To proceed we need to further specify properties of the thermal reservoir. To this extent we need to discuss properties of so-called bath time-correlation functions.

Note: The last term of Eq. (2.12) contains contributions of at least $O(V^3)$ and hence can be dropped in a second order calculation. Its role for fourth order calculations is however crucial.

2.3.2 Time correlation functions

Let us assume a bilinear system-bath interaction:

$$\hat{H}_{S-B} = \hat{V} = \sum_i \hat{Q}_i \hat{F}_i \qquad (2.13)$$

where $\hat{Q}_i$ only acts on S and $\hat{F}_i$ on B.

In the interaction picture

$$\hat{V}_I(t) = U_0^+(t)\,\hat{V}\,\hat{U}_0(t) = \hat{U}_B^+\hat{U}_S^+\,\hat{V}\,\hat{U}_S\hat{U}_B = \sum_i \hat{Q}_i(t)\hat{F}_i(t) \quad (2.14)$$

where

$$\hat{F}_i(t) = \hat{U}_B^+\hat{F}_i\hat{U}_B\,, \qquad \hat{Q}_i(t) = \hat{U}_S^+\hat{Q}_i\hat{U}_S\,. \quad (2.15)$$

Inserting (2.14) in (2.12), using that $\hat{F}_i$ and $\hat{Q}_i$ commute and the cyclic property of the trace, one finds:

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{i}{\hbar}\sum_i \Big[\hat{Q}_i(t)\hat{\rho}_S(0)\,\mathrm{Tr}_B\{\hat{F}_i(t)\hat{\rho}_B(0)\} - \hat{\rho}_S(0)\hat{Q}_i(t)\,\mathrm{Tr}_B\{\hat{F}_i(t)\hat{\rho}_B(0)\}\Big]$$

$$-\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt'\Big[\hat{Q}_i(t)\hat{Q}_j(t')\hat{\rho}_{red,I}(t') - \hat{Q}_j(t')\hat{\rho}_{red,I}(t')\hat{Q}_i(t)\Big]\mathrm{Tr}_B\{\hat{F}_i(t)\hat{F}_j(t')\hat{\rho}_B\}$$

$$-\Big[\hat{Q}_i(t)\hat{\rho}_{red,I}\hat{Q}_j(t') - \hat{\rho}_{red,I}(t')\hat{Q}_j(t')\hat{Q}_i(t)\Big]\mathrm{Tr}_B\{\hat{F}_j(t')\hat{F}_i(t)\hat{\rho}_B\}$$

$$+\ O(V^3) \qquad (2.16)$$

where we neglected the last term in Eq. (2.12). We also replaced

$$\mathrm{Tr}_B \{ [\hat{V}_I(t), [\hat{V}_I(t'), \hat{\rho}_{S,I}(t') \rho_B(0)]] \} \to \mathrm{Tr}_B \{ [\hat{V}_I(t), [\hat{V}_I(t'), \hat{\rho}_{red,I}(t') \rho_B(0)]] \}$$

which is correct to $O(\hat{V}^2)$.

Consider now the expectation values

$$\langle \hat{F}_i(t) \rangle_B = \mathrm{Tr}_B \{ \hat{F}_i(t) \hat{\rho}_B \} \quad \text{and}$$

$$\langle \hat{F}_i(t) \hat{F}_j(t') \rangle_B = \mathrm{Tr}_B \{ \hat{F}_i(t) \hat{F}_j(t') \hat{\rho}_B \}$$

i) $$\langle \hat{F}_i(t) \rangle_B = \mathrm{Tr}_B \{ \hat{F}_i(t) \hat{\rho}_B \} = \sum_{n,m} \langle n | \hat{F}_i(t) | m \rangle \langle m | \hat{\rho}_B | n \rangle$$

$$= \sum_n Z^{-1} \langle n | \hat{F}_i(t) | n \rangle \, e^{-\beta E_n}$$

$\{|n\rangle\}$ is the eigenbasis of H_B (and $\hat{N}_B$).

