Eq. (2.34) can be recast in the form:

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t dt' \, K_I^{(2)}(t,t') \, \hat{\rho}_{red,I}(t') + O(\hat{V}^3) \qquad (2.35)$$

where $K_I^{(2)}(t,t')$ is a superoperator acting on the reduced density operator $\hat{\rho}_{red,I}$. The superscript (2) indicates that only contributions up to 2nd order in $\hat{V}$ are included. It is possible (see later the projection-operator formalism) to extend (2.35) to all orders and obtain thus a $K_I(t,t')$ which is a power series in $\hat{V}$.

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^t dt' \, K_I(t,t') \, \hat{\rho}_{red,I}(t') \qquad (2.36)$$

Both (2.35) and (2.36) are called generalized master equations (GME) and $K_I(t,t')$ is the propagation Kernel in interaction picture, which can be perturbatively calculated to the desired order.

2.3.3 Convolutive form of the Kernel

It is important to notice that, if we transform (2.35) into the Schrödinger picture, and we assume $\hat{H}$ not explicitly time dependent, we can write:

$$\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}\left[\hat{H}_S, \hat{\rho}_{red}\right] + \int_0^t dt' \, K^{(2)}(t-t') \, \hat{\rho}_{red}(t') \qquad (2.37)$$

i.e the Kernel of the evolution in the Sch. picture has a convolutive form. Once again the result is also valid to all orders (see later).

proof of (2.37)

We start from (2.34) truncated to 2nd order in $\hat V$.

$$\dot{\rho}_{red,I}(t) = -\frac{1}{\hbar^2}\int_0^t dt' \Big\{ \big[\hat Q_i(t), \hat Q_j(t')\hat\rho_{red,I}(t')\big] F^{(B)}_{ij}(t-t') - \big[\hat Q_i(t), \hat\rho_{red,I}(t')\hat Q_j(t')\big] F^{(B)}_{ji}(t'-t) \Big\}$$

where $F^{(B)}_{ij}(\tau) = Tr_B\{\hat F_i(\tau)\hat F_j(0)\hat\rho_B\}$. We further observe that

$$\frac{\partial}{\partial t}\hat\rho_{red,I}(t) = \frac{\partial}{\partial t}\big[U_s^+(t)\hat\rho_{red}\hat U_s(t)\big] = \frac{i}{\hbar}\big[\hat U_s^+(t)\hat H_s\hat\rho_{red}\hat U_s(t) - \hat U_s^+(t)\hat\rho_{red}\hat H_s\hat U_s(t)\big] + \hat U_s^+(t)\Big(\frac{\partial}{\partial t}\hat\rho_{red}\Big)\hat U_s(t) = \hat U_s^+\frac{i}{\hbar}\big[\hat H_s,\hat\rho_{red}\big]\hat U_s + \hat U_s^+\dot{\hat\rho}_{red}\hat U_s$$

$\Rightarrow$ it follows
$$\dot{\hat\rho}_{red} = -\frac{i}{\hbar}\big[\hat H_s,\hat\rho_{red}\big] + \hat U_s(t)\,\dot{\hat\rho}_{red,I}\,\hat U_s^+(t) \qquad (2.38)$$

We can now analyze (2.34)

$$\hat\rho_{red,I}(t) = -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{\Big[U_s^+(t)\hat Q_i\hat U_s(t),\ \hat U_s^+(t')\hat Q_j\overbrace{\hat U_s(t')\hat U_s^+(t')}^{=1_s}\hat\rho_{red}^{(t)}\hat U_s(t')\Big] F^{(B)}_{ij}(t-t') - \Big[\hat U_s^+(t)\hat Q_i\hat U_s(t),\ \hat U_s^+(t')\hat\rho_{red}^{(t')}\underbrace{\hat U_s(t')\hat U_s^+(t')}_{=1_s}\hat Q_j\ \hat U_s(t')\Big] F^{(B)}_{ji}(t'-t)\Big\}$$

$$= -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{\Big[\hat U_s^+(t)\hat Q_i\hat U_s(t-t')\hat Q_j\hat\rho_{red}^{(t')}\hat U_s(t') - \hat U_s^+(t)\hat Q_j\hat\rho_{red}^{(t')}\hat U_s(t'-t)\hat Q_i\hat U_s^{(t)}\Big]F^{(B)}_{ij}(t-t - \Big[\hat U_s^+(t)\hat Q_i\hat U_s(t-t')\hat\rho_{red}^{(t')}\hat Q_j U_s(t') - \hat U_s^+(t')\hat\rho_{red}^{(t')}\hat Q_j\hat U_s(t'-t)\hat Q_i\hat U_s(t)\Big]F^{(B)}_{ji}(t'-t$$

And, combining all the observations above:

$$\dot{\hat\rho}_{red} = -\frac{i}{\hbar}\big[\hat H_s,\hat\rho_{red}\big] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{\Big[\hat Q_i\hat U_s(t-t')\hat Q_j\hat\rho_{red}^{(t')}\hat U_s(t'-t) - \hat U_s(t-t')\hat Q_j\hat\rho_{red}^{(t')}\hat U_s(t'-t)\hat Q_i\Big] F^{(B)}_{ij}(t-t') + - \Big[\hat Q_i U_s^+(t'-t)\hat\rho_{red}(t')\hat Q_j\hat U_s(t'-t) - \hat U_s^+(t'-t)\hat\rho_{red}(t')\hat Q_j\hat U_s(t'-t)\hat Q_i\Big] F^{(B)}_{ji}(t'-t)\Big\}$$

In a more compact form we can write:

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

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

$$-\left[\hat{Q}_i, \hat{U}_S^+(t'-t)\,\hat{\rho}_{red}(t')\,\hat{Q}_j U_S(t'-t)\right] F_{ji}^{(B)}(t'-t)\Big\} \qquad (2.39)$$

It is interesting to check the Hermiticity of the result:

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

Under the only fundamental condition $\hat{H} = \hat{H}^+$ which implies $\sum_i \hat{F}_i\hat{Q}_i = \sum_i \hat{Q}_i^+\hat{F}_i^+$.

