The system oscillates between the pure state $|\uparrow\rangle\langle\uparrow|$ and $|\downarrow\rangle\langle\downarrow|$ passing through the maximally incoherent state $\frac{1}{4}\left(|0\rangle\langle 0| + \sum_{\sigma} |\sigma\rangle\langle\sigma| + |2\rangle\langle 2|\right)$ for $\omega t = \frac{\pi}{2} + k\pi$.

Notice: the average particle number and the average energy of the level 1 remain constant $\langle N_1\rangle = 1$ and $\langle E_1\rangle = \varepsilon$. Their dispersion, though, fluctuates:

$$\sqrt{\langle \hat{N}^2\rangle - \langle \hat{N}\rangle^2} = \sqrt{\frac{1}{4}\left(2 + 2\cos^2\omega t + 4\sin^2\omega t\right) - 1} = \frac{|\sin(\omega t)|}{\sqrt{2}}$$

$$\langle \Delta E\rangle = \varepsilon \langle \Delta N\rangle = \varepsilon \frac{|\sin(\omega t)|}{\sqrt{2}}.$$

End of the example.

As we derived formally in (2.4) and (2.5), the information over the system Φ_1 is contained in $\hat{\rho}_{red}$. In the previous example we have explicitly calculated the dynamics of a reduced density matrix. In general

▲ $\boxed{\text{Which is the dynamics of } \hat{\rho}_{red}\text{ ?}}$

The dynamics of a QM system which is "closed", i.e. is isolated from the rest of the world, has an "Hamiltonian" character. In other words, its time evolution is determined by the SE or, in the density operator description, by the Liouville-von Neumann eq. => in particular a pure state remains pure and no mixtures are created.

Suppose now that $\Phi_1 \cup \Phi_2$, the combined system, is closed, but that Φ_2 is left unobserved. In this case Φ_1 is referred to as an open system.

The dynamics of open system is qualitatively different from that of closed ones, as, due to interaction with Φ_2, Φ_1 can be found in a mixed state even if before interaction it was prepared in a pure state. Hence:

The dynamics of an open system, and hence of $\hat{\rho}^{red}$, cannot be described by the Liouville-von Neumann eq.

Rather, from (2.4) and (1.17) it follows:

$$i\hbar \frac{\partial}{\partial t} \hat{\rho}^{red} = Tr_{\Phi_2}\{[\hat{H}, \hat{\rho}(t)]\} \qquad (2.16)$$

Note: The dynamics of the composite system is reversible as far as the initial state $\hat{\rho}(0)$ can be obtained mathematically from the formula:

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

where $U^+(t)$ is a unitary operator associated to the Hamiltonian $\hat{\hat{H}} = -\hat{H}$, thus a legitimate time evolution. In the case of an open system, if the unobserved component system is large (virtually an infinite number of degrees of freedom) the loss of coherence cannot be cured. On the small subsystem this is interpreted as irreversibility.

Example <u>Dynamics of an infinite chain</u>

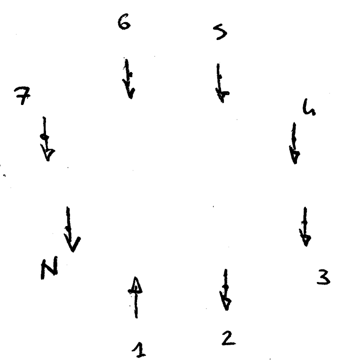
Consider a chain of N sites described by the Hamilton operator

$$\hat{H} = \sum_{\alpha\sigma} \varepsilon\, c^{+}_{\alpha\sigma} c_{\alpha\sigma} + b \sum_{\alpha} \left(c^{+}_{\alpha\sigma} c_{\alpha+1\sigma} + c^{+}_{\alpha+1\sigma} c_{\alpha\sigma} \right) \qquad (2.17)$$

with periodic boundary conditions $c^{+}_{N+1\sigma} := c^{+}_{1\sigma}$. As initial state of the system we consider the "factorized" configuration

$$|\uparrow\rangle \otimes |\downarrow \downarrow \ldots\ldots \downarrow\rangle$$

grafically represented by



Since the Hamiltonian conserves particle number and spin, the relevant Hilbert space in which we calculate the dynamics of the total density matrix is spanned by the N^2 states

$$|\alpha\beta\rangle = c^{+}_{\alpha\uparrow} c_{\beta\downarrow} \underbrace{\prod_{\gamma=1}^{N} c^{+}_{\gamma\downarrow} |\emptyset\rangle}_{|\Downarrow\rangle} \qquad (2.18)$$

Notice: if $\alpha = \beta = 1$ we obtain the initial state. If $\alpha = \beta \neq 1$ we obtain a state in which the spin in position α is flipped. If $\alpha \neq \beta$ the position β is empty, while the position α is doubly occupied.