Assuming that $\hat{F}_i$ has no diagonal elements in the energy representation (otherwise the free Hamiltonian could be redefined to include these parts) $\Rightarrow$ $\langle \hat{F}_i(t) \rangle = 0$ (2.17)

In other words the interaction does not produce an average frequency shift.

ii) $$\langle \hat{F}_i(t) \hat{F}_j(t') \rangle_B = \mathrm{Tr}_B \{ \hat{F}_i(t) \hat{F}_j(t') \rho_B \} =$$

$$= \mathrm{Tr}_B \{ \hat{U}_B^+(t) \hat{F}_i \hat{U}_B(t) \hat{U}_B^+(t') \hat{F}_j \hat{U}_B(t') \hat{\rho}_B \} =$$ ρ_B is not evolving in time

cyclic trace property $$\mathrm{Tr}_B \{ \underbrace{\hat{U}_B(t') \hat{U}_B^+(t)}_{U_B^+(t-t')} \hat{F}_i \underbrace{\hat{U}_B(t) U_B^+(t')}_{U_B(t-t')} \hat{F}_j \hat{\rho}_B \} = \langle \hat{F}_i(t-t') \hat{F}_j \rangle_B \quad (2.18)$$

i.e., the correlation function $\langle \hat{F}_i(t) \hat{F}_j(t') \rangle$ is <u>stationary</u> (= it only depends on the time difference.

Inserting (2.17) and (2.18) in (2.16), it follows

$$\boxed{\begin{aligned}\dot{\hat{\rho}}_{red,I}(t) = -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{ & [\hat{Q}_i(t), \hat{Q}_j(t')\hat{\rho}_{red,I}(t')] \langle \hat{F}_i(t)\hat{F}_j(t')\rangle_B \\ & - [\hat{Q}_i(t), \hat{\rho}_{red,I}(t')\hat{Q}_j(t')] \langle \hat{F}_j(t')\hat{F}_i(t)\rangle_B \Big\} + O(V^3)\end{aligned} \qquad (2.19)}$$

<u>Note</u>: All information on the reservoir is, to second order in $\hat{V}$, contained in the correlation functions $\langle \hat{F}_i(t)\hat{F}_j(t')\rangle_B$ and $\langle \hat{F}_j(t')\hat{F}_i(t)\rangle_B$. In reality the correlators to be calculated are only $\langle \hat{F}_i(t)\hat{F}_j(t')\rangle = C_{ij}(t-t')$ since $\langle \hat{F}_j(t')\hat{F}_i(t)\rangle = C_{ji}(t'-t)$.

<u>2.3.3 Generalized master equation for the RDM</u>

Eq. (2.19) can be recast in the form

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t dt'\, K^{(2)}(t,t')\,\hat{\rho}_{red,I}(t') + O(V^3) \qquad (2.20)$$

where $K^{(2)}(t,t')$ is a <u>superoperator</u> acting on the reduced density operator $\hat{\rho}_{red,I}$. Here the superscript (2) indicates that only contributions up to 2^{nd} order in $\hat{V}$ are included.

If (2.12) is iterated to all orders, analogously to (2.20), the exact equation is found:

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

where the superoperator K is now a power series in the interaction $\hat{V}$. This integro-differential eq. is called generalized master equation (GME).

2.3.4 Markov approximation

Frequently a Markov approximation is performed on the GME. Specifically, the Markov approximation relies on the observation that the correlation function $\langle \hat{F}_i(t-t')\hat{F}_j \rangle_B$ vanishes for time intervals $t-t' > \tau$ where τ is the so-called correlation time of the reservoir:

$$\langle \hat{F}_i(t)\, \hat{F}_j(t') \rangle \simeq \langle \hat{F}_i(t) \rangle \langle \hat{F}_j(t') \rangle = 0 \quad \text{if} \quad t-t' > \tau \qquad (2.22)$$

This relation expresses the concept that the reservoir "forgets" the correlations induced by interactions occurring at times t and t' on the time scale τ. If one now compares τ with the characteristic time $1/\gamma$ (we will see it as damping time, decay rate) required for $\hat{\rho}(t)_{red,I}$ to change appreciably, and it holds

$$\tau \ll 1/\gamma \qquad (2.23)$$

$\Rightarrow$ $\hat{\rho}_{red,I}(t') \approx \hat{\rho}_{red,I}(t)$ in Eq. (2.21) on the time-scale in which the correlation functions are not vanishing.

