

3 Equation of Motion for the Reduced Density Operator

3.1 The Interaction Representation of the Reduced Density Operator

formal solution of the Liouville–von Neumann

$$\hat{W}(t) = U(t - t_0)\hat{W}(t_0)U^+(t - t_0)$$

the time–evolution operator $U(t - t_0)$ is defined with respect to the total Hamiltonian H ;

one can separate this operator into the “free” time–evolution operator

$$U_0(t - t_0) = \exp\left(-\frac{i}{\hbar}H_S(t - t_0)\right) \exp\left(-\frac{i}{\hbar}H_R(t - t_0)\right) \equiv U_S(t - t_0) U_R(t - t_0)$$

and the related S –operator

$$S(t, t_0) = T \exp\left(-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{S-R}^{(I)}(\tau)\right)$$

it contains the system–reservoir coupling Hamiltonian in the interaction representation

$$H_{S-R}^{(I)}(t) = U_0^+(t - t_0)H_{S-R}U_0(t - t_0)$$

for the total density operator we can write

$$\hat{W}(t) = U_0(t - t_0)\hat{W}^{(I)}(t)U_0^+(t - t_0)$$

density operator in the interaction representation

$$\hat{W}^{(I)}(t) = U_0^+(t - t_0)\hat{W}(t)U_0(t - t_0) = S(t, t_0)\hat{W}(t_0)S^+(t, t_0)$$

using this equation the following time derivative can be written as

$$\frac{\partial}{\partial t}\hat{W}(t) = -\frac{i}{\hbar}[H_0, \hat{W}(t)]_- + U_0(t - t_0)\frac{\partial}{\partial t}\hat{W}^{(I)}(t)U_0^+(t - t_0)$$

we set this expression equal to the right-hand side of the Liouville-von Neumann equation

$$\frac{\partial}{\partial t}\hat{W}^{(I)}(t) = -\frac{i}{\hbar}[H_{S-R}^{(I)}(t), \hat{W}^{(I)}(t)]_-$$

next, we transform the RDO into the interaction representation

$$\hat{\rho}(t) = \text{tr}_R\{\hat{W}(t)\} = \text{tr}_R\left\{U_0(t - t_0)\hat{W}^{(I)}(t)U_0^+(t - t_0)\right\} = U_S(t - t_0)\text{tr}_R\left\{U_R(t - t_0)\hat{W}^{(I)}(t)U_R^+(t - t_0)\right\}U_S^+(t - t_0)$$

using the cyclic invariance of the trace we can write $\hat{\rho}(t) = U_S(t - t_0)\hat{\rho}^{(I)}(t)U_S^+(t - t_0)$

with the RDO in the interaction representation defined as $\hat{\rho}^{(I)}(t) = \text{tr}_R\left\{\hat{W}^{(I)}(t)\right\}$

with these definitions the equation of motion for $\rho^{(I)}(t)$ follows as

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t) = -\frac{i}{\hbar}\text{tr}_R\left\{[H_{S-R}^{(I)}(t), \hat{W}^{(I)}(t)]_-\right\}$$

3.2 The Projection Superoperator

the generation of equations for the RDO of higher order in the system–reservoir coupling requires the combination of a perturbation theory with a scheme for restricting the operator equations to the state space of the relevant system;

suppose \hat{O} is an operator acting in the space of the system and the reservoir states; let us consider the quantity \mathcal{P} which acts on \hat{O} as follows

$$\mathcal{P}\hat{O} = \hat{R} \operatorname{tr}_R\{\hat{O}\}$$

\mathcal{P} separates \hat{O} into the part $\operatorname{tr}_R\{\hat{O}\}$ acting only in the system space and an operator \hat{R} which exclusively acts in the state space of the reservoir;

if we apply \mathcal{P} to the full density operator we obtain the RDO $\hat{\rho}$ and some reservoir operator

$$\mathcal{P}\hat{W}(t) = \hat{R} \hat{\rho}(t)$$

if $\operatorname{tr}_R\{\hat{R}\} = 1$, which we will assume in the following, the superoperator \mathcal{P} is a **projection superoperator**

$$\mathcal{P}^2\hat{O} = \hat{R} \operatorname{tr}_R\{\hat{R} \operatorname{tr}_R\{\hat{O}\}\} = \hat{R} \operatorname{tr}_R\{\hat{R}\} \operatorname{tr}_R\{\hat{O}\} = \mathcal{P}\hat{O}$$