Since the Hamiltonian (2.15) is invariant under rotation $\alpha \to \alpha+1$, it is convenient to construct states which are respecting this symmetry.

$$|l m\rangle = \frac{1}{N}\sum_{\alpha\beta} e^{i\frac{2\pi}{N}(\alpha l - \beta m)} |\alpha\beta\rangle \qquad l,m=0\ldots N-1 \quad (2.19)$$

The states $|lm\rangle$ are eigenstates of $\hat{H}$ in the Hilbert space which shares the same particle number and S_z of the initial condition. This statement follows from the consideration that:

i) $|\downarrow\downarrow\rangle$ is an eigenstate of $\hat{H}$ with eigenvalue $N\varepsilon$ since no hopping can take place due to the Pauli exclusion principle.

ii) $\hat{H}$ is diagonal in the l basis:

proof: $$c^+_{l\sigma} = \frac{1}{\sqrt{N}}\sum_{\alpha} e^{i\frac{2\pi}{N}\alpha l} c^+_{\alpha\sigma}$$

This relation can be easily inverted

$$c^+_{\alpha\sigma} \overset{\text{Ansatz}}{=} \frac{1}{\sqrt{N}}\sum_{l} e^{-i\frac{2\pi}{N}\alpha l} c^+_{l\sigma} \overset{\text{def of } c^+_l}{=} \frac{1}{N}\sum_{\beta l} e^{-i\frac{2\pi}{N}(\alpha-\beta)l} c^+_{\beta\sigma} =$$

$$= \underbrace{\sum_{\beta}\frac{1}{N}\sum_{l} e^{-i\frac{2\pi}{N}(\alpha-\beta)l}}_{\delta_{\alpha\beta}} c^+_{\beta\sigma} = c^+_{\alpha\sigma}.$$

$$\hat{H} = \sum_{\alpha\sigma} \varepsilon\, c^+_{\alpha\sigma} c_{\alpha\sigma} + b\sum_{\alpha}\left(c^+_{\alpha\sigma} c_{\alpha+1\sigma} + c^+_{\alpha+1\sigma} c_{\alpha\sigma}\right) =$$

$$= \sum_{lm\sigma} \underbrace{\frac{1}{N}\sum_{\alpha} e^{i\frac{2\pi}{N}\alpha(l-m)}}_{=\delta_{lm}} \left(\varepsilon + b e^{i\frac{2\pi}{N}m} + b e^{-i\frac{2\pi}{N}l}\right) c^+_{l\sigma} c_{m\sigma}$$

$$\hat{H} = \sum_{l\sigma}\left[\varepsilon + 2b\cos\left(\frac{2\pi}{N}l\right)\right] c^{+}_{l\sigma} c_{l\sigma} .$$

iii)
$$|lm\rangle = c^{+}_{l\uparrow} c_{m\downarrow} |\Downarrow\rangle$$

$$\Rightarrow \hat{H}|lm\rangle = \left(N\varepsilon + 2b\left[\cos\left(\frac{2\pi}{N}l\right) - \cos\left(\frac{2\pi}{N}m\right)\right]\right)|lm\rangle = \mathcal{E}_{l,m}|lm\rangle$$

Following the same relation written in (2.10) we obtain, for the time propagation of the factorized state:

$$|\alpha=1,\beta=1,t\rangle = \sum_{lm} \langle lm|\alpha=1,\beta=1\rangle\, e^{-\frac{i}{\hbar}\mathcal{E}_{l,m}t}\, |lm\rangle$$

$$\stackrel{(2.19)}{=} \frac{1}{N}\sum_{lm} e^{-i\frac{2\pi}{N}(l-m) - \frac{i}{\hbar}\mathcal{E}_{lm}t}\, |lm\rangle \qquad (2.20)$$

Consequently, we can write, for the total density matrix

$$\hat{\rho}_{tot} = \frac{1}{N^2}\sum_{lm}\sum_{l'm'} |lm\rangle\langle l'm'|\, e^{-i\frac{2\pi}{N}(l-m-l'+m') - \frac{i}{\hbar}(\mathcal{E}_{lm}-\mathcal{E}_{l'm'})t} \qquad (2.21)$$

In order to calculate the partial trace leading to the reduced density matrix associated to the position $\alpha=1$ it is useful to change basis and write:

$$\hat{\rho}_{tot} = \frac{1}{N^4}\sum_{lm}\sum_{l'm'}\sum_{\alpha\beta}\sum_{\alpha'\beta'} |\alpha\beta\rangle\langle\alpha'\beta'|\, e^{-i\frac{2\pi}{N}[l(1-\alpha)-m(1-\beta)-l'(1-\alpha')+m'(1-\beta')]} \cdot$$
$$\cdot\, e^{-\frac{i}{\hbar}(\mathcal{E}_{lm}-\mathcal{E}_{l'm'})t} \qquad (2.22)$$

The partial trace imposes $\alpha=\alpha'$ and $\beta=\beta'$. Moreover, it follows directly from (2.18) and consideration thereafter that:

i) $\alpha = 1$ $\beta = 1$ contributes to $|\uparrow\rangle\langle\uparrow| P_\uparrow$

ii) $\alpha = 1$ $\beta \neq 1$ contribute to $|2\rangle\langle 2| P_2$

iii) $\alpha \neq 1$ $\beta = 1$ " $|0\rangle\langle 0| P_0$

iv) $\alpha \neq 1$ $\beta \neq 1$ " $|\downarrow\rangle\langle\downarrow| P_\downarrow$