$\Rightarrow$ the Markov approximation to (2.21)

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t dt' \, K(t,t') \, \rho_{red,I}(t) \quad (2.24)$$

$\leftarrow$ This is not any more an integro differential equation

One can also further analyze (2.24) to make further approximations.
Let us go back to Eq. (2.19) and perform the variable transformation

$$t - t' = t'' \Rightarrow dt' = -dt'' \text{ which brings } \int_0^t dt' \to \int_0^t dt'' \quad (2.25)$$

The Markov approx allows, if $t \gg \tau$ to replace

$$\int_0^t dt'' \sim \int_0^\infty dt'' \quad (2.26)$$

This yields the Markovian master equation (MME)

$$\boxed{\dot{\hat{\rho}}_{red,I}(t) = \int_0^\infty dt'' \, K(t, t-t'') \, \hat{\rho}_{red,I}(t)} \quad (2.27)$$

In other terms (2.27) can be written as

$$\boxed{\dot{\hat{\rho}}_{red,I}(t) = \mathcal{L}_I(t) \, \hat{\rho}_{red,I}(t)} \quad (2.27b)$$

where we have introduced the superoperator $\mathcal{L}_I$: the Liouvillean in interaction picture.

Convolution form of the Kernel.

The statement that we want to make is that the GME (to second order) can be written, in the Schrödinger picture, as:

$$\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] + \int_0^t dt'\, K^{(2)}(t-t')\, \hat{\rho}_{red}(t')$$

if the system hamiltonian is not explicitly time dependent.

<u>proof</u>:

We start from Eq. (2.19)

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{ [\hat{Q}_i(t), \hat{Q}_j(t')\hat{\rho}_{red,I}(t')] \langle \hat{F}_i(t)\hat{F}_j(t')\rangle_B$$
$$- [\hat{Q}_i(t), \hat{\rho}_{red,I}(t')\hat{Q}_j(t')] \langle \hat{F}_j(t')\hat{F}_i(t)\rangle_B \Big\}$$

The following observations follow:

i)
$$\langle \hat{F}_i(t)\hat{F}_j(t')\rangle_B = \langle \hat{F}_i(t-t')\hat{F}_j(0)\rangle_B = C_{ij}(t-t')$$
$$\langle \hat{F}_j(t')\hat{F}_i(t)\rangle_B = \langle \hat{F}_j(t'-t)\hat{F}_i(0)\rangle_B = C_{ji}(t'-t) \qquad \text{cfr. (2.18)}$$

ii)
$$\frac{\partial}{\partial t}\hat{\rho}_{red,I}(t) = \frac{\partial}{\partial t}\left[\hat{U}_s^+(t)\,\hat{\rho}_{red}\,\hat{U}_s(t)\right] = \frac{i}{\hbar}\left[U_s^+(t)\hat{H}_s\hat{\rho}_{red}\hat{U}_s(t) - \hat{U}_s^+\hat{\rho}_{red}\hat{H}_s\hat{U}\right]$$
$$+ \hat{U}_s^+\dot{\hat{\rho}}_{red}\hat{U}_s = U_s^+\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}]\hat{U}_s + \hat{U}_s^+\dot{\hat{\rho}}_{red}\hat{U}_s$$

$$\Rightarrow \dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] + U_s(t)\,\dot{\hat{\rho}}_{red,I}\,U_s^+(t)$$

iii) Now we can ~~just~~ analyze (2.19) and write

$$\dot{\hat{\rho}}_{red,2}(t) = -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{ \Big[\hat{U}_s^+(t)\hat{Q}_i\hat{U}_s(t), \hat{U}_s^+(t')\hat{Q}_j \overbrace{\cancel{\hat{U}_s(t')}\,\cancel{\hat{U}_s^+(t')}}^{\mathbb{1}_s}\hat{\rho}_{red}\hat{U}_s(t')\Big] \langle \hat{F}_i(t-t')\hat{F}_j\rangle_B$$