we specify

$$\mathcal{P}\dots = \hat{R}_{\text{eq}} \operatorname{tr}_R\{\dots\}$$

with the reservoir equilibrium statistical operator

$$\hat{R}_{\text{eq}} = \frac{1}{\mathcal{Z}} e^{-H_R/k_B T}$$

orthogonal complement to projection superoperator $\mathcal{Q} = 1 - \mathcal{P}$ $\mathcal{Q}\mathcal{P} = \mathcal{P}\mathcal{Q} = 0$
the action of \mathcal{Q} on the total density operator leads to $\mathcal{Q}\hat{W}(t) = \hat{W}(t) - \hat{\rho}(t)\hat{R}_{\text{eq}}$
this is often called irrelevant part of the statistical operator;

\mathcal{P} and \mathcal{Q} can be used to systematically develop a perturbation expansion with respect to $H_{\text{S-R}}$; we start our considerations in the interaction representation

$$\mathcal{P}\hat{W}^{(\text{I})}(t) = \hat{R}_{\text{eq}}\text{tr}_{\text{R}}\{\hat{W}^{(\text{I})}(t)\} = \hat{R}_{\text{eq}}\hat{\rho}^{(\text{I})}(t)$$

using the identity $\hat{W}^{(\text{I})}(t) = \mathcal{P}\hat{W}^{(\text{I})}(t) + \mathcal{Q}\hat{W}^{(\text{I})}(t)$ the Liouville–von Neumann equation can be split into two coupled equations

$$\mathcal{P}\frac{\partial}{\partial t}\hat{W}^{(\text{I})}(t) = -\frac{i}{\hbar}\mathcal{P}\left[H_{\text{S-R}}^{(\text{I})}(t), \mathcal{P}\hat{W}^{(\text{I})}(t) + \mathcal{Q}\hat{W}^{(\text{I})}(t)\right]_{-}$$

taking the trace with respect to the reservoir states it follows that

$$\text{tr}_{\text{R}}\left\{\mathcal{P}\frac{\partial}{\partial t}\hat{W}^{(\text{I})}(t)\right\} = \frac{\partial}{\partial t}\hat{\rho}^{(\text{I})}(t) = -\frac{i}{\hbar}\text{tr}_{\text{R}}\left\{\left[H_{\text{S-R}}^{(\text{I})}(t), \hat{R}_{\text{eq}}\hat{\rho}^{(\text{I})}(t) + \mathcal{Q}\hat{W}^{(\text{I})}(t)\right]_{-}\right\}$$

in a similar manner one obtains

$$\frac{\partial}{\partial t}\mathcal{Q}\hat{W}^{(\text{I})}(t) = -\frac{i}{\hbar}\mathcal{Q}\left[H_{\text{S-R}}^{(\text{I})}(t), \hat{R}_{\text{eq}}\hat{\rho}^{(\text{I})}(t) + \mathcal{Q}\hat{W}^{(\text{I})}(t)\right]_{-}$$

3.3 The Nakajima–Zwanzig Equation

to have a more compact notation we introduce the interaction Liouville superoperator

$$\mathcal{L}_{S-R}^{(I)} = \frac{1}{\hbar} [H_{S-R}^{(I)}, \dots]$$

and the time–ordered superoperator

$$\mathcal{S}_{\mathcal{Q}}(t, \bar{t}) = \mathcal{T} \exp \left\{ -i \int_{\bar{t}}^t d\tau \mathcal{Q} \mathcal{L}_{S-R}^{(I)}(\tau) \right\}$$

the expansion of $\mathcal{S}_{\mathcal{Q}} \hat{O}$ in powers of $\mathcal{Q} \mathcal{L}_{S-R}^{(I)}(\tau)$ introduces multiple commutators with $H_{S-R}^{(I)}$ (the quantity \hat{O} is an arbitrary operator);

those $H_{S-R}^{(I)}$ appearing left from \hat{O} are ordered with increasing time from right to left while the $H_{S-R}^{(I)}$ appearing right from \hat{O} are arranged in the reverse manner;

these two different types of time ordering have been abbreviated by the symbol \mathcal{T} ;

the equation of motion for $\mathcal{Q} \hat{W}^{(I)}(t)$ is solved as

$$\mathcal{Q} \hat{W}^{(I)}(t) = \mathcal{S}_{\mathcal{Q}}(t, t_0) \mathcal{Q} \hat{W}^{(I)}(t_0) - i \int_{t_0}^t d\bar{t} \mathcal{S}_{\mathcal{Q}}(t, \bar{t}) \mathcal{Q} \mathcal{L}_{S-R}^{(I)}(\bar{t}) \hat{R}_{\text{eq}} \hat{\rho}^{(I)}(\bar{t}) .$$

since we are not interested in the problem of initial correlations the first term on the right–hand side will be neglected by assuming that at time t_0 the density operator of the total system factorizes into the density operator of the relevant system and the reservoir, $W(t_0) = \hat{\rho}(t_0) \hat{R}_{\text{eq}}$;

inserting $\mathcal{Q}\hat{W}^{(I)}(t)$ in the equation for $\mathcal{P}\hat{W}^{(I)}(t)$ we get an equation of motion which allows an **exact** determination of the reduced statistical operator of the relevant system; this so-called **Nakajima–Zwanzig equation** reads

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t) = -i \operatorname{tr}_R \left\{ \mathcal{L}_{S-R}^{(I)}(t) \hat{R}_{\text{eq}} \right\} \hat{\rho}^{(I)}(t) - \int_{t_0}^t d\bar{t} \operatorname{tr}_R \left\{ \mathcal{L}_{S-R}^{(I)}(t) \mathcal{S}_{\mathcal{Q}}(t, \bar{t}) \mathcal{Q} \mathcal{L}_{S-R}^{(I)}(\bar{t}) \hat{R}_{\text{eq}} \right\} \hat{\rho}^{(I)}(\bar{t})$$

the system–reservoir interaction enters the right–hand side in **infinite** order;

to have a more compact notation we introduce

$$\langle \dots \rangle_R = \operatorname{tr}_R \{ \dots \hat{R}_{\text{eq}} \}$$

the equation of motion for the RDO follows as

$$\frac{\partial}{\partial t}\hat{\rho}^{(I)}(t) = -i \langle \mathcal{L}_{S-R}^{(I)}(t) \rangle_R \hat{\rho}^{(I)}(t) - \int_{t_0}^t d\bar{t} \mathcal{M}^{(I)}(t, \bar{t}) \hat{\rho}^{(I)}(\bar{t})$$

the first term can be identified as as the mean–field contribution; the second term introduced the memory kernel superoperator (in the interaction representation)

$$\mathcal{M}^{(I)}(t, \bar{t}) = \langle \mathcal{L}_{S-R}^{(I)}(t) \mathcal{S}_{\mathcal{Q}}(t, \bar{t}) \mathcal{Q} \mathcal{L}_{S-R}^{(I)}(\bar{t}) \rangle_R .$$

according to the definition of the kernel we have $t > \bar{t}$, and, additionally, any expansion of the S –superoperator guarantees time–ordered expressions;

3.4 Second–Order Equation of Motion for the Reduced Statistical Operator

replacing \mathcal{S}_Q by unity we obtain the equation of motion for the RDO which is of second–order with respect to H_{S-R}

$$\frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) = -\frac{i}{\hbar} \text{tr}_R \left\{ \hat{R}_{\text{eq}} \left[H_{S-R}^{(I)}(t), \hat{\rho}^{(I)}(t) \right]_- \right\} - \frac{1}{\hbar^2} \int_{t_0}^t d\tau \text{tr}_R \left\{ \left[H_{S-R}^{(I)}(t), (1 - \mathcal{P}) \left[H_{S-R}^{(I)}(\tau), \hat{R}_{\text{eq}} \hat{\rho}^{(I)}(\tau) \right]_- \right]_- \right\}$$

in the following we use the factorized form of the system–reservoir coupling;
the mean–field contribution (in the interaction representation) becomes

$$\text{tr}_R \left\{ \hat{R}_{\text{eq}} \left[H_{S-R}^{(I)}(t), \hat{\rho}^{(I)}(t) \right]_- \right\} = \sum_u \left[K_u^{(I)}(t) \langle \Phi_u \rangle_R, \hat{\rho}^{(I)}(t) \right]_- \equiv \left[H_{\text{mf}}^{(I)}(t), \hat{\rho}^{(I)}(t) \right]_-$$

