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

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

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 $2^{nd}$ order in $\hat{V}$.

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

where $F_{ij}^{(B)}(\tau) = \mathrm{Tr}_B\{\hat{F}_i(\tau)\hat{F}_j(0)\hat{\rho}_B\}$. We further observe that

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

$$\Rightarrow \text{ it follows } \quad \dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] + \hat{U}_s(t)\,\dot{\hat{\rho}}_{red,I}\,\hat{U}_s^+(t) \qquad (2.38)$$

We can now analyze (2.34)

$$\hat{\rho}_{red,I}(t) = -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \Big\{ [U_s^+(t)\hat{Q}_i\hat{U}_s(t), \hat{U}_s^+(t')\hat{Q}_j\overbrace{\hat{U}_s(t')\hat{U}_s^+(t')}^{=\mathbb{1}_s}\hat{\rho}_{red}^{(t)}\hat{U}_s(t')]\, F_{ij}^{(B)}(t-t')$$
$$- [\hat{U}_s^+(t)\hat{Q}_i\hat{U}_s(t), \hat{U}_s^+(t')\hat{\rho}_{red}^{(t')}\underbrace{\hat{U}_s(t')\hat{U}_s^+(t')}_{=\mathbb{1}_s}\hat{Q}_j\hat{U}_s(t')]\, F_{ji}^{(B)}(t'-t)\Big\}$$

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

And, combining all the observation above:

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

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

In a more compact form we can write:

$$\dot{\hat{\rho}}_{red}(t) = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}(t)] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt'$$
$$\{[\hat{Q}_i, \hat{U}_s(t-t')\hat{Q}_j\,\hat{\rho}_{red}(t')\,\hat{U}_s^+(t-t')]\,F_{ij}^{(B)}(t-t')$$
$$-[\hat{Q}_i, \hat{U}_s^+(t'-t)\,\hat{\rho}_{red}(t')\,\hat{Q}_j U_s(t'-t)]\,F_{ji}^{(B)}(t'-t)\} \qquad (2.39)$$

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 $\sum_i \hat{F}_i\hat{Q}_i = \sum_i \hat{Q}_i^+\hat{F}_i^+$, for the interaction component of the Hamiltonian.

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

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

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 [ $\hat{U}_s(t) = \hat{U}_s^+(-t)$ ]

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

$\Rightarrow$ in conclusion

$$\dot{\hat{\rho}}_{red}(t) = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}(t)] - \frac{1}{\hbar^2}\sum_{ij}\int_0^t dt'\,\{[\hat{Q}_i, \hat{U}_s(t-t')\hat{Q}_j\,\hat{\rho}_{red}(t')\,\hat{U}_s^+(t-t')]\,F_{ij}^{(B)}(t-t') + h.c.\} \qquad (2.40)$$

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.

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

## 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 loosing 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 $\tau$ is the correlation time of the reservoir.

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

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 $\tau$.

We can now compare $\tau$ with the characteristic time $1/\gamma$ ($\gamma$ 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 $\tau$.

Consider (2.34) and do the change of variables:

$$t - t' = t'' \Rightarrow \quad dt' = -dt'' \Rightarrow \int_0^t dt' \longrightarrow -\int_t^0 dt'' = \int_0^t dt''$$

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)

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

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.

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

## 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)

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

$$- [\hat{Q}_i(t), \hat{\rho}_{red,I}(t)\hat{Q}_j(t-t'')] \langle \hat{F}_j \hat{F}_i(t'')\rangle_B \Big\} \quad (2.46)$$

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

$$\langle m|\hat{Q}_i(t)|n\rangle = e^{i\omega_{mn}t}\langle m|\hat{Q}_i|n\rangle \quad (2.47)$$

with $$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (2.48)$$

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 (2.49)

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

$$\underbrace{\Big\{-\sum_k \delta_{mn}\Gamma^+_{m'kkn'} + \Gamma^+_{nmm'n'} + \Gamma^-_{nmm'n'} - \sum_k \delta_{n'm'}\Gamma^-_{nkkm}\Big\}}_{\equiv R_{m'mn'n}\ \text{Redfield tensor: time independent!}} \quad (2.50)$$

Proof of (2.50) starting from (2.46)

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

We project on the system eigenstates:

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

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

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

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 (2.51) $\Gamma^{+}$ associated to $\langle \hat{F}_i(t'') F_j \rangle$ and $\Gamma^{-}$ associated to $\langle \hat{F}_j F_i(t'') \rangle_B$ and obtain (2.50).

