2.3.6   Rotating wave approximation (RWA)

Inspection of (2.33b) suggests a further approximation, based on the observation that contributions which are _slowly oscillating_ dominate. These are called _secular terms_ satisfy

$$\omega_{m'n'} - \omega_{mn} \approx 0 \iff E_{m'} - E_{n'} - E_m + E_n \approx 0 \qquad (2.37)$$

whereby $\approx$ means that we do not have necessarily an exact zero but that $|\omega_{m'n'} - \omega_{mn}| < R_{m'm\,n'n}$ or R reflects the energy level spread $\Delta\omega$ induced by the coupling to the reservoir. One has to distinguish 2 cases:

I) __Non-degenerate levels__   It follows that

$$(m', m) \neq (n', n) \Rightarrow \omega_{m'n'} \neq 0 \text{ or } \omega_{mn} \neq 0$$

$\Rightarrow$ the oscillatory contribution can only vanish if $\omega_{m'n'} = \omega_{mn}$

$$\boxed{\text{i.e.,} \quad m' = m \text{ and } n' = n} \qquad (2.38)$$

$\Rightarrow$ (RWA):
$$\boxed{\left(\dot{\rho}_{red,I}\right)_{m'm} = \left(\rho_{red,I}\right)_{m'm} R_{m'm\,m'm} + \delta_{m'm} \sum_{n \neq m} \left(\rho_{red,I}\right)_{nn} R_{mm\,nn}} \qquad (2.39)$$

(2.39) leads to the conclusion that in the RWA populations and coherences are decoupled in the non-degenerate case.

II) Degenerate levels

Besides for the condition (2.38) one finds that (2.37) 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 $\bar{m}'$, $E_n = E_{n'} \iff n = n'$

$$\text{(RWA)} \quad \left(\dot{\rho}_{red,I} \right)_{\bar{m}'\bar{m}} = R_{\bar{m}'\bar{m}\bar{m}'\bar{m}} \left(\rho_{red,I} \right)_{\bar{m}'\bar{m}} + \tag{2.40}$$

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

An alternative, perhaps more intuitive, way of dealing with the (RWA) starts from the analysis of the MME in Schrödinger picture
Eq. (2.35)

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

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

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

$$\left(\rho_{red} \right)_{m'm}(t) = \left(\rho_{red}^{\circ} \right)_{m'm} e^{-i\omega_{m'm}t} \tag{2.41}$$

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

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

$$\left. + R_{mmnn'}\left(\rho_{red}\right)_{nn'}e^{-i\omega_{nn'}t}\right] \qquad (2.42)$$

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

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

Since $\quad \Gamma^+_{mkkn} = \Gamma^{-\,*}_{nkkn} \quad \Rightarrow \quad R_{mmnn'} = R_{mmn'n}^{\,*}\quad$ and (2.42)

becomes

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

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 & quasi-degenerate levels:</u> $\exists\, m \neq m' : \omega_{m'm} \lesssim R_{m'mn'n}$.

The equation of motion for the coherences depends on ω 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 (2.39) it follows that

$$\left(\dot{\hat{\rho}}_{red,I}\right)_{m'm} = \delta_{m'm} \sum_{n\neq m} W_{mn} \left(\hat{\rho}_{red,I}\right)_{nn} - \gamma_{m'm} \left(\hat{\rho}_{red,I}\right)_{m'm} \qquad (2.40)$$

with

$$W_{mn} = \Gamma^{+}_{nmmn} + \Gamma^{-}_{nmmn} \qquad (2.41)$$

$$\gamma_{m'm} = \sum_{k} \left(\Gamma^{+}_{m'kkm'} + \Gamma^{-}_{mkkm} \right) - \Gamma^{+}_{mmm'm'} - \Gamma^{-}_{mmm'm'} \qquad (2.42)$$

Notice that W_{mn} is real and $\gamma_{m'm} = \gamma^{*}_{mm'}$.
The proof relies on the observation that:

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

In fact:

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

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

Using the relation $\sum_i \hat{Q}_i^{+}\hat{F}_i^{+} = \hat{V}^{+} = \hat{V} = \sum_i \hat{Q}_i\cdot\hat{F}_i$ 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 γ

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

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

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Back to the Schrödinger picture and introducing

$$\rho_{mm'}(t) := \langle m'| \hat{\rho}_{red}(t)|m\rangle \qquad (2.43)$$

one finds the MME in the RWA

$$\boxed{\dot{\rho}_{m'm} = -i\omega_{m'm}\rho_{m'm} + \delta_{m'm}\sum_{n\neq m} W_{mn}\rho_{nn} - \gamma_{m'm}\rho_{m'm}} \qquad (2.44)$$

