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Dr. Christian Caron
Springer Heidelberg
Physics Editorial Department I
Tiergartenstrasse 17
69121 Heidelberg/Germany
christian.caron@springer.com

Robert Alicki Karl Lendi

Quantum Dynamical Semigroups and Applications

Springer

Authors

Robert Alicki
University Gdansk
Institute of Theoretical Physics
and Astrophysics
Wita Stwosza 57
80-952 Gdańsk, Poland
E-mail: fizra@univ.gda.pl

Karl Lendi
University of Zürich
Institute of Physical Chemistry
Winterthurer Str. 190
8057 Zürich, Switzerland
E-mail: carlen@pci.unizh.ch

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Preface

The first edition has been out of print soon after appearance. Over the years, a strongly increasing citation rate and numerous demands for copies led to the desire for a second edition. We may say that our original idea, i.e., making the mathematical theory related to the fundamental concept of complete positivity and derived Markovian master equations more easily accessible to a wider community, has finally borne its fruits.

For the present second edition various corrections and improvements have been necessary in addition to a clean typesetting. We also found it important to give at the end a survey of further developments in this field over the past 20 years together with a list of appropriate references.

We would like to express our particular acknowledgement and thanks to Prof. Jürg Hutter who has taken the labour of translating the entire text into LaTeX.

Gdańsk *R. Alicki*
Zürich *K. Lendi*
December 2006

Preface to the First Edition

The original idea of publishing lecture notes on this topic arose spontanously after invited talks given by the authors at the *XXth Symposium of Theoretical Chemistry* held in 1984 in Emmetten, Switzerland. As a result of many discussions we felt a real need for popularization of the unifying and fruitful, but apparently widely unknown, concept of complete positivity. The associated semigroup dynamics of open quantum systems covers so many different types of interesting irreversible processes that this theory should be made more easily accessible to a wider public. Our common desire to give a rather broad presentation of the subject soon caused the manuscripts to loose their original character of contributions to conference proceedings. During the continuous attempts to improve upon the actual versions and to include more and more topics and the latest research results, much time elapsed, and now we can say that many conference talks, many special lecture courses given at the Universities of Gdańsk and Zürich and various recently published and also unpublished papers, as well as discussions with colleagues, contributed to the final versions.

Each author's contribution reflects strongly the area of his own research activities, but we could not resist the challenge of a joint presentation as a synthesis of a whole with a broad spectrum ranging from the abstract theory up to very concrete applications, even to recent experiments.

We hope that this book provides a valuable survey of many relevant aspects of the quantum theory of irreversible processes.

Gdańsk — *R. Alicki*
Zürich — *K. Lendi*
June 1987

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General Theory and Applications to Unstable Particles

Robert Alicki

1 General Theory

1.1 Introduction

The aim of the first part of these lecture notes is to give a concise and self-contained introduction into a mathematically sound theory of quantum Markovian master equations. The text is intended for those who are interested in practical applications and are not experts in mathematical physics. Therefore the original proofs are highly simplified or replaced by heuristic ones. However, the final results are always consistent with the rigorous mathematical theory.

Subsection 1.2 is devoted to the general properties of an irreversible evolution for a quantum open system. In contrast to the classical theory the problem of the most general admissible dynamical transformation of quantum mixed states is not a trivial one and leads to the notion of complete positivity. The main result of this discussion is the general form of the Markovian master equation satisfying the complete positivity condition.

Three methods of derivation of Markovian master equations from the underlying Hamiltonian dynamics of the open system coupled to the reservoir are presented in Subsect. 1.3. In contrast to many of the derivations which can be found in the literature the attention is paid to a mathematically proper form of the obtained equations of motion.

The next subsection contains few examples of possible extensions of the presented formalism. The open systems influenced by varying external conditions, systems with different "channels of evolution" and the simplified description of many-body open systems in terms of nonlinear single-particle evolution equations are briefly discussed.

In Subsect. 1.5 a model of N 2-level atoms interacting with the electromagnetic field in thermal equilibrium is worked out in some details and serves as an illustration of the general result.

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1.2 Completely Positive Dynamical Semigroups

1.2.1 Reduced Dynamics

In the following we consider a quantum open system $\mathcal{S}$. The Hilbert space associated with $\mathcal{S}$ is denoted by $\mathcal{H}_{\rm S}$ and the corresponding scalar product by $\langle\varphi \mid \psi\rangle$, $\varphi, \psi \in \mathcal{H}_{\rm S}$. We shall use two complex Banach spaces of operators acting on $\mathcal{H}_{\rm S}$ which are described in Appendix A.1. The first one is the Banach space $\mathcal{T}(\mathcal{H}_{\rm S})$ of trace class operators with a trace norm $\|\cdot\|_1$. The (mixed) states are defined as positive[1] operators of trace one (density matrices) and they form a convex set $\mathcal{P}(\mathcal{H}_{\rm S})$ whose extreme points are the pure states given by projections on 1-dimensional subspaces. In the Dirac notation we denote pure states by $|\varphi\rangle\langle\varphi|, \quad \|\varphi\| = 1$. An arbitrary density matrix $\rho \in \mathcal{P}(\mathcal{H}_{\rm S})$ may be represented in the following form

$$\rho = \sum_k \lambda_k |\psi_k\rangle\langle\psi_k| \tag{1}$$

$$\text{with } \langle\psi_k \mid \psi_l\rangle = \delta_{kl} \ , \quad \lambda_k \geq 0 \ , \quad \sum_k \lambda_k = 1 \ .$$

The second Banach space is a set of all linear and bounded operators $\mathcal{B}(\mathcal{H}_{\rm S})$ with an operator norm $\|\cdot\|_\infty$. $\mathcal{B}(\mathcal{H}_{\rm S})$ is also an algebra with respect to multiplication of operators. The bounded observables of $\mathcal{S}$ are represented by self-adjoint elements of $\mathcal{B}(\mathcal{H}_{\rm S})$. Unbounded observables are treated as limits of sequences of bounded ones. A mean value of an observable A in a state ρ is given by $\mathrm{Tr}(\rho \mathrm{A})$.

A state of the quantum open system $\mathcal{S}$ is changed due to the internal dynamics of $\mathcal{S}$ and the interaction with the external world (reservoir $\mathcal{R}$). The Hilbert space of the total system is a tensor product $\mathcal{H}_{\rm S} \otimes \mathcal{H}_{\rm R}$ of the corresponding Hilbert spaces. We assume that we are able to prepare at a time $t_0 = 0$ the initial state of the total system as an uncorrelated product state $\rho \otimes \omega_{\rm R}$ where ρ is a varying initial state of $\mathcal{S}$ and $\omega_{\rm R}$ is the fixed reference state of $\mathcal{R}$. By U we denote the unitary operator $e^{-iH_{\rm tot}t}$, $(\hbar \equiv 1)$ representing the reversible evolution governed by the Hamiltonian $H_{\rm tot}$ of the total system from $t_0 = 0$ to a certain moment $t > 0$. Then the transformation describing a state change for our open system may be written as

$$\rho \mapsto \Lambda\,\rho = \mathrm{Tr}_{\rm R}(U\rho \otimes \omega_{\rm R} U^\star) \ . \tag{2}$$

Here $\mathrm{Tr}_{\rm R}$ is a partial trace operation from $\mathcal{T}(\mathcal{H}_{\rm S} \otimes \mathcal{H}_{\rm R})$ into $\mathcal{T}(\mathcal{H}_{\rm S})$ defined by

$$\langle\varphi \mid \mathrm{Tr}_{\rm R}\gamma \mid \psi\rangle = \sum_\nu \langle\varphi \otimes f_\nu \mid \gamma \mid \psi \otimes f_\nu\rangle \tag{3}$$

[1] In Sects. 1 & 2 of these notes the word "positive" used for numbers, functions, matrices, operators and maps means "non-negative" "positive-semidefinite" etc. The corresponding relation is denoted by "$\geq$".

with $\gamma \in \mathcal{T}(\mathcal{H}_S \otimes \mathcal{H}_R)$, $\varphi, \psi \in \mathcal{H}_S$ and $\{f_\nu\}$ – an arbitrary orthonormal basis in $\mathcal{H}_R$. It is possible to characterize the class of dynamical maps Λ defined as in (2) in terms of the Hilbert space $\mathcal{H}_S$ only [1, 2]. Namely using the spectral decomposition $\omega_R = \sum_\nu \lambda_\nu |f_\nu\rangle\langle f_\nu|$ with the orthonormal basis $\{f_\nu\}$ and choosing the orthonormal basis $\{\psi_k\}$ in $\mathcal{H}_S$ we obtain the following matrix representation of (2)

$$(\Lambda\,\rho)_{kl} = \sum_{\substack{\mu,\nu \\ m,n}} \lambda_\nu\, U_{\mu k,\nu m}\, \rho_{mn}\, \overline{U}_{\nu n,\mu l} \tag{4}$$

Hence *the dynamical map* Λ may be written as

$$\Lambda\,\rho = \sum_\alpha W_\alpha\,\rho\,W_\alpha^\star \tag{5a}$$

$$\text{where} \qquad W_\alpha \in \mathcal{B}(\mathcal{H}_S)\,, \qquad \sum_\alpha W_\alpha^\star\, W_\alpha = \mathbb{1}\,. \tag{5b}$$

The correspondence between (4) and (5) is given by $\{\alpha\} \equiv \{(\mu,\nu)\}$, $(W_\alpha)_{km} = \sqrt{\lambda_\nu}\, U_{\mu k,\nu m}$.

The converse construction for a map defined by (5) is also possible. We take as $\mathcal{H}_R$ the Hilbert space of complex sequences $\{\xi_\alpha\}$ with a scalar product $\langle\xi|\eta\rangle = \sum_\alpha \overline{\xi}_\alpha \eta_\alpha$ and as ω_R a pure state $|e\rangle\langle e|$ with $e = (1, 0, 0, \ldots)$. Then it remains to show that there exists a unitary operator U acting on $\mathcal{H}_S \otimes \mathcal{H}_R$ which may be written as a matrix $(U_{\alpha\beta})$ with values in $\mathcal{B}(\mathcal{H}_S)$ and with $U_{\alpha 1} = W_\alpha$. Such an operator always exists because the condition $\sum_\alpha W_\alpha^\star W_\alpha = \mathbb{1}$ is consistent with the unitarity condition $\sum_\alpha U_{\mu\alpha} U_{\alpha\nu}^\star = \delta_{\mu\nu}\mathbb{1}$. Summarizing, the maps given by (5) are the only candidates for dynamical maps describing irreversible time evolutions of open quantum systems in the Schrödinger picture.

1.2.2 Completely Positive Maps

There exists an equivalent characterization of a dynamical map (5) in terms of the so-called complete positivity which is often very convenient for mathematical reasons. The importance of this notion in quantum statistical physics was recognized by Kraus [1], Lindblad [2, 3], Gorini, Kossakowski and Sudarshan [4].

Because complete positivity is traditionally defined for maps on algebras we introduce now *a dynamical map in the Heisenberg picture*. This map denoted by $\Lambda^\star$ acts on $\mathcal{B}(\mathcal{H}_S)$ such that for any $\rho \in \mathcal{T}(\mathcal{H}_S)$ and $A \in \mathcal{B}(\mathcal{H}_S)$

$$\mathrm{Tr}\,\{(\Lambda\,\rho)A\} = \mathrm{Tr}(\rho\,\Lambda^\star A) \tag{6}$$

Therefore for Λ given by (5) we obtain

$$\Lambda^\star A = \sum_\alpha W_\alpha^\star A\, W_\alpha \ , \tag{7a}$$

$$W_\alpha \in \mathcal{B}(\mathcal{H}_{\rm S}) \ , \qquad \sum_\alpha W_\alpha^\star\, W_\alpha = \mathbb{1} \ . \tag{7b}$$

We forget now for a moment the origin of Λ as reduced dynamics and we discuss necessary mathematical conditions which should be imposed on $\Lambda^\star$. Because Λ maps density matrices into density matrices then $\Lambda^\star$ must be at least a linear positive (i.e. $\Lambda^\star$ transforms positive operators into positive ones) and unity preserving map on $\mathcal{B}(\mathcal{H}_{\rm S})$. Consider now the n-level system with a trivial Hamiltonian $H = 0$ placed far away from our open system $\mathcal{S}$. Hence, because both systems do not interact the joint dynamical map in the Heisenberg picture $\Lambda_n^\star$ must be given by a tensor product $\Lambda^\star \otimes \mathbb{1}$ acting on $\mathcal{B}(\mathcal{H}_{\rm S} \otimes \mathbb{C}^n)$. Obviously $\Lambda_n^\star$ should be positive for all $n = 1, 2, \ldots$. This is a new condition on $\Lambda^\star$ which is called *complete positivity* and is much stronger then usual positivity.