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

ii) $\left\{\left[\hat{Q}_i, \hat{U}_S(t-t')\hat{Q}_j\,\hat{\rho}_{red}(t')\,\hat{U}_S^+(t-t')\right] F_{ij}^{(B)}(t-t')\right\}^+ =$

$$= -\left[\hat{Q}_i^+, U_S(t-t')\,\hat{\rho}_{red}(t')\,\hat{Q}_j^+\,U_S^+(t-t')\right] F_{ij}^{(B)*}(t-t') = (*)$$

But, if $F_{ij}^{(B)}(t-t') = \langle \hat{F}_i(t-t')\hat{F}_j\rangle_B \Rightarrow F_{ij}^{(B)*}(t-t') = \langle \hat{F}_j^+ F_i^+(t-t')$ $= \langle \hat{F}_j^+(t'-t)\hat{F}_i^+\rangle$ If we let recombine F_i^+ and Q_i^+ we reconstruct $\hat{V}$ and obtain [$\hat{U}_S(t) = \hat{U}_S^+(-t)$]

$$(*) = -\left[\hat{Q}_i, \hat{U}_S^+(t-t')\,\hat{\rho}_{red}(t')\,\hat{Q}_j\,\hat{U}_S(t'-t)\right] F_{ji}^{(B)}(t'-t)$$

$\Rightarrow$ in conclusion

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

(2.40)

Notice: $\hat{U}_s(t)\hat{U}_s^{+}(t') = \hat{U}_s(t,t')$, i.e. it is ALWAYS the propagator of the vector states in the Schrödinger picture from $t \to t'$.

But $\hat{U}_s(t,t') = \hat{U}_s(t-t')$ only if $\hat{H}_s$ is NOT explicitly time dependent.

$$U_s(t,t') \underset{\substack{\uparrow \\ \text{general}}}{=} T_{\leftarrow} \exp\left[-\frac{i}{\hbar}\int_t^{t'} dt''\, H_s(t'')\right] \underset{\substack{\uparrow \\ H_s \text{ indep} \\ \text{of time.}}}{=} e^{-i/\hbar (t-t')\hat{H}_s}$$

2.3.4 Markov approximation

Frequently the Markov approximation is performed on the GME. The latter simplifies the calculation of the time evolution of $\hat{\rho}_{red}$ at the price of losing the memory of the evolution kernel. Specifically, the Markov approximation relies on the observation that the correlation function vanishes for time intervals $t'-t \gg \tau$ where τ is the correlation time of the reservoir.

$$\langle \hat{F}_i(t)\hat{F}_j(t')\rangle \simeq \langle \hat{F}_i(t)\rangle\langle \hat{F}_j(t')\rangle = 0 \quad \text{if } t-t' \gg \tau \quad (2.41)$$

Eq. (2.41) expresses the concept that the reservoir considers as independent the excitations $\hat{F}_i$ and $\hat{F}_j$ induced by the coupling to the system if they occur at times t and t' separated much more than a characteristic time τ.

We can now compare τ with the characteristic time $1/\gamma$ (γ is a damping or decay rate) required for $\hat{\rho}_{red,I}$ to change appreciably. If it holds:

$$\tau \ll 1/\gamma \quad (2.42)$$

it follows that:

$$\hat{\rho}_{red,I}(t') \approx \hat{\rho}_{red,I}(t)$$

in Eq. (2.36) on the time scale on which the bath correlation function are NOT vanishing. Thus the Markov approximation:

$$\dot{\hat{\rho}}_{red}(t) = \int_0^t dt' \, K_I(t,t') \, \hat{\rho}_{red,I}(t) \tag{2.43}$$

The first observation is that (2.43) is not any more an integro-differential equation. One can further manipulate (2.34) under the same assumption on the bath correlation time τ.

Consider (2.34) and do the change of variables:

$$t - t' = t'' \Rightarrow dt' = -dt'' \Rightarrow \int_0^t dt' \rightarrow \int_0^t dt''$$

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

$$\int_0^t dt'' \sim \int_0^\infty dt'' \tag{2.44}$$

which yields the Markovian master equation (MME)

$$\dot{\hat{\rho}}_{red,I}(t) = \int_0^\infty dt \, K(t, t-t'') \, \hat{\rho}_{red,I}(t) \tag{2.45}$$

In other terms (2.45) can be written as:

$$\dot{\hat{\rho}}_{red,I}(t) = \mathcal{L}_I(t) \, \hat{\rho}_{red,I}(t) \tag{2.45b}$$

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

<u>Notice</u>: by transforming (2.45) back to the Schr. picture one appreciates that the Markov approximation breaks the convolutive form of the propagating Kernel: