$\boxed{\begin{aligned} T_\alpha(t) &= c(t) T^0_\alpha \\ \mu_\alpha(t) &= c(t)\mu^0_\alpha + v(t) \end{aligned}}$$

is intuitively clear, since lifting all energies by $v(t)$ corresponds to changing μ
when stretching/squeezing the spectrum via $c(t)$, populations can only be kept constant if the temperature changes.

Charge and energy currents

particle current flowing out of reservoir α

$$I_\alpha^N = -\frac{d}{dt}\langle \hat{N}_\alpha \rangle$$

$$= \frac{i}{\hbar}\langle [\hat{N}_\alpha, H_{tot}] \rangle$$

$$= \frac{i}{\hbar}\langle [\hat{N}_\alpha, H_{tun,\alpha}] \rangle$$

charge / particle currents are conserved !! This can easily be shown exploiting

$$[\hat{N}_\alpha, H_{tun,\alpha}] = -[\hat{n}, H_{tun,\alpha}]$$

$$\Rightarrow \sum_\alpha I_\alpha^N = \frac{i}{\hbar}\sum_\alpha \langle [\hat{N}_\alpha, H_{tun,\alpha}] \rangle = -\frac{i}{\hbar}\langle [\hat{n}, H_{tun}] \rangle = \frac{d}{dt}\langle \hat{n} \rangle$$

$\Rightarrow$ sum over all particles tunneling out of the reservoirs is equal to the amount of particles tunneling into the system!

Note that $\frac{d}{dt}\langle \hat{n} \rangle$ can only be finite on short times (and not in the stationary case) since the total charge that can be stored in the system is bounded!

concrete evaluation of I_α^N

$$I_\alpha^N = -\frac{d}{dt}\langle \hat{N}_\alpha \rangle = \frac{i}{\hbar}\langle [\hat{N}_\alpha, H_{tun,\alpha}] \rangle = \frac{i}{\hbar}\,\mathrm{Tr}\,\mathrm{Tr}_{res}\left\{[\hat{N}_\alpha, H_{tun,\alpha}]\,\rho^{tot}(t)\right\}$$

$$= -\frac{i}{\hbar}\,\mathrm{Tr}\,\mathrm{Tr}_{res}\left\{[\hat{n}, H_{tun,\alpha}]\,\rho^{tot}(t)\right\}$$

$$= \mathrm{Tr}\left\{\hat{n}\,\underbrace{\mathrm{Tr}_{res}\left\{-\frac{i}{\hbar}[H_{tun,\alpha}, \rho^{tot}(t)]\right\}}_{\text{This is what leads to the master equation (here wrt } W_\alpha \text{ only)}}\right\}$$

$$\Rightarrow \quad I_\alpha^N = \mathrm{Tr}\{\hat{n}\, W_\alpha \rho\}$$

small exercise: show that this leads to the expression given in 1.3.
take the simple SIAM and use the Stückelberg relation.

we will later write this in the more compact way

$$I_\alpha^N = (n|W_\alpha|\rho)$$

energy current flowing out of reservoir α

$$I_\alpha^E = -\frac{d}{dt}\langle H_\alpha\rangle = \frac{i}{\hbar}\langle[H_\alpha, H_{tot}]\rangle - \langle\dot{H}_\alpha\rangle$$

↑ power due to external driving

we now assume $\dot{H}_\alpha = 0$
(while H, H_{tun} can still be time-dep.)

$$\rightarrow \quad I_\alpha^E = \frac{i}{\hbar}\langle[H_\alpha, H_{tun,\alpha}]\rangle$$

Note that the situation is very different from the charge current since in general $\left[\sum_{\alpha'} H_{\alpha'} + H,\ H_{tun,\alpha}\right] \neq 0$

$\Rightarrow$ energy currents out of reservoirs do not equal energy currents into the system!

We rather have:

$$\sum_\alpha I_\alpha^E + \sum_\alpha I^E_{tun,\alpha} = \frac{d}{dt}\langle H\rangle$$

↑ energy current into barriers

The important question arises, whether the tunneling barriers are part of the system or of the environment

→ relevant for thermodynamics considerations of time-dependent systems!!

see e.g. Ludovico et al. PRB 94, 035436 (2016)

Esposito ...

Concrete evaluation of I^E_α

$$I_E^\alpha = -\frac{d}{dt}\langle H_\alpha\rangle = \frac{i}{\hbar}\langle [H_\alpha, H_{tun,\alpha}]\rangle$$

$$= \frac{i}{\hbar} \operatorname{Tr} \operatorname{Tr}_{res}\left\{[H_\alpha, H_{tun,\alpha}]\, \rho^{tot}(t)\right\}$$

We now assume that tunneling to reservoir α conserves the energy of the total system.
This means that we do not consider photon-emission due to tunneling etc.

namely: $[H_{tot}, H_{tun,\alpha}] = 0 = [\sum_\alpha H_\alpha + H + \sum_{\alpha'} H_{tun,\alpha'}, H_{tun,\alpha}]$

and also $[H_\alpha + H + \sum_{\alpha'\neq\alpha} H_{tun,\alpha'}, H_{tun,\alpha}] = 0$

$$\Rightarrow I_E^\alpha = -\frac{i}{\hbar} \operatorname{Tr} \operatorname{Tr}_{res}\left\{[H, H_{tun,\alpha}]\, \rho^{tot}(t)\right\} - \frac{i}{\hbar} \operatorname{Tr}\operatorname{Tr}_{res}\left\{\Big[\sum_{\alpha'\neq\alpha} H_{tun,\alpha'}, H_{tun,\alpha}\Big]\rho^{tot}(t)\right\}$$

$$= -\frac{i}{\hbar} \operatorname{Tr}\left\{H \operatorname{Tr}_{res}\left\{[H_{tun,\alpha}, \rho^{tot}(t)]\right\}\right\} - \frac{i}{\hbar} \operatorname{Tr}\operatorname{Tr}_{res}\left\{\Big[\sum_{\alpha'\neq\alpha} H_{tun,\alpha'}, H_{tun,\alpha}\Big]\rho^{tot}(t)\right\}$$

↑ at least second order in Γ !!

$$\Rightarrow \quad I_E^{\alpha} \approx \mathrm{Tr}\left\{ H\, W_\alpha\, \rho(t) \right\}$$

$$\rightarrow \quad (H \,|\, W_\alpha \,|\, \rho)$$

$\Rightarrow$ this can again be shown to coincide with the expression shown in 1.3.