the term

$$- \int_{t_0}^t d\tau \mathcal{M}^{(I)}(t, \tau) \hat{\rho}^{(I)}(\tau) = -\frac{1}{\hbar^2} \int_{t_0}^t d\tau \text{tr}_R \left\{ \left[H_{S-R}^{(I)}(t), (1 - \mathcal{P}) \left[H_{S-R}^{(I)}(\tau), \hat{R}_{\text{eq}} \hat{\rho}^{(I)}(\tau) \right]_- \right]_- \right\}$$

is considered in more detail;

due to the factor $(1 - \mathcal{P})$ there are altogether eight terms where those containing the factor \mathcal{P} include two trace operations;

we consider the four terms corresponding to the unit operator of $(1 - \mathcal{P})$ and write

$$\hbar^2 \mathcal{M}_1^{(I)} \hat{\rho}^{(I)} = \text{tr}_R \{ [H_{S-R}^{(I)}(t), [H_{S-R}^{(I)}(\tau), \hat{R}_{\text{eq}} \rho^{(I)}(\tau)]_-]_- \}$$

or in more detail

$$\begin{aligned} \hbar^2 \mathcal{M}_1^{(I)} \hat{\rho}^{(I)} = & \sum_{u,v} \left(\text{tr}_R \{ \Phi_u^{(I)}(t) \Phi_v^{(I)}(\tau) \hat{R}_{\text{eq}} \} K_u^{(I)}(t) K_v^{(I)}(\tau) \hat{\rho}^{(I)}(\tau) \right. \\ & - \text{tr}_R \{ \Phi_u^{(I)}(t) \hat{R}_{\text{eq}} \Phi_v^{(I)}(\tau) \} K_u^{(I)}(t) \hat{\rho}^{(I)}(\tau) K_v^{(I)}(\tau) \\ & - \text{tr}_R \{ \Phi_v^{(I)}(\tau) \hat{R}_{\text{eq}} \Phi_u^{(I)}(t) \} K_v^{(I)}(\tau) \hat{\rho}^{(I)}(\tau) K_u^{(I)}(t) \\ & \left. + \text{tr}_R \{ \hat{R}_{\text{eq}} \Phi_v^{(I)}(\tau) \Phi_u^{(I)}(t) \} \hat{\rho}^{(I)}(\tau) K_v^{(I)}(\tau) K_u^{(I)}(t) \right) \end{aligned}$$

for the second term proportional to \mathcal{P} we write

$$\begin{aligned} \hbar^2 \mathcal{M}_2^{(I)} \hat{\rho}^{(I)} = & \text{tr}_R \{ [H_{S-R}^{(I)}(t), \hat{R}_{\text{eq}} \text{tr}_R \{ [H_{S-R}^{(I)}(\tau), \hat{R}_{\text{eq}} \hat{\rho}^{(I)}(\tau)]_- \}]_- \} \\ = & \sum_{u,v} \langle \Phi_u \rangle_R \langle \Phi_v \rangle_R [K_u^{(I)}(t), [K_v^{(I)}(\tau), \hat{\rho}^{(I)}(\tau)]_-]_- \end{aligned}$$

we rewrite the expectation values of the reservoir part of H_{S-R} in $\mathcal{M}_1^{(I)}$

$$\text{tr}_R \{ \Phi_u^{(I)}(t) \Phi_v^{(I)}(\tau) \hat{R}_{\text{eq}} \} = \text{tr}_R \{ U_R^+(t - \tau) \Phi_u U_R(t - \tau) \Phi_v \hat{R}_{\text{eq}} \} = \langle \Phi_u^{(I)}(t - \tau) \Phi_v^{(I)}(0) \rangle_R$$

we get for the remaining terms

$$\text{tr}_R \{ \Phi_u^{(I)}(t) \hat{R}_{\text{eq}} \Phi_v^{(I)}(\tau) \} = \langle \Phi_v^{(I)}(0) \Phi_u^{(I)}(t - \tau) \rangle_R$$

$$\text{tr}_R \{ \Phi_v^{(I)}(t) \hat{R}_{\text{eq}} \Phi_u^{(I)}(\tau) \} = \langle \Phi_u^{(I)}(t - \tau) \Phi_v^{(I)}(0) \rangle_R$$