One obtains thus:

$$\hat{\rho}_{red} = |\uparrow\rangle\langle\uparrow| \frac{1}{N^4} \sum_{ll'}\sum_{mm'} e^{-i/\hbar (E_{lm} - E_{l'm'})t} +$$

$$+ |2\rangle\langle 2| \frac{1}{N^3} \sum_{ll'}\sum_{mm'} \Big(\underbrace{\frac{1}{N}\sum_\beta e^{-i\frac{2\pi}{N}[(m'-m)(1-\beta)]}}_{\delta_{mm'}} - \frac{1}{N} \Big) e^{-i/\hbar (E_{ll'} - E_{m'm})t} +$$

$$+ |0\rangle\langle 0| \frac{1}{N^3} \sum_{ll'}\sum_{mm'} \Big(\frac{1}{N}\sum_\alpha e^{-i\frac{2\pi}{N}[(l-l')(1-\alpha)]} - \frac{1}{N} \Big) e^{-i/\hbar (E_{ll'} - E_{m'm})t} +$$

$$+ |\downarrow\rangle\langle\downarrow| \frac{1}{N^2} \sum_{ll'}\sum_{mm'} \Big(\frac{1}{N}\sum_\alpha e^{-i\frac{2\pi}{N}[(l-l')(1-\alpha)]} - \frac{1}{N} \Big)\Big(\frac{1}{N}\sum_\beta e^{-i\frac{2\pi}{N}[(m'-m)(1-\beta)]} - \frac{1}{N} \Big) \cdot$$

$$\cdot e^{-i/\hbar (E_{ll'} - E_{m'm})t}$$

$$= |\uparrow\rangle\langle\uparrow| \left| \frac{1}{N}\sum_l e^{-i\omega t \cos(\frac{2\pi}{N}l)} \right|^4 +$$

$$+ \big(|2\rangle\langle 2| + |0\rangle\langle 0| \big) \left| \frac{1}{N}\sum_l e^{-i\omega t \cos(\frac{2\pi}{N}l)} \right|^2 \left(1 - \left| \frac{1}{N}\sum_l e^{-i\omega t \cos(\frac{2\pi}{N}l)} \right|^2 \right)$$

$$+ |\downarrow\rangle\langle\downarrow| \left(1 - \left| \frac{1}{N}\sum_l e^{-i\omega t \cos(\frac{2\pi}{N}l)} \right|^2 \right)^2 \qquad (2.23)$$

$$\omega = \frac{2b}{\hbar}$$

Notice that in the limit $N = 2 \Rightarrow l = 0, 1$ the formula above reproduces the result discussed at page 25.

We are here interested, though, into the limit $N \to \infty$. The (angular) momenta l become continuous variables with the usual procedure:

$$\frac{2\pi}{N} l = x \qquad \frac{1}{N}\sum_{l=0}^{N-1} \longrightarrow \frac{1}{2\pi}\int_0^{2\pi} dx$$

consequently we can write:

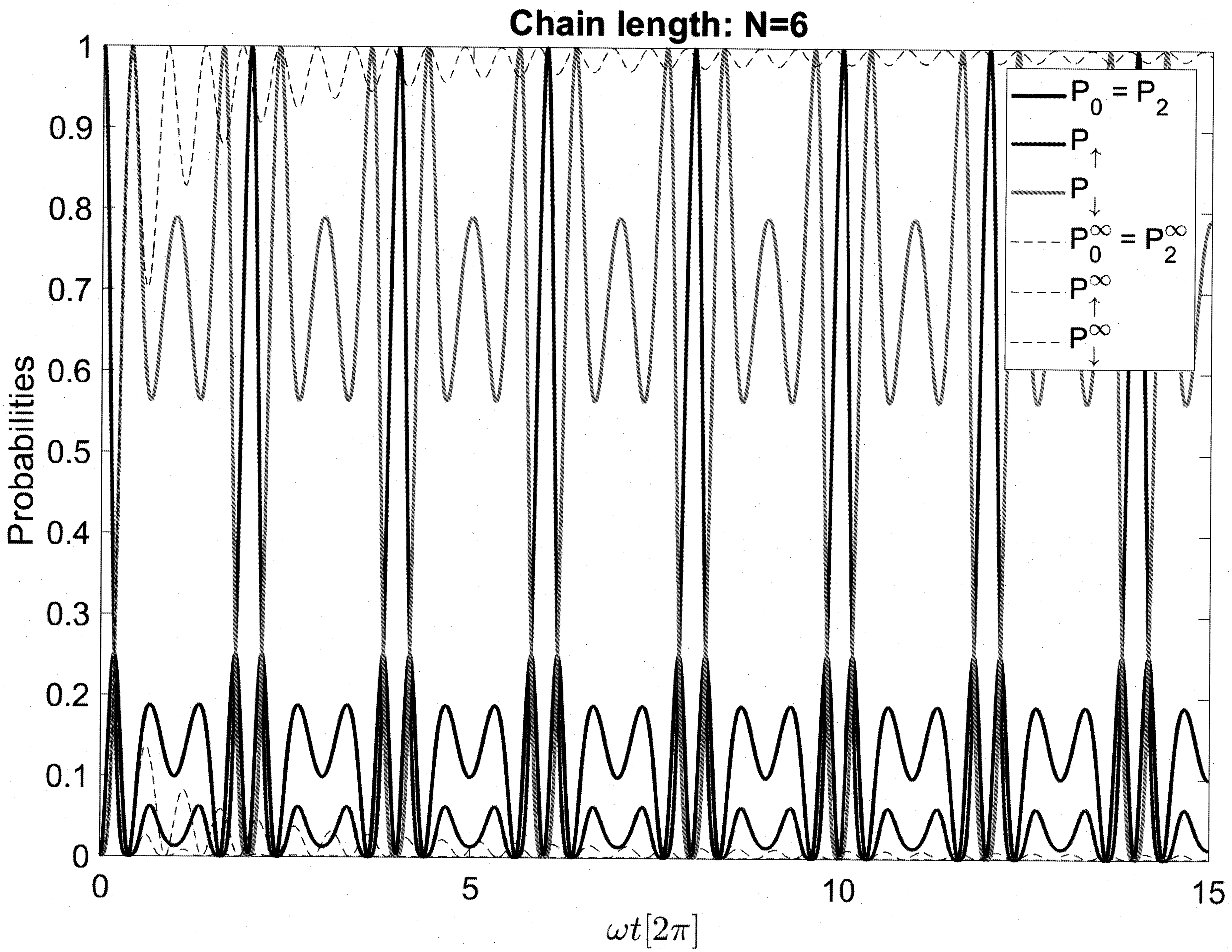
$$\lim_{N\to\infty} \frac{1}{N}\sum_{l} e^{-i\omega t \cos\left(\frac{2\pi}{N} l\right)} = \frac{1}{2\pi}\int_0^{2\pi} e^{-i\omega t \cos(x)}\, dx = J_0(\omega t)$$

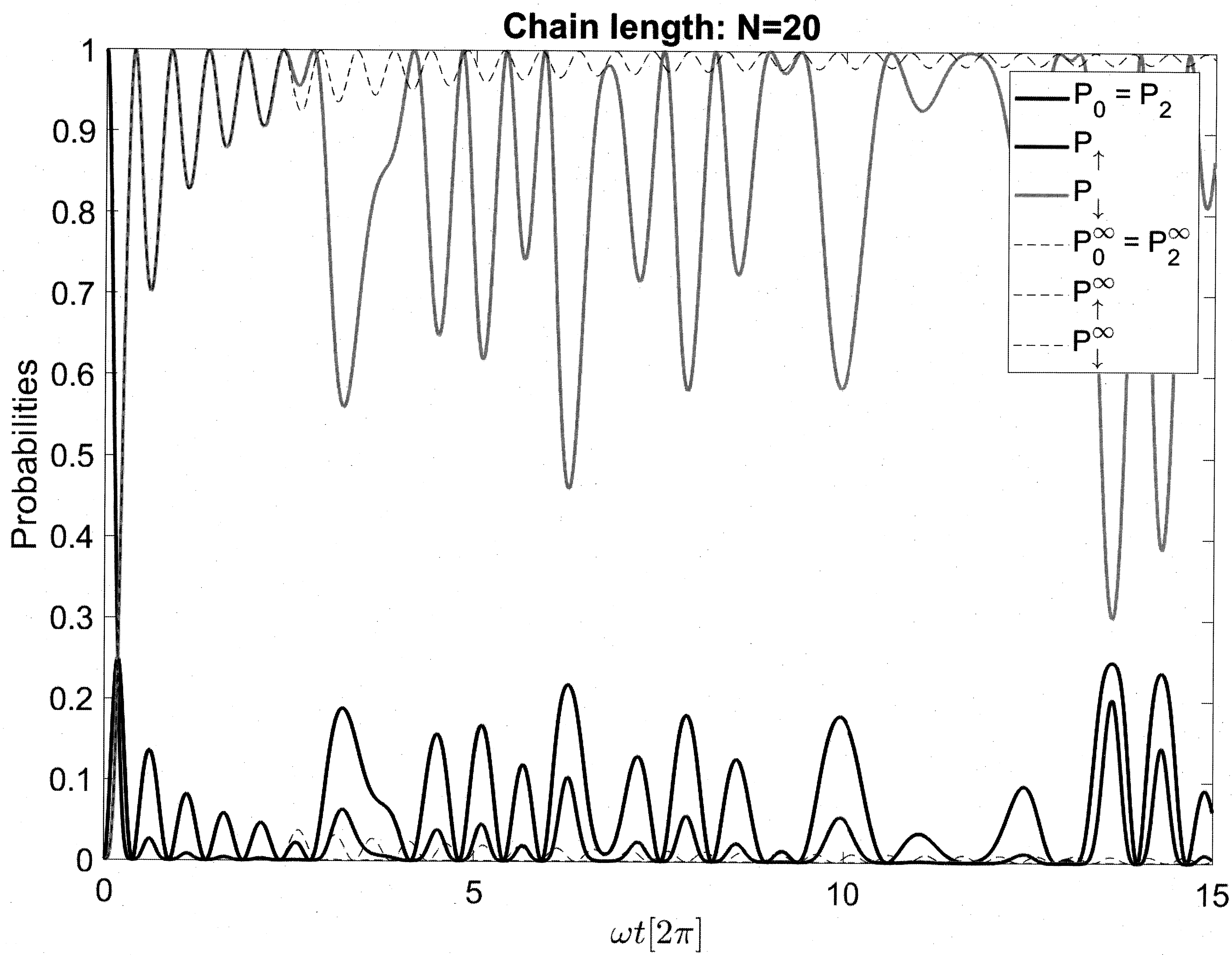
where $J_0(x)$ is the Bessel function.