The dynamical map $\Lambda^\star$ given by (7) obviously satisfies the following conditions

$$\Lambda^\star \text{ is completely positive} \tag{8a}$$

$$\Lambda^\star \mathbb{1} = \mathbb{1} \tag{8b}$$

The converse statement is also true. Let $\Lambda^\star$ fulfill (8a), (8b). Then for any vectors Φ, Ψ from $\mathcal{H}_{\rm S} \otimes \mathbb{C}^n$ we have

$$\langle \Psi \mid \Lambda_n^\star(|\Phi\rangle\langle\Phi|) \mid \Psi\rangle \geq 0 \ . \tag{9}$$

Introducing orthonormal basis $\{f_\nu\}$, $\{e_k\}$ in $\mathcal{H}_{\rm S}$ and $\mathbb{C}^n$ respectively we may write (9) in the matrix representation

$$\begin{aligned} 0 &\leq \sum_{\substack{\nu,k\\ \mu,l\\ \sigma,\rho}} \Psi_{\nu k}\, \overline{\Psi}_{\mu l}\, \Lambda^\star_{\nu\mu,\sigma\rho}\, \Phi_{\sigma k}\, \overline{\Phi}_{\rho l} \\ &= \sum_{\substack{\mu,\nu\\ \sigma,\rho}} \Lambda^\star_{\nu\mu,\sigma\rho} \left(\sum_k \Psi_{\nu k}\, \Phi_{\sigma k} \right) \left(\overline{\sum_k \Psi_{\mu k}\, \Phi_{\rho k}} \right) \ . \end{aligned} \tag{10}$$

For a new matrix $T_{AB} = \Lambda^\star_{\nu\mu,\sigma\rho}$ with indices $A = (\nu, \sigma)$, $B = (\mu, \rho)$ we see that (T_{AB}) is positive definite and hence can be written as $T_{AB} = \sum_\alpha \overline{W}_A^\alpha\, W_B^\alpha$.

It means that

$$\Lambda^\star_{\nu\mu,\sigma\rho} = \sum_\alpha \overline{W}^\alpha_{\nu\sigma} W^\alpha_{\mu\rho} \ . \tag{11}$$

This is a matrix representation of $\Lambda^\star$ given by (7b). Obviously (7b) follows from (8b).

Now we may use (7) and (8) as equivalent definitions of the dynamical map in the Heisenberg picture $\Lambda^\star$ dual to the dynamical map in the Sachrödinger picture Λ given by (2).

To close this section we quote a useful *Kadison inequality* valid for all $\Lambda^\star$ defined as above,

$$\Lambda^\star(AA^\star) \geq \Lambda^\star A(\Lambda^\star A)^\star \ . \tag{12}$$

1.2.3 Generalized H-theorem

A dynamical map Λ defined in previous sections describes an irreversible evolution of a quantum open system. Usually irreversibility is related to certain H-theorems for entropy functionals. The von Neumann extension of Boltzmann and Gibbs *entropy* is given by the following definition

$$S(\rho) = \begin{cases} -\mathrm{Tr}\rho\ln\rho & \text{if } \rho\ln\rho \in \mathcal{T}(\mathcal{H}) \\ +\infty & \text{otherwise} \end{cases} \tag{13}$$

Using (1) we obtain

$$S(\rho) = -\sum_k \lambda_k \ln\lambda_k \qquad (\text{or } +\infty) \ . \tag{14}$$

For a pair of states $\rho, \sigma \in \mathcal{P}(\mathcal{H})$ one can define a *relative entropy*

$$S(\rho \mid \sigma) = \mathrm{Tr}(\rho\ln\rho - \rho\ln\sigma) \ , \tag{15}$$

if it exists.