$$\text{tr}_R \{ \hat{R}_{\text{eq}} \Phi_v^{(I)}(\tau) \Phi_u^{(I)}(t) \} = \langle \Phi_v^{(I)}(0) \Phi_u^{(I)}(t - \tau) \rangle_R$$

the total memory kernel can be cast into a form which has only four terms each containing the following type of function (the superscript I on the bath operators will be suppressed in the following)

$$C_{uv}(t) = \frac{1}{\hbar^2} \langle \Phi_u(t) \Phi_v(0) \rangle_R - \frac{1}{\hbar^2} \langle \Phi_u \rangle_R \langle \Phi_v \rangle_R = \frac{1}{\hbar^2} \langle \Delta \Phi_u(t) \Delta \Phi_v(0) \rangle_R$$

we introduced

$$\Delta \Phi_u(t) = \Phi_u(t) - \langle \Phi_u \rangle_R$$

this operator describes the **fluctuations** of the reservoir part of H_{S-R} with respect to its average value; the function $C_{uv}(t)$ is called **reservoir correlation function**;

it establishes a connection between the fluctuations of the operators Φ_v and Φ_u at different times;

the correlations of the fluctuations decay after a certain **correlation time** τ_c ;

if Φ_u is a Hermitian operator we have

$$\langle \Phi_v(0) \Phi_u(t) \rangle_R = [\langle \Phi_u(t) \Phi_v(0) \rangle_R]^* = \langle \Phi_v(-t) \Phi_u(0) \rangle_R$$

from which we get the important property

$$C_{uv}^*(t) = C_{vu}(-t)$$

using the definition of the correlation function the equation of motion for the RDO follows as

$$\frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) = -\frac{i}{\hbar} \sum_u \langle \Phi_u \rangle_R [K_u^{(I)}, \hat{\rho}^{(I)}(t)]_- - \sum_{u,v} \int_{t_0}^t d\tau \left(C_{uv}(t-\tau) [K_u^{(I)}(t), K_v^{(I)}(\tau) \hat{\rho}^{(I)}(\tau)]_- - C_{vu}(-t+\tau) [K_u^{(I)}(t), \hat{\rho}^{(I)}(\tau) K_v^{(I)}(\tau)]_- \right)$$

since every term on the right-hand side is given by a commutator it is easy to demonstrate that the RDO equation ensures conservation of total probability, i.e. $\text{tr}_S \{ \partial \hat{\rho}(t) / \partial t \} = 0$;

by computing the Hermitian conjugated of the right-hand side one may demonstrate that the Hermiticity of $\hat{\rho}^{(I)}$ is assured for all times (note that in the case of non-Hermitian operators K_u and Φ_u the whole u, v -summation realizes Hermitian operators);

the equation is called **Quantum Master Equation** (QME) since it generalizes ordinary rate equations (Master equations); alternatively, the term **density matrix equation in the second Born approximation** is common (one refers to the second-order perturbation theory);

the right-hand side of this equation reveals that the change in time of the RDO is not only determined by its actual value but by the history of its own time dependence; the equation is specified as the QME with memory effects;

4 Quantum Master Equation

we transform the equation of motion for the RDO from the interaction representation into the Schrödinger representation

$$\frac{\partial}{\partial t} \hat{\rho}(t) = \frac{\partial}{\partial t} [U_S(t - t_0) \hat{\rho}^{(I)}(t) U_S^\dagger(t - t_0)]_- = -\frac{i}{\hbar} [H_S, \hat{\rho}(t)]_- + U_S(t - t_0) \frac{\partial}{\partial t} \hat{\rho}^{(I)}(t) U_S^\dagger(t - t_0)$$

this gives

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} \left[H_S + \sum_u \langle \Phi_u \rangle_R K_u, \hat{\rho}(t) \right]_-$$

$$\begin{aligned} & -U_S(t - t_0) \times \sum_{u,v} \int_{t_0}^t d\bar{t} \left\{ C_{uv}(t - \bar{t}) \left[U_S^\dagger(t - t_0) K_u U_S(t - t_0), U_S^\dagger(\bar{t} - t_0) K_v U_S(\bar{t} - t_0) U_S^\dagger(\bar{t} - t_0) \hat{\rho}(\bar{t}) U_S(\bar{t} - t_0) \right]_- \right. \\ & \left. - C_{vu}(-t + \bar{t}) \left[U_S^\dagger(t - t_0) K_u U_S(t - t_0), U_S^\dagger(\bar{t} - t_0) \hat{\rho}(\bar{t}) U_S(\bar{t} - t_0) U_S^\dagger(\bar{t} - t_0) K_v U_S(\bar{t} - t_0) \right]_- \right\} \times U_S^\dagger(t - t_0) \end{aligned}$$

combining products of time–evolution operators and replacing $t - \bar{t}$ by τ , we obtain the QME in the Schrödinger representation