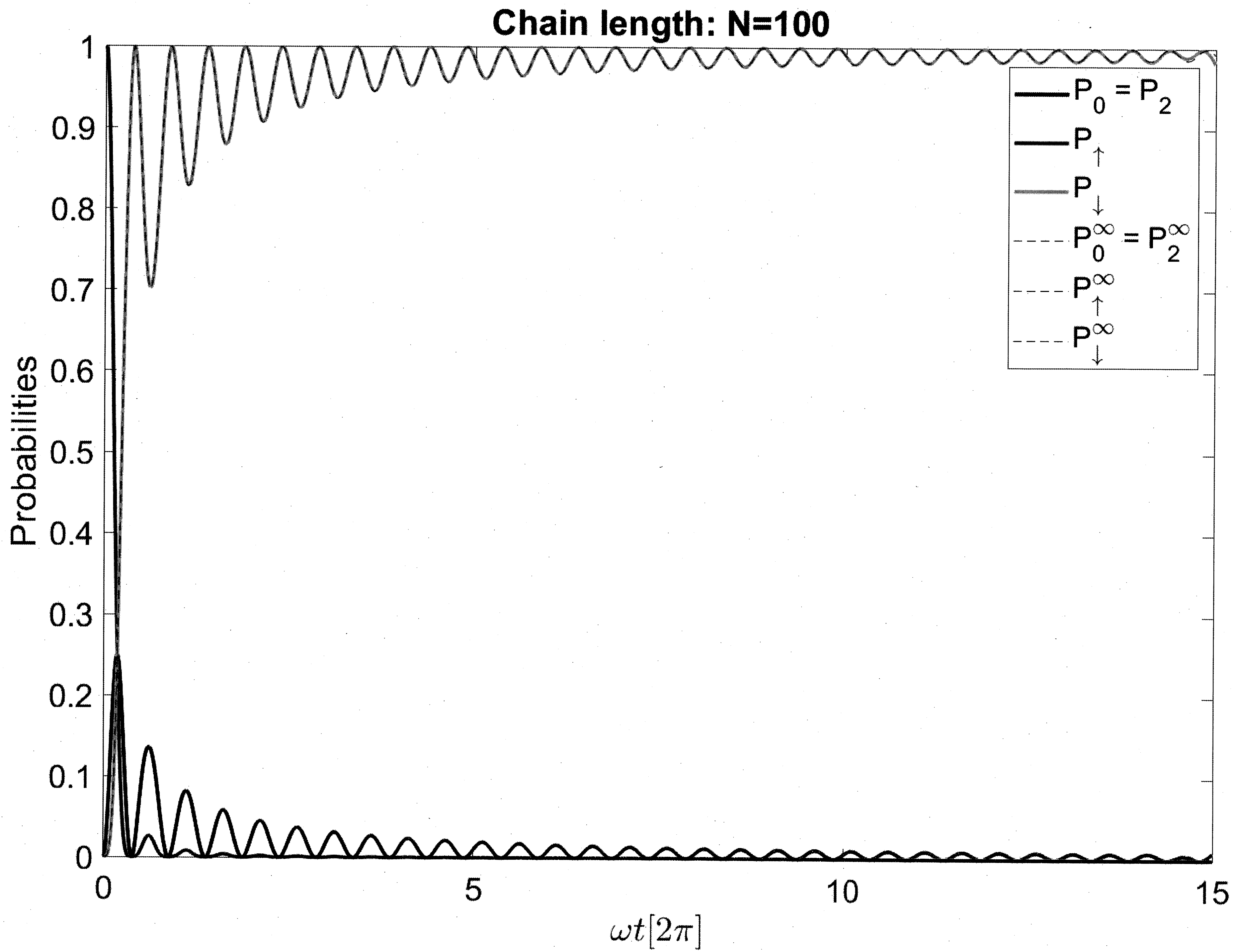
$$\hat{\rho}_{red}(t) = |\uparrow\rangle\langle\uparrow| \, |J_0(\omega t)|^4 + \left(|0\rangle\langle 0| + |2\rangle\langle 2|\right) |J_0(\omega t)|^2 \left(1 - |J_0(\omega t)|^2\right)$$
$$+ |\downarrow\rangle\langle\downarrow| \left(1 - |J_0(\omega t)|^2\right)^2 . \qquad (2.24)$$

Notice:

- As for the case $N=2$ in the dynamics of the reduced system mixed states emerge.
- The presence of a continuum spectrum in the "leads" introduces irreversibility into the reduced system which reaches a stationary limit, with no more revivals of pure states.
- The stationary limit has a clear physical meaning since the "impurity" at site 1 is tunnel coupled to a "reservoir" polarized $\downarrow$.