In other words, it holds

$$\langle m'|\dot{\hat{\rho}}_{red,I}|m\rangle = \sum_{nn'} \langle n'|\hat{\rho}_{red,I}(t)|n\rangle\, e^{i(\omega_{m'n'}-\omega_{mn})t}\, R_{m'mn'n} \qquad (2.52)$$

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

$$\dot{\rho}^{I}_{m'm} = R_{m'mm'm}\,\rho^{I}_{m'm} + \sum_{\substack{n\neq m \\ \text{or} \\ n'\neq m'}} e^{i(\omega_{m'n'}-\omega_{mn})t} R_{m'mn'n}\,\rho^{I}_{n'n} \qquad (2.53)$$

or, alternatively

$$\dot{\rho}^{I}_{m'm} = \sum_{nn'} e^{i(\omega_{m'm}-\omega_{n'n})t} R_{m'mn'n}\,\rho^{I}_{n'n} \qquad (2.53b)$$

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

$$(\rho_{red})_{m'm} = e^{-i\omega_{m'm}t}(\rho_{red\,I})_{m'm} \qquad (2.54a)$$

$$(\dot{\rho}_{red})_{m'm} = \underbrace{-i\omega_{m'm}e^{-i\omega_{m'm}t}(\rho_{red,I})_{m'm}}_{(\rho_{red})_{m'm}} + e^{-i\omega_{m'm}t}(\dot{\rho}_{red\,I})_{m'm} \qquad (2.54b)$$

It follows

$$\boxed{\langle m'|\dot{\hat{\rho}}_{red}|m\rangle = -i\omega_{m'm}\langle m'|\hat{\rho}_{red}|m\rangle + \sum_{nn'}\langle n'|\hat{\rho}_{red}|n\rangle R_{m'mn'n}} \qquad (2.55)$$

or, in operatorial terms (cfr. Eq. 2.36)

$$\boxed{\dot{\hat{\rho}}_{red} = -\frac{i}{\hbar}[\hat{H}_s, \hat{\rho}_{red}] + \mathcal{L}\hat{\rho}_{red}} \qquad (2.56)$$

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.

## 2.3.6 Rotating wave approximation

Inspection of (2.536) suggests a further approximation, based on the observation that contributions which are <u>slowly oscillating</u> dominate the equation of motion. These so called <u>secular terms</u> satisfy the condition

$$\omega_{m'n'} - \omega_{mn} \cong 0 \quad \Leftrightarrow \quad \omega_{m'm} - \omega_{n'n} \cong 0 \qquad (2.57)$$

In principle one could retain terms $|\omega_{m'n'} - \omega_{mn}| \ll \max_{nmkl} \| R_{nmkl} \|$ since the oscillation frequency should be compared to the rate of change of $\rho_{red,I}$.

We can now distinguish 2 cases:

(I) <u>Non-degenerate levels</u>:

For a generic non-degenerated spectrum we always fulfill the RWA condition (2.57) if

$$m = m' \text{ and } n = n' \quad \text{or} \quad m = n \text{ and } m' = n' \qquad (2.58)$$

and obtain the equation

$$\boxed{(\dot{\rho}_{red,I})_{m'm} = R_{m'm\,m'm} (\rho_{red,I})_{m'm} + \delta_{m'm} \sum_{n \neq m} R_{mm\,nn} (\rho_{red,I})_{nn}} \qquad (2.59)$$

leading to the conclusion that populations and coherences have decoupled dynamics for systems without degeneracies. The condition $\omega_{m'm} = \omega_{n'n}$ can also be obtained for $m' \neq m$ and $n' \neq n$ and $m \neq n$.