$$- \Big[\hat{U}_s^+(t)\hat{Q}_i\hat{U}_s(t), \hat{U}_s^+(t')\hat{\rho}_{red}\overbrace{\cancel{\hat{U}_s(t')}\,\cancel{\hat{U}_s^+(t')}}^{\mathbb{1}_s}\hat{Q}_j\hat{U}_s(t')\Big]\langle \hat{F}_j(t-t')\hat{F}_i\rangle_B \Big\}$$

$$= -\frac{1}{\hbar^2}\sum_{ij}\int dt' \Big\{\Big[\hat{U}_s^+(t)\hat{Q}_i\hat{U}_s(t-t')\hat{Q}_j\hat{\rho}_{red}\hat{U}_s(t') - \hat{U}_s^+(t')\hat{Q}_j\hat{\rho}_{red}\hat{U}_s(t'-t)\hat{Q}_i\hat{U}_s(t)\Big]$$

$$\times \langle \hat{F}_i(t-t')\hat{F}_j\rangle_B$$

$$- \Big[\hat{U}_s^+(t)\hat{Q}_i\hat{U}_s(t-t')\hat{\rho}_{red}\hat{Q}_jU_s(t') - U_s^+(t')\hat{\rho}_{red}\hat{Q}_j\hat{U}_s(t'-t)\hat{Q}_i\hat{U}_s(t)\Big]$$

$$\times \langle \hat{F}_j(t-t')\hat{F}_i\rangle_B \Big\} .$$

Putting all 3 observations together:

$$\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{\Big[\hat{Q}_i\hat{U}_s(t-t')\hat{Q}_j\hat{\rho}_{red}\hat{U}_s(t'-t) - \hat{U}_s(t-t')\hat{Q}_j\hat{\rho}_{red}\hat{U}_s(t'-t)\hat{Q}_i\Big]$$

$$C_{ij}(t-t')$$

$$- \Big[\hat{Q}_i\hat{U}_s^+(t'-t)\hat{\rho}_{red}\hat{Q}_jU_s(t'-t) - U_s^+(t'-t)\hat{\rho}_{red}\hat{Q}_j\hat{U}_s(t'-t)\hat{Q}_i\Big]$$

$$C_{ji}(t'-t)\Big\}$$

this closes the proof.

$$\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt'$$

$$\Big\{\left[\hat{Q}_i, \hat{U}_S(t-t')\hat{Q}_j\,\hat{\rho}_{red}\,U_S^+(t-t')\right] c_{ij}(t-t')$$

$$-\left[\hat{Q}_i, U_S^+(t'-t)\,\hat{\rho}_{red}\,\hat{Q}_j\,U_S(t'-t)\right] c_{ji}(t'-t)\Big\}$$

It is an interesting check to understand if we calculated thing properly to ask the following question:

$$\dot{\hat{\rho}}_{red}^{\,+} \stackrel{?}{=} \dot{\hat{\rho}}_{red}$$

The only fundamental condition is that $H_{S-B}^+ = H_{S-B}$ at ~~each~~ every time $\Rightarrow \sum_i \hat{F}_i\hat{Q}_i = \sum_i \hat{Q}_i^+\hat{F}_i^+$. ~~Bisse~~

$$\left(-\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right]\right)^+ = \frac{i}{\hbar}\left[\hat{\rho}_{red}\hat{H}_S - \hat{H}_S\hat{\rho}_{red}\right] = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right]$$

$$\left[\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt'\left[\hat{Q}_i, \hat{U}_S(t-t')\hat{Q}_j\,\hat{\rho}_{red}\,U_S^+(t-t')\right] \langle \hat{F}_i(t-t')\hat{F}_j\rangle_B\right]^+ =$$

$$= \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' - \left[\hat{Q}_i^+, U_S(t-t')\,\hat{\rho}_{red}\,\hat{Q}_j^+ U_S^+(t-t')\right] \langle \hat{F}_j^+ F_i^+(t-t')\rangle = (*)$$

Now we can take Tr_B out and bring together $Q_i^+F_i^+$ and $Q_j^+F_j^+$. all together this will reconstruct $Q_i F_i$ and $Q_j F_j$ due to Hermiticity of $H_{S-B} = V$.