Chain length: N=6
Probabilities
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
$\omega t[2\pi]$
$P_0 = P_2$
$P_\uparrow$
$P_\downarrow$
$P_0^\infty = P_2^\infty$
$P_\uparrow^\infty$
$P_\downarrow^\infty$


Chain length: N=20
Probabilities
$\omega t[2\pi]$
$P_0 = P_2$
$P_\uparrow$
$P_\downarrow$
$P_0^\infty = P_2^\infty$
$P_\uparrow^\infty$
$P_\downarrow^\infty$
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
5
10
15



Chain length: N=100
Probabilities
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
5
10
15
$\omega t[2\pi]$
$P_0 = P_2$
$P_\uparrow$
$P_\downarrow$
$P_0^\infty = P_2^\infty$
$P_\uparrow^\infty$
$P_\downarrow^\infty$

2.3 Generalized master equation (GME) for the RDM

In the two examples just discussed, we have calculated explicitly the time evolution of the RDM for a closed isolated system. We have calculated

$$\hat{\rho}_{red}(t) \equiv Tr_B \{ \hat{\rho}_{tot}(t) \}.$$

The main results were: i) the appearance of mixed states within the time evolution, ii) the emergence of "irreversibility" in presence of an infinite unobserved subsystem. The systems considered here were, though, very idealized.

▲ Can we derive an equation of motion for $\hat{\rho}_{red}$ in a general context, whose solution is $\hat{\rho}_{red}(t)$?

2.3.1 System-bath model

The most generic framework for the derivation of a RDM is the one of a system-bath model: i.e.

$\Phi_1 \dashrightarrow$ S small subsystem characterized by $\hat{H}_S$ SYSTEM

$\Phi_2 \longrightarrow$ B large subsystem " " $\hat{H}_B$ BATH

The SYSTEM and the BATH interact via the Hamiltonian $\hat{V}$ which implies transfer of energy and/or particles between the two subsystems. The total Hamiltonian is given by

$$\hat{H} = \underbrace{\hat{H}_S + \hat{H}_B}_{=\hat{H}_0} + \hat{V} \qquad (2.25)$$

Notice: The BATH it is so large that it remains in thermal equilibrium despite the energy and/or particles exchanged with S through $\hat{V}$.

The Liouville-von Neumann equation for $\hat\rho_{tot}$ in interaction picture can be recast into the integro differential equation:

$$\dot{\hat\rho}_I(t) = -\frac{i}{\hbar}\left[\hat V_I(t), \hat\rho_I(0)\right] - \frac{1}{\hbar^2}\int_0^t dt' \left[\hat V_I(t), \left[\hat V_I(t'), \hat\rho_I(t')\right]\right] \quad (1.27)$$

which yields for the RDM, $\hat\rho_{red}(t) = Tr_B\,\hat\rho(t)$ in I-picture:

$$\dot{\hat\rho}_{I,red}(t) = -\frac{i}{\hbar} Tr_B\left\{\left[\hat V_I(t), \hat\rho_I(0)\right]\right\} - \frac{1}{\hbar^2}\int_0^t dt'\, Tr_B\left\{\left[\hat V_I(t), \left[\hat V_I(t'), \hat\rho_I(t')\right]\right]\right\} \quad (2.26)$$

Eq. (2.26) is still <u>not</u> a closed equation for $\hat\rho_{red,I}$. Two points should still be solved

$\boxed{A}$ $\quad \hat\rho_{I,red} = \hat\rho_{red,I} \quad (2.27)$

proof:

$$\hat\rho_{I,red}(t) = Tr_B\left\{U_0^+(t)\,\hat\rho_{tot}(t)U_0(t)\right\} = Tr_B\left\{U_B^+(t)\,U_S^+(t)\,\hat\rho_{tot}(t)\,U_S(t)\,U_B(t)\right\}$$

The last equality follows from the observation that $[H_S(t), H_B(t')] = 0 \;\; \forall\, t, t'$ even assuming explicitly time dependent Hamiltonians for the system and the bath.

$$U_S(t) = T_\leftarrow \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, H_S(t')\right] \qquad U_B(t) = T_\leftarrow \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, H_B(t')\right]$$

as follows from the condition $i\hbar\,\partial_t U_{S/B}(t) = H_{S/B}(t)\,U(t)$ and $U_{S/B}(0) = 1$.

$U_0(t)$ is defined instead by $i\hbar\,\partial_t U_0 = (H_S(t) + H_B(t))\,U_0(t)$ and $U_0(0) = 1$.