One should rather write

$$\left(\dot{\rho}_{red,I}\right)_{m'm} = \sum_{n' \neq n} R_{m'mn'n}\, \delta(\omega_{m'm} - \omega_{n'n}) \left(\rho_{red,I}\right)_{n'n} + \delta_{m'm} R_{mmnn} \left(\rho_{red,I}\right)_{nn} \qquad (2.59b)$$

which still confirms the decoupled dynamics of population and coherences.

## II) Degenerate levels

Besides for the condition (2.58) one finds that (2.57) is verified also for

$$E_{M'} = E_{M} \quad \text{and} \quad E_{N'} = E_{N} \quad \text{but} \quad m' \neq m \quad \text{or} \quad n' \neq n$$

For example let us assume $\bar{m}$ and $\bar{m}'$ : $E_{\bar{m}'} = E_{\bar{m}}$ but $\bar{m}' \neq \bar{m}$

On the other hand $\forall\, n, n' \neq \bar{m}$ and $\bar{m}'$ $E_n = E_{n'} \Leftrightarrow n = n'$

$$(RWA)\quad \left(\dot{\rho}_{red,I}\right)_{\bar{m}'\bar{m}} = R_{\bar{m}'\bar{m}\bar{m}'\bar{m}} \left(\rho_{red,I}\right)_{\bar{m}'\bar{m}} + \tag{2.60}$$

$$+ R_{\bar{m}'\bar{m}\bar{m}\bar{m}'} \left(\rho_{red,I}\right)_{\bar{m}\bar{m}'} + \sum_{\substack{n \neq m \\ \text{or} \\ n \neq m'}} R_{\bar{m}'\bar{m}nn} \left(\rho_{red,I}\right)_{nn} .$$

An alternative, *perhaps more intuitive*, way of dealing with the (RWA) starts from the analysis of the MME in Schrödinger picture Eq. (2.55)

$$\left(\dot{\rho}_{red}\right)_{m'm} = -i\omega_{m'm} \left(\rho_{red}\right)_{m'm} + \sum_{n'n} R_{m'mn'n} \left(\rho_{red}\right)_{n'n}$$

I) Non degenerate levels: i.e. $\omega_{m'm} \gg R_{m'mn'n}$ if $m' \neq m$.

$m' \neq m$ $\quad \left(\dot{\rho}_{red}\right)_{m'm} \cong -i\omega_{m'm} \left(\rho_{red}\right)_{m'm}$ $\rightarrow$ The equation for the coherences is easily solved

$$\left(\rho_{red}\right)_{m'm}(t) = \left(\overset{\circ}{\rho}_{red}\right)_{m'm} e^{-i\omega_{m'm} t} \tag{2.61}$$

$m' = m$

$$\left(\dot{\rho}_{red}\right)_{mm} = \sum_{n} R_{mmnn} \left(\rho_{red}\right)_{nn} + \sum_{n' \neq n} R_{mmn'n} \left(\overset{\circ}{\rho}_{red}\right)_{n'n} e^{-i\omega_{n'n} t}$$

$$(\dot{\rho}_{red})_{mm} = \sum_n R_{mmnn}(\rho_{red})_{nn} + \sum_{n'<n}\Big[R_{mmn'n}(\rho^0_{red})_{n'n}\, e^{-i\omega_{n'n}t}$$

$$+ R_{mmnn'}(\rho^0_{red})_{nn'}\, e^{-i\omega_{nn'}t}\Big] \qquad (2.62)$$

$$R_{mmn'n} = \Big\{ -\sum_k \delta_{mn}\Gamma^+_{mkkn'} + \Gamma^+_{nmmn'} + \Gamma^-_{nmmn'} - \sum_k \delta_{n'm}\Gamma^-_{nkkm} \Big\}$$

$$R_{mmnn'} = \Big\{ -\sum_k \delta_{mn'}\Gamma^+_{mkkn} + \Gamma^+_{n'mmn} + \Gamma^-_{n'mmn} - \sum_k \delta_{nm}\Gamma^-_{n'kkm} \Big\}$$

Since $\Gamma^+_{mkkn} = \Gamma^{-\,*}_{nkkm}$ $\Rightarrow$ $R_{mmnn'} = R_{mmn'n}^*$ and (2.62) becomes

$$(\dot{\rho}_{red})_{mm} = \sum_n R_{mmnn}(\rho_{red})_{nn} + \underbrace{2\sum_{n'<n} \mathrm{Re}\Big[R_{mmn'n}(\rho^0_{red})_{n'n}\, e^{-i\omega_{n'n}t}\Big]}_{}$$

strongly oscillating and can be omitted from the equations. It gives random "kicks" to $(\rho_{red})_{mm}$.

$\rightarrow$ populations and coherences have decoupled evolution.

II) <u>degenerate or quasi-degenerate levels</u>: $\exists\, m \neq m' : \omega_{m'm} \lesssim R_{m'mm'm}$.

The equation of motion for the coherences depends on $\omega$ and $R$. Moreover populations and coherences cannot be separated.

## 2.3.7 RWA in the non degenerate case: Pauli master equation

These are equations for the diagonal elements of the RDM.
(Pauli master eq. 1928) They are widely spread in physics.
From (2.50) it follows that, in the RWA for non-deg. systems (2.59)

$$(\dot{\hat{\rho}}_{red,I})_{m'm} = \delta_{m'm} \sum_{n\neq m} W_{mn} (\hat{\rho}_{red,I})_{nn} - \gamma_{m'm} (\hat{\rho}_{red,I})_{m',m} \quad (2.63)$$

with

$$W_{mn} = \Gamma^{+}_{nmmn} + \Gamma^{-}_{nmmn} \quad (2.64a)$$

$$\gamma_{m'm} = \sum_k (\Gamma^{+}_{m'kkm'} + \Gamma^{-}_{mkkm}) - \Gamma^{+}_{mmm'm'} - \Gamma^{-}_{mmm'm'} \quad (2.64b)$$

Notice that $W_{mn}$ is real and $\gamma_{m'm} = \gamma^*_{mm'}$.

The proof relies on the observation that:

$$(\Gamma^{-}_{mkln})^* = \Gamma^{+}_{nlkm}$$

In fact:

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

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

Using the relation $\sum_i \hat{Q}_i^+ \hat{F}_i^+ = \hat{V}^+ = \hat{V} = \sum_i \hat{Q}_i \hat{F}_i$ we can remove the dagger

$$= \frac{1}{\hbar^2} \sum_{ij} \langle n| Q_i|l\rangle\langle k|Q_j|m\rangle \int_0^\infty dt''\, e^{-i\omega_{km}t''} \langle \hat{F}_i(t'') F_j\rangle_B = \Gamma^{+}_{nlkm}.$$

Hence, it holds for $W$:

$$W^*_{mn} = \Gamma^{+*}_{nmmn} + \Gamma^{-*}_{nmmn} = \Gamma^{-}_{nmmn} + \Gamma^{+}_{nmmn} = W_{mn} \iff W_{mn} \in \mathbb{R}.$$

And, for $\gamma$

$$\gamma^*_{m'm} = \sum_k (\Gamma^{+*}_{m'kkm'} + \Gamma^{-*}_{mkkm}) - \Gamma^{+*}_{mmm'm'} - \Gamma^{-*}_{mmm'm'} = \sum_k (\Gamma^{-}_{m'kkm'} + \Gamma^{+}_{mkkm}) - \Gamma^{-}_{m'm'mm} - \Gamma^{+}_{m'm'mm}$$

$$= \gamma_{mm'}.$$

Back to the Schrödinger picture and introducing

$$\rho_{m'm}(t) := \langle m' | \hat{\rho}_{red}(t) | m \rangle \qquad (2.65)$$

one finds the MME in the RWA

$$\boxed{\dot{\rho}_{m'm} = -i\omega_{m'm}\,\rho_{m'm} + \delta_{m'm} \sum_{n \neq m} W_{mn}\,\rho_{nn} - \gamma_{m'm}\,\rho_{m'm}} \qquad (2.66)$$

In particular, the dynamics of the coherences is given by

$$\rho_{m'm}(t) = \rho_{m'm}(0)\, e^{-i(\omega_{m'm} + \mathrm{Im}\,\gamma_{m'm})t}\, e^{-\mathrm{Re}\,\gamma_{m'm} t} \qquad (2.67)$$

i.e. the coupling to the environment induces a frequency shift, called Lamb shift, given by $\mathrm{Im}\,\gamma_{m'm}$. Moreover, $\mathrm{Re}\,\gamma_{m'm}$ is called dephasing rate. It sets the time scale for the loss of quantum coherence due to the interaction with the bath. Notice that $\mathrm{Re}\,\gamma_{m'm} \geq 0$ or the positivity of $\rho$ would be lost at some point.
The dynamics of the populations is governed by rate equations

$$\dot{\rho}_{mm} = \sum_{n \neq m} W_{mn}\,\rho_{nn} - \gamma_{mm}\,\rho_{mm} \qquad (2.68)$$

From (2.64) it follows $\gamma_{mm} = \sum_{k \neq m} (\Gamma^{+}_{mkkm} + \Gamma^{-}_{mkkm})$ and hence

$$\boxed{\dot{\rho}_{mm} = \sum_{n \neq m} W_{mn}\,\rho_{nn} - \Big(\sum_{n \neq m} W_{nm}\Big)\rho_{mm}} \qquad (2.69)$$

The physical meaning of (2.69) is that the rate of change of the populations is given by the general relation

$$\dot{\rho}_{mm} = \underline{\underline{\text{gain}}} \text{ in } |m\rangle\langle m| - \underline{\underline{\text{loss}}} \text{ from } |m\rangle\langle m| \qquad (2.70)$$

Hence the parameters $W_{mn}$ are interpreted as <u>probabilities per unit time</u> that a transition $|m\rangle \to |n\rangle$ can be induced by an interaction with the reservoir. This eq. plays a crucial role in statistical physics, chemistry and biology. (see e.g. Haken, Synergetics, Springer, Berlin (1978)). We shall discuss important applications in quantum transport.

Now, we want to have a closer look to the <u>transition rates</u>

$$W_{mn} = \Gamma^{+}_{nmmn} + \Gamma^{-}_{nmmn}.$$

Let us consider (from (2.49))

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

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

and, in particular, their integral part: (for $\Gamma^+$)

$$\int_0^\infty dt''\, e^{-i\omega_{mn}t''}\langle \hat{F}_i(t'')\hat{F}_j\rangle_B = \int_0^\infty dt''\, e^{-i\omega_{mn}t''}\,\mathrm{Tr}_B\{\hat{F}_i(t'')\hat{F}_j\,\rho_B\}$$

$$= \sum_{N'N} \langle N'|\hat{F}_i|N\rangle\langle N|\hat{F}_j|N'\rangle\langle N'|\rho_B|N'\rangle \int_0^\infty dt''\, e^{i(E_{N'}-E_N-\hbar\omega_{mn})t''/\hbar} \qquad (2.71)$$

likewise for $\Gamma^-$

$$\int_0^\infty dt''\, e^{-i\omega_{nm}t''}\langle \hat{F}_j\hat{F}_i(t'')\rangle_B = \sum_{N'N}\langle N'|\hat{F}_j|N\rangle\langle N|\hat{F}_i|N'\rangle\langle N'|\rho_B|N'\rangle \int_0^\infty dt''\, e^{-i(E_{N'}-E_N-\hbar\omega_{mn})t''/\hbar} \qquad (2.71\,b)$$

We recall the form of the interaction Hamiltonian (230):

$$\hat{H}_{S-B} = \hat{V} = \sum_i \hat{Q}_i \hat{F}_i .$$

Hence

$$\sum_i \langle m|\hat{Q}_i|n\rangle \langle N'|\hat{F}_i|N\rangle = \langle mN'|\hat{V}|nN\rangle \qquad (2.72)$$