Continuing from above

$$(*) = \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \; - \left[\hat{Q}_i \,,\, U_S(t-t')\hat{\rho}_{red}\hat{Q}_j U_S^{+}(t-t')\right] \langle \hat{F}_j \hat{F}_i(t-t')\rangle$$

but $\langle \hat{F}_j \hat{F}_i(t-t')\rangle = \langle \hat{F}_j(t'-t)\hat{F}_i\rangle$. Finally using again the relation $U_S^{+}(t) = U_S(-t)$ closes the proof.

$$\Rightarrow \quad \dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \left\{\left[\hat{Q}_i, \hat{U}_S(t-t')\hat{Q}_j\hat{\rho}_{red}U_S^{+}(t-t')\right]C_{ij}(t-t') + h.c.\right.$$

$$= -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right] + \int_0^t dt' \, K^{(2)}(t-t')\,\hat{\rho}_{red}(t') .$$

Note: in the Markov approximation

i) $\int_0^t dt' \, K^{(2)}(t-t')\,\hat{\rho}_{red}(t') \longrightarrow \int_0^t dt' \, K^{(2)}(t-t')\,\hat{\rho}_{red}(t)$

ii) $\left[\int_0^t dt' \xrightarrow{t''=t-t'} \int_0^t dt''\right] \quad \int_0^t dt'' \, K^{(2)}(t'')\,\hat{\rho}_{red}(t) \longrightarrow \int_0^\infty dt'' \, K^{(2)}(t'')\,\hat{\rho}_{red}(t)$

the convolution form is lost.

In other words, it holds

$$\langle m'|\dot{\hat{\rho}}_{red,I}|m\rangle = \sum_{nn'} \langle n'|\hat{\rho}_{red,I}(t)|n\rangle \, e^{i(\omega_{m'n'}-\omega_{mn})t} \, R_{m'mn'n} \qquad (2.33)$$

or, with a more compact notation $\langle m'|\rho_{red,I}|m\rangle = \rho^I_{m'm}$

$$\dot{\rho}^I_{m'm} = R_{m'mm'm}\,\rho^I_{m'm} + \sum_{\substack{n\neq m \\ \text{or} \\ n'\neq m'}} e^{i(\omega_{m'n'}-\omega_{mn})t} R_{m'mn'n}\,\rho^I_{n'n} \qquad (2.33b)$$

or, alternatively

$$\dot{\rho}^I_{m'm} = \sum_{nn'} e^{i(\omega_{m'm}-\omega_{n'n})t} R_{m'mn'n}\,\rho^I_{n'n} \qquad (2.33c)$$

Note: in the Schrödinger picture. Let us recall (1.24...)

$$\hat{\rho}_{red} = e^{-i\hat{H}_s t/\hbar}\,\hat{\rho}_{red,I}\,e^{i\hat{H}_s t/\hbar}$$

which, when projected in the energy eigenbasis yields

$$(\rho_{red})_{m'm} = e^{-i\omega_{m'm}t}(\rho_{red\,I})_{m'm} \qquad (2.34a)$$

$$(\dot{\rho}_{red})_{m'm} = -i\omega_{m'm}\underbrace{e^{-i\omega_{m'm}t}(\rho_{red,I})_{m'm}}_{(\rho_{red})_{m'm}} + e^{-i\omega_{m'm}t}(\dot{\rho}_{red\,I})_{m'm} \qquad (2.34b)$$

It follows

$$\boxed{\begin{aligned}\langle m'|\dot{\hat{\rho}}_{red}|m\rangle &= -i\omega_{m'm}\langle m'|\hat{\rho}_{red}|m\rangle + \\ &+ \sum_{nn'}\langle n'|\hat{\rho}_{red}|n\rangle R_{m'mn'n}\end{aligned}} \qquad (2.35)$$

or, in operatorial terms (cfr. Eq. 2.27b)

$$\boxed{\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] + \mathcal{L}\hat{\rho}_{red}} \qquad (2.36)$$

The eq. of motion for the RDM in the Schrödinger picture is made up of two contributions, a unitary part and the one $\mathcal{L}\hat{\rho}_{red}$ describing irreversible processes.