Suppose $\quad U_0(t) = U_S(t)\,U_B(t)$

$$i\hbar\,\partial_t\left[U_S(t)\,U_B(t)\right] = H_S(t)\,U_S(t)\,U_B(t) + \overline{U_S(t)\,H_B(t)}\,U_B(t) = \left(H_S(t) + H_B(t)\right)U_S(t)\,U_B(t).$$

Analogously it works for $U_B(t)U_S(t)$. Moreover $U_S(0)U_B(0) = 1$ as it follows from the initial conditions for U_S and U_B separately. But the propagator is unique => $U_S U_B$ $(= U_B U_S)$ makes the job.

$$\mathrm{Tr}_B\left\{ U_B^+(t)\, U_S^+(t)\, \hat{\rho}_{tot}(s)\, U_S(t) U_B(t) \right\} =$$

$$= \sum_{ijk} \langle \phi_k^{(B)} | U_B^+(t) | \phi_i^{(B)} \rangle \langle \phi_i^{(B)} | U_S^+(t)\, \hat{\rho}_{tot}(t)\, U_S(t) | \phi_j^{(B)} \rangle \langle \phi_j^{(B)} | U_B(t) | \phi_k^{(B)} \rangle$$

$$= \sum_{ij} \overbrace{\langle \phi_j^{(B)} | \underbrace{U_B(t) U_B^+(t)}_{1_B} | \phi_i^{(B)} \rangle}^{\delta_{ij}} \langle \phi_i^{(B)} | U_S^+(t)\, \hat{\rho}_{tot}(t)\, U_S(t) | \phi_j^{(B)} \rangle$$

$$= \sum_i U_S^+(t) \langle \phi_i^{(B)} | \hat{\rho}_{tot}(t) | \phi_i^{(B)} \rangle U_S(t) = \hat{\rho}_{red,I}$$

$\boxed{B}$ How does $\hat{\rho}_{red,I}$ appears on the RHS of (2.26) ?

We assume first of all that at until the initial time $t=0$ the system and the bath are uncorrelated => $\hat{\rho}_{tot}(0) = \hat{\rho}_S \otimes \hat{\rho}_B$ with $\mathrm{Tr}_{S/B}\, \hat{\rho}_{S/B} = 1$. Additionally B is in thermal equilibrium:

$$\hat{\rho}_B(0) = \frac{e^{-\beta(\hat{H}_B - \mu \hat{N}_B)}}{Z_B} \qquad (1.296)$$

and its state is defined by the temperature $T = \frac{1}{k_B \beta}$ and chemical potential μ. Moreover

$$\rho_I(t) = U_I(t)\, \rho_S(0) \otimes \rho_B(0)\, U_I^+(t) = \rho_S(0) \otimes \rho_B(0) + \left(-\frac{i}{\hbar}\right) \int_0^t dt' \left[V_I(t'), \rho_S(0) \otimes \rho_B \right] + O(\hat{V}^2)$$

$$\Rightarrow \mathrm{Tr}_B\{ \rho_I(t) \} \otimes \rho_B(0) = \rho_S(0) \otimes \rho_B(0) + O(\hat{V})$$

We can thus conclude

$$\rho_I(t) = \mathrm{Tr}_B\{\rho_I(t)\} \otimes \rho_B(0) + O(\hat{V}) \qquad (2.28)$$

The statement above is almost trivial if one understands it as: the coupling $\hat{V}$ introduces entanglements between system and bath, which we formally separate from the disentangled evolution $\rho_{red} \otimes \rho_B$. At a still formally exact level we can write:

$$\hat{\rho}_I(t) = \mathrm{Tr}_B\{\hat{\rho}_I(t)\} \otimes \hat{\rho}_B(0) + \Delta\hat{\rho}.$$

And, consequently the equation:

$$\begin{aligned}\dot{\hat{\rho}}_{red,I}(t) = &-\frac{i}{\hbar}\mathrm{Tr}_B\{[\hat{V}_I(t), \hat{\rho}_S(0)\otimes\hat{\rho}_B(0)]\} \\ &-\frac{1}{\hbar^2}\int_0^t dt'\,\mathrm{Tr}_B\{[\hat{V}_I(t),[\hat{V}_I(t'), \hat{\rho}_{red,I}(t')\otimes\hat{\rho}_B(0)]]\} \\ &-\frac{1}{\hbar^2}\int_0^t dt'\,\mathrm{Tr}_B\{[\hat{V}_I(t),[\hat{V}_I(t'), \Delta\hat{\rho}]]\}\end{aligned} \qquad (2.29)$$

In a perturbative approach which stops at the II order in the interaction, the last line in (2.29) can be neglected and a GME is formally derived.

<u>Notice</u>:
- In the case of higher order perturbative approaches $\Delta\hat{\rho}$ cannot be neglected.
- Eq. (2.29), even in its perturbative sense ($\Delta\hat{\rho} \to 0$) has memory since $\dot{\hat{\rho}}_{red,I}(t)$ depends on $\rho_{red,I}(t')$ with $0 \le t' \le t$.