This yields

$$W_{mn} = \Gamma^{+}_{nmmn} + \Gamma^{-}_{nmmn} =$$

$$= \frac{1}{\hbar^2} \sum_{NN'} \langle nN'|\hat{V}|mN\rangle\langle mN|\hat{V}|nN'\rangle \rho_{B,NN'} \int_{-\infty}^{+\infty} dt'' \, e^{i(E_{N'} - E_N - \hbar\omega_{mn})t''/\hbar}$$

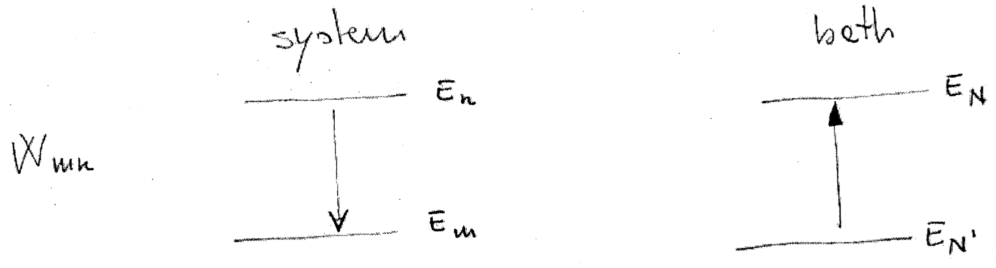
or

$$\boxed{W_{mn} = \frac{2\pi}{\hbar} \sum_{NN'} |\langle mN|\hat{V}|nN'\rangle|^2 \rho_{B,NN'} \, \delta(E_{N'} - E_N - \hbar\omega_{mn})} \qquad (2.73)$$

which resembles Fermi's golden rule expression for the transition probability per unit time.

Note: Because $\hat{V}$ is hermitian $\Rightarrow$ $|\langle mN|\hat{V}|nN'\rangle|^2 = |\langle nN'|\hat{V}|mN\rangle|^2$

This however does not imply $W_{mn} = W_{nm}$. The asymmetry comes from the statistical weight $\rho_{B,N'N'} = \frac{1}{Z} e^{-\beta E_{N'}}$. For clarity let us assume $E_m < E_n$ $\Rightarrow$ $\omega_{mn} < 0$ and the $\delta$ in (2.73) implies that relevant contributions to the rate $W_{mn}$ are given by bath states with $E_N > E_{N'}$




The total energy is conserved!

Mathematical parenthesis

$$\int_{-\infty}^{+\infty} dx\, e^{ikx} = \int_0^{\infty} dx\, e^{ikx} + \int_{-\infty}^{0} dx\, e^{ikx} =$$

$$= \int_0^{\infty} dx\, e^{ikx} + \int_0^{\infty} dx\, e^{-ikx} = 2\mathrm{Re} \int_0^{\infty} dx\, e^{ikx}$$

$$\int_0^{\infty} dx\, e^{ikx} = \lim_{\eta\to 0^+} \int_0^{\infty} dx\, e^{ix(k+i\eta)} = \lim_{\eta\to 0^+} \frac{1}{ik-\eta} e^{ikx-\eta x}\Big|_0^{\infty}$$

$$= \lim_{\eta\to 0^+} \frac{i}{k+i\eta}$$

$$2\,\mathrm{Re} \lim_{\eta\to 0^+} \frac{i}{k+i\eta} = \lim_{\eta\to 0^+} 2\,\mathrm{Re} \frac{i(k-i\eta)}{k^2+\eta^2} = \lim_{\eta\to 0^+} \frac{+2\eta}{k^2+\eta^2} = +2\pi\,\delta(k)$$

The last result stems from:

$$\int_{-\infty}^{+\infty} dk\, \frac{\eta}{k^2+\eta^2} \overset{x=\frac{k}{\eta}}{=} \int_{-\infty}^{+\infty} dx\, \frac{1}{1+x^2} = \operatorname{arctg} x \Big|_{-\infty}^{+\infty} = \pi \quad \forall\, \eta.$$