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho} &= -\frac{i}{\hbar} [H_S + \sum_u \langle \Phi_u \rangle_R K_u, \hat{\rho}]_- \\ & - \sum_{u,v} \int_0^{t-t_0} d\tau \left(C_{uv}(\tau) \left[K_u, U_S(\tau) K_v \hat{\rho}(t - \tau) U_S^\dagger(\tau) \right]_- - C_{vu}(-\tau) \left[K_u, U_S(\tau) \hat{\rho}(t - \tau) K_v U_S^\dagger(\tau) \right]_- \right) \end{aligned}$$

let us assume that the integrand is constant within the memory time; then the contribution of the integral to the right-hand side of the QME is of the order of $\tau_{\text{mem}} \langle H_{S-R} \rangle^2 / \hbar^2$; in order to justify the perturbation expansion, this quantity (which has the dimension of a rate) has to be small compared to the first term on the right-hand side $\langle H_S \rangle / \hbar$;

the term $\sim \langle \Phi_u \rangle_R$ contains the mean-field contribution to the system dynamics which is of first order in the system-reservoir interaction; the dynamics including this mean-field term is reversible; the second term on the right-hand side which depends on the complex-valued correlation function $C_{uv}(t)$ leads to a quite different behavior; it is responsible for energy dissipation from the relevant system into the reservoir; the QME also guarantees Hermiticity of $\hat{\rho}$ and conservation of total probability;

in the QME the RDO $\hat{\rho}$ appears with an retarded time argument, $t - \tau$, in the integrand; this means that the actual change of probabilistic information in time is not determined by the probabilistic information at the same time t but also by that of earlier times $t - \tau$; this type of equation is known from probabilistic theory as a **non-Markovian** equation; it is encountered whenever time-local equations of motion are reduced to equations which only describe a part of the original set of degrees of freedom; the characteristic feature of non-Markovian behavior is the appearance of **memory** effects in the determination of the time dependence of the RDO;

4.1 Markov Approximation

let us assume that a characteristic time τ_{mem} (*memory time*) exists which characterizes the time span of memory effects;

if the reduced density operator $\hat{\rho}$ does not change substantially on the time scale given by τ_{mem} , memory effects will be negligible;

one can invoke the **Markov approximation**

$$\hat{\rho}(t - \tau) \approx \hat{\rho}(t)$$

for a slight improvement of this approximation we use the interaction representation of the RDO

$$\begin{aligned}\hat{\rho}(t - \tau) &= U_S(t - \tau - t_0)\hat{\rho}^{(I)}(t - \tau)U_S^+(t - \tau - t_0) \approx U_S(-\tau)U_S(t - t_0)\hat{\rho}^{(I)}(t)U_S^+(t - t_0)U_S^+(-\tau) \\ &= U_S^+(\tau)\hat{\rho}(t)U_S(\tau)\end{aligned}$$

this procedure guarantees that dynamical effects caused by the relevant system time–evolution operators are accounted for (need to carry out the Markov approximation in the interaction representation);

the dissipative part of the QME becomes

$$\left(\frac{\partial \hat{\rho}}{\partial t}\right)_{\text{diss}} = - \sum_{u,v} \int_0^\infty d\tau \left\{ C_{uv}(\tau) \left[K_u, K_v^{(I)}(-\tau)\hat{\rho}(t) \right]_- - C_{vu}(-\tau) \left[K_u, \hat{\rho}(t)K_v^{(I)}(-\tau) \right]_- \right\}$$

where

$$K_v^{(I)}(-\tau) = U_S(\tau)K_vU_S^+(\tau)$$

a more compact form of this equation is obtained after introduction of the operator