2.3.2 Bath correlation functions

Let's assume a bilinear system-bath interaction:

$$\hat{V} = \sum_i \hat{Q}_i \hat{F}_i \tag{2.30}$$

where $\hat{Q}_i$ only acts on the system and $\hat{F}_i$ on the bath B. In the interaction picture we obtain:

$$\hat{V}_I(t) = \hat{U}_0^+(t)\,\hat{V}\,\hat{U}_0(t) = \hat{U}_B^+(t)\,\hat{U}_S^+(t)\,V\,\hat{U}_S(t)\hat{U}_B(t) =$$

$$= \sum_i \hat{Q}_i(t)\hat{F}_i(t) = \sum_i \hat{U}_B^+(t)\hat{F}_i\hat{U}_B(t)\,\hat{U}_S^+(t)\,\hat{Q}_i\,\hat{U}_S(t) \tag{2.31}$$

The last equality in (2.31) is obtained under the conditions $[\hat{F}_i, \hat{U}_S(t)] = [\hat{Q}_i, \hat{U}_B(t)] = 0$ which is very natural for $\hat{H}_S$ and $\hat{H}_B$ which CONSERVE the particle number in S and B respectively => are formed by terms containing an even number of creation, annihilation operators.

By inserting (2.31) into (2.29) and using the cyclic property of the (partial) trace in the Bath subspace, one finds:

$$\begin{aligned}
\dot{\hat{\rho}}_{red,I}(t) = & -\frac{i}{\hbar}\sum_i [\hat{Q}_i(t), \hat{\rho}_S(0)]\,\mathrm{Tr}_B\{\hat{F}_i(t)\,\hat{\rho}_B(0)\} \\
& -\frac{1}{\hbar^2}\sum_{ij}\int_0^t dt' \,\Big[\hat{Q}_i(t)\hat{Q}_j(t')\hat{\rho}_{red,I}(t') - \hat{Q}_j(t')\hat{\rho}_{red,I}\hat{Q}_i(t)\Big]\,\mathrm{Tr}_B\{\hat{F}_i(t)\hat{F}_j(t')\,\hat{\rho}_B\} \\
& \qquad - \Big[\hat{Q}_i(t)\hat{\rho}_{red,I}(t')\hat{Q}_j(t') - \hat{\rho}_{red,I}\hat{Q}_j(t')\hat{Q}_i(t)\Big]\,\mathrm{Tr}_B\{\hat{F}_j(t')\hat{F}_i(t)\,\hat{\rho}_B\} \\
& + O(\hat{V}^3)
\end{aligned} \tag{2.32}$$

Consider now the expectation values

$$\langle \hat{F}_i(t)\rangle_B \equiv \mathrm{Tr}_B\{\hat{F}_i(t)\,\rho_B\} \quad \text{and}$$

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

i)

$$\langle \hat{F}_i(t) \rangle_B = \sum_{Nn,Mm} \langle Nn| F_i(t) |Mm\rangle\langle Mm| \rho_B |Nn\rangle$$
$$= \sum_{Nn} \frac{1}{Z} \langle Nn| F_i |Nn\rangle \, e^{-\beta(E_{N,n} - N\mu)} = \langle \hat{F} \rangle_B$$

In case $\langle \hat{F} \rangle_B \neq 0$ one can redefine the interaction Hamiltonian as $\tilde{V} = \sum_i (\hat{F}_i - \langle \hat{F}_i \rangle) \hat{Q}_i$ and $\tilde{\hat{H}}_S = \hat{H}_S + \sum_i \langle F_i \rangle \hat{Q}_i$. It is thus not a loss of generality to assume $\langle F_i \rangle = 0$ and neglect the linear order in $\hat{V}$ in (2.32)

ii)

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

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

$$\overset{\text{cyclic property of } Tr_B}{=} Tr_B \{ \hat{U}_B(t') \hat{U}_B^+(t) \hat{F}_i \hat{U}_B(t) \hat{U}_B^+(t') \hat{F}_j \hat{\rho}_B \} =$$

$$= Tr_B \{ \hat{F}_i(t-t') \hat{F}_j \hat{\rho}_B \} = \langle \hat{F}_i(t-t') \hat{F}_j \rangle_B \qquad (2.33)$$

The function $\langle \hat{F}_i(t) \hat{F}_j(t') \rangle_B$ - the bath correlation function - only depends on the time difference. Summarizing:

$$\dot{\hat{\rho}}_{red,I}(t) = -\frac{1}{\hbar^2} \sum_{ij} \int_0^t dt' \{ [\hat{Q}_i(t), \hat{Q}_j(t') \rho_{red,I}(t')] F_{ij}^{(B)}(t-t')$$
$$- [\hat{Q}_i(t), \rho_{red,I}(t') \hat{Q}_j(t')] F_{ji}^{(B)}(t'-t) \} + O(V^3)$$

where $F_{ij}^{(B)}(\tau) = Tr_B \{ \hat{F}_i(\tau) \hat{F}_j(0) \hat{\rho}_B \}$. (2.34)