But $$\lim_{\eta\to 0^+} \frac{\eta}{k^2+\eta^2} = 0 \quad \forall\, k \neq 0.$$

More in detail. From (1.29)

$$\langle N'|\rho_B|N'\rangle = \frac{1}{Z_B}\, e^{-\beta E_{N'}}$$

$$\Rightarrow \quad W_{mn} = \frac{2\pi}{\hbar}\frac{1}{Z_B}\sum_{NN'} |\langle mN|\hat{V}|nN'\rangle|^2\, e^{-\beta E_{N'}}\, \delta(E_{N'}-E_N-\hbar\omega_{mn})$$

and

$$W_{nm} = \frac{2\pi}{\hbar}\frac{1}{Z_B}\sum_{NN'} |\langle nN'|\hat{V}|mN\rangle|^2\, e^{-\beta E_N}\, \delta(E_N-E_{N'}-\hbar\omega_{nm})$$

Using the symmetry of the matrix element and the energy conservation

$$E_N = E_{N'} + \hbar\omega_{nm}$$

$$W_{nm} = \frac{2\pi}{\hbar}\frac{1}{Z_B}\sum_{NN'} |\langle mN|\hat{V}|nN'\rangle|^2 e^{-\beta E_{N'}}\, \delta(E_{N'}-E_N-\hbar\omega_{mn})\; e^{-\beta\hbar\omega_{nm}}$$

and hence

$$\boxed{\frac{W_{mn}}{W_{nm}} = e^{-\beta(E_m-E_n)}} \qquad (2.74)$$

If $E_n > E_m$, the transition $|n\rangle \to |m\rangle$ is more probable than $|m\rangle \to |n\rangle$.

Example: two level system described by the states $|1\rangle$ and $|2\rangle$ with energies $E_1$ and $E_2$. From eqs. (2.69) and (2.74) we obtain:

$$\dot{\rho}_{11} = W_{12}\rho_{22} - W_{21}\rho_{11} = W_{21}\left[e^{-\beta(E_1-E_2)}\rho_{22} - \rho_{11}\right] = -\dot{\rho}_{22}$$

In equilibrium is $\dot{\rho}_{11} = \dot{\rho}_{22} = 0$ $\Rightarrow$ one gets the Boltzmann distribution

$$\boxed{\frac{\rho_{11}^{(\infty)}}{\rho_{22}^{(\infty)}} = \frac{e^{-\beta E_1}}{e^{-\beta E_2}}} \qquad (2.75)$$

Note: The result $W_{nm} \neq W_{mn}$ follows formally from the fact that the reservoir operators $\hat{F}_i, \hat{F}_j$ in general do not commute. In theories in which the reservoir is treated classically it follows

$$\Gamma^{\pm}_{nmmn} = \Gamma^{\pm}_{mnnm} \quad \text{and thus also} \quad W_{nm} = W_{mn}$$

## 2.4 Non perturbative methods

The approach considered so far is perturbative in the coupling to the bath. Instead our approach to evaluate $\hat{\rho}_{red} = \mathrm{Tr}_B\{\hat{\rho}\}$ was: first evaluate $\hat{\rho}(t)$ perturbatively in $\hat{H}_{S-B}$ and after perform the trace over the bath.

In a situation in which we do not want to perform an approximation on $\hat{H}_{S-B}$ one has first to calculate $\mathrm{Tr}_B$ and only afterwards to perform approximations. For linear baths (e.g. a bath of non-interacting harmonic oscillators) the trace operation can be performed exactly. In these cases a convenient starting point is Eq. (1.16)

$$\hat{\rho}(t) = \hat{U}(t)\hat{\rho}(0)U^+(t)$$

This approach, though, goes beyond the scope of the present lectures. We will, nevertheless study also master equations where the perturbation $H_{S-B}$ is considered to all orders. The method will be though a perturbative one.