In particular, the dynamics of the underlined <u>coherences</u> is given by

$$\rho_{m'm}(t) = \rho_{m'm}(0)\; e^{-i(\omega_{m'm} + Im\,\gamma_{m'm})t}\; e^{-Re\,\gamma_{m'm}t} \qquad (2.45)$$

i.e. the coupling to the environment induces a <u>frequency shift</u>, called <u>Lamb shift</u>, given by $Im\,\gamma_{m'm}$. Moreover, $Re\,\gamma_{m'm}$ is called <u>dephasing rate</u>. It sets the time scale for the <u>loss of quantum coherence</u> due to the interaction with the bath.

The dynamics of the <u>populations</u> is governed by rate equations

$$\dot{\rho}_{mm} = \sum_{n\neq m} W_{mn}\rho_{nn} - \gamma_{mm}\rho_{mm} \qquad (2.46)$$

From (2.42) it follows $\gamma_{mm} = \sum_{k\neq m}\left(\Gamma^{+}_{mkkm} + \Gamma^{-}_{mkkm}\right)$ and hence

$$\boxed{\dot{\rho}_{mm} = \sum_{n\neq m} W_{mn}\rho_{nn} - \left(\sum_{n\neq m} W_{nm}\right)\rho_{mm}} \qquad (2.47)$$

The physical meaning of (2.47) is that the rate of change

of the populations is given by the general relation

$$\dot{\rho}_{mm} = \text{gain in } |m\rangle\langle m| - \text{loss from } |m\rangle\langle m| \qquad (2.48)$$

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 (2.31))

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

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

and, in particular, their integral part: (for Γ^+)

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

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

$$(2.49)$$

likewise for Γ^-

$$\int_0^\infty dt'' \, e^{-i\omega_{nm}t''} \langle \hat{F}_j \, \hat{F}_i(t'')\rangle_B = \sum_{N'N} \langle N'|\hat{F}_j|N\rangle\langle N|\hat{F}_i|N'\rangle\langle N'|\rho_B|N'\rangle$$

$$\int_0^\infty dt'' \, e^{-i(E_{N'}-E_N - \hbar\omega_{mn})t''/\hbar} \qquad (2.49b)$$

We recall the form of the interaction Hamiltonian (2.13):
$$\hat{H}_{S-B} = \hat{V} = \sum_i \hat{Q}_i \hat{F}_i.$$

Hence
$$\sum_i \langle m | \hat{Q}_i | n \rangle \langle N' | \hat{F}_i | N \rangle = \langle mN' | \hat{V} | nN \rangle \qquad (2.50)$$

This yields:
$$W_{mn} = \Pi^+_{nmmn} + \Pi^-_{nmmn} =$$

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

or

$$\boxed{ W_{mn} = \frac{2\pi}{\hbar} \sum_{NN'} |\langle mN | \hat{V} | nN' \rangle|^2 \, \rho_{B,NN'} \, \delta(E_{N'} - E_N - \hbar\omega_{mn}) } \qquad (2.51)$$

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 δ in (2.51) implies that relevant contributions to the rate W_{mn} are given by bath states with $E_N > E_{N'}$

W_{mn}
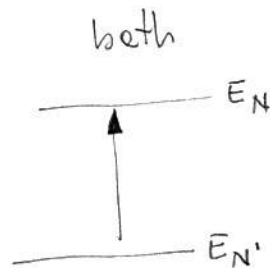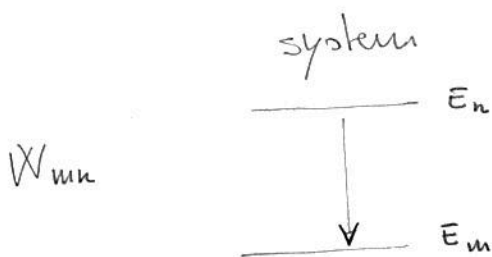
More in detail. From (1.29)

$$\langle N' | \rho_B | N' \rangle = \frac{1}{Z_B} e^{-\beta \bar{E}_{N'}}$$

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

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

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

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

and hence

$$\boxed{\frac{W_{mn}}{W_{nm}} = e^{-\beta(E_m - E_n)}} \qquad (2.52)$$

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. (2.47) and (2.52) 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

$$\boxed{\frac{\rho_{11}(\infty)}{\rho_{22}(\infty)} = \frac{e^{-\beta E_1}}{e^{-\beta E_2}}} \qquad (2.53)$$

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 also 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 $\hat{\rho}_{red} = \text{Tr}_B\{\hat{\rho}\}$ 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 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.