2.3.5. Bloch-Redfield (or Wangsness-Bloch-Redfield) equations

The Markovian master eq. yields the so called WBR equations when the superoperator kernel is evaluated up to 2nd order.
These are a set of coupled differential eq. for the elements of the RDM evaluated in the basis which diagonalizes $\hat{H}_S$.

In other words, starting point is the MME (for simplicity we assume $\hat{H}_S$ to be time-independent)

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{1}{\hbar^2}\int_0^\infty dt'' \sum_{ij} \Big\{ \big[\hat{Q}_i(t), \hat{Q}_j(t-t'')\hat{\rho}_{red,I}(t)\big] \langle \hat{F}_i(t'')\hat{F}_j\rangle_B$$

$$- \big[\hat{Q}_i(t), \hat{\rho}_{red,I}(t)\hat{Q}_j(t-t'')\big]\langle \hat{F}_j \hat{F}_i(t'')\rangle_B \Big\} \qquad (2.28)$$

We now introduce the eigenstates $|m\rangle$ of $\hat{H}_S$ of energy E_m. It holds:

$$\langle m|\hat{Q}_i(t)|n\rangle = e^{i\omega_{mn}t}\langle m|\hat{Q}_i|n\rangle \qquad (2.29)$$

with $$\omega_{mn} = \frac{E_m - E_n}{\hbar} \qquad (2.30)$$

Introducing the tensors:

$$\Gamma^+_{mkln} = \frac{1}{\hbar^2}\sum_{ij}\langle m|\hat{Q}_i|k\rangle\langle l|\hat{Q}_j|n\rangle \int_0^\infty dt''\, e^{-i\omega_{ln}t''}\langle \hat{F}_i(t'')\hat{F}_j\rangle_B$$

$$\Gamma^-_{mkln} = \frac{1}{\hbar^2}\sum_{ij}\langle m|\hat{Q}_j|k\rangle\langle l|\hat{Q}_i|n\rangle \int_0^\infty dt''\, e^{-i\omega_{mk}t''}\langle \hat{F}_j\hat{F}_i(t'')\rangle_B$$

one obtains (2.31)

$$\langle m'|\dot{\hat{\rho}}_{red,I}|m\rangle = \sum_{nn'}\langle n'|\hat{\rho}_{red,I}(t)|n\rangle\, e^{i(\omega_{m'n'}-\omega_{mn})t}$$

$$\underbrace{\Big\{ -\sum_k \delta_{mn}\Gamma^+_{m'kkn'} + \Gamma^+_{nmm'n'} + \Gamma^-_{nmm'n'} - \sum_k \delta_{n'm'}\Gamma^-_{nkkm}\Big\}}_{\equiv R_{m'mn'n} \text{ Redfield tensor}} \qquad (2.32)$$

Proof of (2.32) starting from (2.28)

$$\dot{\rho}_{red,I}(t) = -\frac{1}{\hbar^2}\int_0^\infty dt'' \sum_{ij} \Big\{ \big[\hat{Q}_i(t), \hat{Q}_j(t-t'')\,\hat{\rho}_{red,I}(t)\big] \langle \hat{F}_i(t'')\hat{F}_j\rangle_B$$
$$- \big[\hat{Q}_i(t), \hat{\rho}_{red,I}(t)\,\hat{Q}_j(t-t'')\big]\langle \hat{F}_j\,\hat{F}_i(t'')\rangle_B \Big\}$$