$$\Lambda_u = \sum_v \int_0^{\infty} d\tau C_{uv}(\tau) K_v^{(I)}(-\tau)$$

and the operator $\Lambda_u^{(+)}$ following from Λ_u upon replacing $C_{uv}(\tau)$ by $C_{vu}(-\tau)$; if any term of H_{S-R} is Hermitian, then $\Lambda_u^{(+)} = \Lambda_u^+$;

it follows

$$\left(\frac{\partial \hat{\rho}}{\partial t}\right)_{\text{diss}} = - \sum_u \left[K_u, \Lambda_u \hat{\rho}(t) - \hat{\rho}(t) \Lambda_u^{(+)} \right]_-$$

carrying out the commutator the resulting expression suggests to supplement the system Hamiltonian by non-Hermitian contributions which are proportional to $K_u \Lambda_u$

$$H_S^{(\text{eff})} = H_S + \sum_u K_u [\langle \Phi_u \rangle_R - i\hbar \Lambda_u]$$

we obtain for the QME in the Markov approximation as

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -\frac{i}{\hbar} \left(H_S^{(\text{eff})} \hat{\rho}(t) - \hat{\rho}(t) H_S^{(\text{eff})+} \right) + \sum_u \left(K_u \hat{\rho}(t) \Lambda_u^{(+)} + \Lambda_u \hat{\rho}(t) K_u \right)$$

$H_S^{(\text{eff})+}$ has to be understood as the Hermitian conjugated of $H^{(\text{eff})}$ except that all Λ_u have been replaced by $\Lambda_u^{(+)}$

this equation can be interpreted as follows:

we first note that the part of the dissipative contributions acting exclusively from the left or from the right on the reduced density operator could be comprised to a non-Hermitian Hamiltonian; its action can be understood as changing of a state vector norm; however, the remaining dissipative part acting on the reduced density operator from the left and the right simultaneously compensates for this normalization change; as a result the condition $\text{tr}_S\{\hat{\rho}\} = 1$ is fulfilled (together, of course, with conservation of total probability);

we give an alternative notation of the QME based on the superoperator formulation in Liouville space; in the present case a Liouville superoperator can only be introduced for the reversible part of the QME

$$\mathcal{L}_S \dots = [H_S, \dots]_- / \hbar$$

we write

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i\mathcal{L}_S \hat{\rho}(t) - \mathcal{D} \hat{\rho}(t)$$

the so-called dissipative (or relaxation) superoperator \mathcal{D} has been introduced; sometimes it is useful to introduce the formal solution of the QME as

$$\hat{\rho}(t) = \mathcal{U}(t - t_0) \hat{\rho}(t_0)$$

with the time-evolution superoperator

$$\mathcal{U}(t - t_0) = \exp \left(-i(\mathcal{L}_S - i\mathcal{D})(t - t_0) \right)$$

the action of \mathcal{D} can be characterized by considering the change of the internal energy of the relevant system (if $\langle \Phi_u \rangle_{\text{R}} \neq 0$, H_{S} can be extended by H_{mf})

$$E_{\text{S}} = \text{tr}_{\text{S}}\{\hat{\rho}(t)H_{\text{S}}\}$$

one immediately obtains

$$\frac{\partial}{\partial t}E_{\text{S}} = -\text{tr}_{\text{S}}\{H_{\text{S}}\mathcal{D}\hat{\rho}(t)\} = -\sum_u \text{tr}_{\text{S}}\{[H_{\text{S}}, K_u]_-(\Lambda_u\hat{\rho}(t) - \hat{\rho}(t)\Lambda_u^{(+)})\}$$

the expression shows that for cases where the commutator of the system Hamiltonian with every operator K_u vanishes, dissipation does not alter the internal energy; this may be interpreted as an action of the environment reduced to elastic scattering processes which do not change the system energy but probably the phase of the system; because of this particular property dissipative processes which do not change the system energy are related to what is known as **pure dephasing**;

assuming that the $|a\rangle$ are *eigenstates* of H_{S} the coupling operator $K_u = |a\rangle\langle a|$ represents an example for a system–reservoir coupling which guarantees the conservation of the internal energy E_{S} ; this has to be expected since the system part K_u of the system–reservoir coupling does not change the system–state;

to be complete we also remark that the internal energy remains constant if the dissipation is of such a type that the second term in the trace expression of vanishes;