We project on the system eigenstates:

$$(\dot{\rho}_{red,I})_{m'm} = -\frac{1}{\hbar^2}\int_0^\infty dt'' \sum_{ij}\sum_{kl} \Big\{ \big[\langle m'|\hat{Q}_i(t)|k\rangle\langle k|\hat{Q}_j(t-t'')|l\rangle\langle l|\hat{\rho}_{red,I}|m\rangle$$
$$- \langle m'|\hat{Q}_j(t-t')|k\rangle\langle k|\hat{\rho}_{red,I}|l\rangle\langle l|\hat{Q}_i(t)|m\rangle\big]\langle F_i(t'')\hat{F}_j\rangle_B$$
$$- \big[\langle m'|\hat{Q}_i(t)|k\rangle\langle k|\hat{\rho}_{red,I}|l\rangle\langle l|\hat{Q}_j(t-t'')|m\rangle$$
$$- \langle m'|\hat{\rho}_{red,I}|k\rangle\langle k|\hat{Q}_j(t-t'')|l\rangle\langle l|\hat{Q}_i(t)|m\rangle\big]\langle \hat{F}_j\,\hat{F}_i(t'')\rangle_B \Big\}$$

$$= -\frac{1}{\hbar^2}\int_0^\infty dt'' \sum_{\substack{nn'\\ij}} \Big\{\Big[\sum_k \langle m'|\hat{Q}_i(t)|k\rangle\langle k|\hat{Q}_j(t-t'')|n'\rangle\langle n'|\hat{\rho}_{red,I}|n\rangle\,\delta_{nm}$$
$$- \langle m'|\hat{Q}_j(t-t'')|n'\rangle\langle n'|\hat{\rho}_{red,I}|n\rangle\langle n|\hat{Q}_i(t)|m\rangle\Big]\langle \hat{F}_i(t'')\hat{F}_j\rangle_B$$
$$- \big[\langle m'|\hat{Q}_i(t)|n'\rangle\langle n'|\rho_{red,I}|n\rangle\langle n|\hat{Q}_j(t-t'')|m\rangle$$
$$- \sum_k \delta_{n'm'}\langle n'|\rho_{red,I}|n\rangle\langle n|\hat{Q}_j(t-t'')|k\rangle\langle k|\hat{Q}_i(t)|m\rangle\big]\langle \hat{F}_j F_i(t'')\rangle_B$$

$$= -\frac{1}{\hbar^2}\int_0^\infty dt'' \sum_{\substack{nn'\\ij}} \Big\{\Big[\sum_k e^{i(\omega_{m'k}+\omega_{kn'})t}\langle m'|\hat{Q}_i|k\rangle\langle k|\hat{Q}_j|n'\rangle e^{-i\omega_{kn'}t''}\delta_{nm}$$
$$- e^{i(\omega_{m'n'}-\omega_{mn})t}\langle m'|\hat{Q}_j|n'\rangle\langle n|\hat{Q}_i|m\rangle e^{-i\omega_{m'n'}t''}\Big]\langle \hat{F}_i(t'')F_j\rangle_B$$
$$- \Big[e^{i(\omega_{m'n'}-\omega_{mn})t}\langle m'|\hat{Q}_i|n'\rangle\langle n|\hat{Q}_j|m\rangle e^{-i\omega_{nm}t''}$$
$$- \sum_k \delta_{n'm'}\,e^{i(\omega_{nk}-\omega_{mk})t}\langle n|\hat{Q}_j|k\rangle\langle k|\hat{Q}_i|m\rangle e^{-i\omega_{nk}t''}\Big]\langle \hat{F}_j\hat{F}_i(t'')\rangle_B$$
$$(\rho_{red,I})_{n'n}$$

but

$$* \quad e^{i(\omega_{m'k} + \omega_{kn'})t} \delta_{nm} = e^{i(\omega_{m'n'} - \omega_{mn})t} \delta_{mn}$$

$$* \quad e^{i(\omega_{nk} - \omega_{mk})t} \delta_{n'm'} = e^{i(\omega_{m'n'} - \omega_{mn})t} \delta_{m'n'}$$

Now we can identify the two types of rates (2.31) Γ^+ associated to $\langle \hat{F}_i(t'') F_j \rangle$ and Γ^- associated to $\langle \hat{F}_j F_i(t'') \rangle_B$ and obtain (2.32).