We present now some useful properties of entropy and relative entropy functionals. The proofs and references may be found in a review paper [5].

$$S(\rho) \geq 0 \ ; \quad S(\rho) = 0 \quad \text{if and only if } \rho = |\psi\rangle\langle\psi| \ . \tag{16}$$

$$S(\rho \mid \sigma) \geq 0 \ ; \quad S(\rho \mid \sigma) = 0 \quad \text{if and only if } \rho = \sigma \ . \tag{17}$$

Let $\lambda_j > 0$, $\sum_j \lambda_j = 1$, $\rho_j, \sigma_j \in \mathcal{P}(\mathcal{H})$ then

$$\sum_j \lambda_j S(\rho_j) \ \leq \ S\left(\sum_j \lambda_j \rho_j\right) \ , \tag{18}$$

$$S\left(\sum_j \lambda_j \rho_j \mid \sum_j \lambda_j \sigma_j\right) \ \leq \ \sum_j \lambda_j S(\rho_j \mid \sigma_j) \ . \tag{19}$$

For a unitary operator U,

$$S(U\,\rho\,U^\star) = S(\rho) \ , \tag{20}$$

$$S(U\,\rho\,U^\star \mid U\,\sigma\,U^\star) = S(\rho \mid \sigma) \ . \tag{21}$$

Let $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$; $\rho, \sigma \in \mathcal{P}(\mathcal{H})$ and $\rho_1 = \mathrm{Tr}_2\,\rho$, $\rho_2 = \mathrm{Tr}_1\,\rho$, $\sigma_1 = \mathrm{Tr}_2\,\sigma$ then

$$S(\rho) \leq S(\rho_1) + S(\rho_2) \tag{22}$$
$$S(\rho_1 \mid \sigma_1) \leq S(\rho \mid \sigma) \ . \tag{23}$$

If now $\rho_1, \sigma_1 \in \mathcal{P}(\mathcal{H}_1)$ and $\sigma_2 \in \mathcal{P}(\mathcal{H}_2)$ then

$$S(\sigma_1 \otimes \sigma_2) = S(\sigma_1) + S(\sigma_2) \ , \tag{24}$$
$$S(\rho_1 \otimes \sigma_2 \mid \sigma_1 \otimes \sigma_2) = S(\rho_1 \mid \sigma_1) \ . \tag{25}$$

Remembering that a dynamical map Λ may be always represented by (2) and using the properties (21), (23), (25) one obtains

$$\begin{aligned} S(\Lambda\rho \mid \Lambda\sigma) &= S(\mathrm{Tr}_{\mathrm{R}}\{U\rho \otimes \omega_{\mathrm{R}} U^\star\} \mid \mathrm{Tr}_{\mathrm{R}}\{U\sigma \otimes \omega_{\mathrm{R}} U^\star\}) \\ &\leq S(U\rho \otimes \omega_{\mathrm{R}} U^\star \mid U\sigma \otimes \omega_{\mathrm{R}} U^\star) \\ &= S(\rho \otimes \omega_{\mathrm{R}} \mid \sigma \otimes \omega_{\mathrm{R}}) = S(\rho \mid \sigma) \ . \end{aligned} \tag{26}$$

Hence a *generalized H-theorem* for quantum dynamical maps proved by Lindblad [3] has the form

$$S(\Lambda\rho \mid \Lambda\sigma) \leq S(\rho \mid \sigma) \ . \tag{27}$$

We discuss now some consequences of (27). Assuming that σ is a *stationary state* for Λ, i.e. $\Lambda\sigma = \sigma$ we obtain the following interesting physical application of (27). Namely

$$\Delta S = S(\Lambda\rho) - S(\rho) = \Delta_p S + \Delta_e S \tag{28}$$

where

$$\Delta_p S = \{S(\rho \mid \sigma) - S(\Lambda\rho \mid \Lambda\sigma)\} \geq 0 \tag{29}$$
$$\Delta_e S = \mathrm{Tr}\{(\Lambda\rho - \rho) \ln \sigma\} \ . \tag{30}$$

According to the principles of phenomenological thermodynamics $\Delta_p S$ may be interpreted as an entropy change due to the positive entropy production in an open system and $\Delta_e S$ is an exchange of entropy with the environment. Consequently the inequality (29) is related to the second law of thermodynamics.

The usual H-theorem: $\Delta S \geq 0$, is true if and only if the central state (called also "infinite temperature state") $\sigma = \frac{1}{N}\mathbb{1}$, where N is the dimension of $\mathcal{H}_{\mathrm{S}}$, is stationary with respect to Λ. The important class of such dynamics is obtained for systems in random external fields. For this case Λ may be always written as

$$\Lambda\,\rho = \int_{\Omega} P(d\omega)\, U_\omega\, \rho\, U_\omega^\star \ , \tag{31}$$

where $P(\cdot)$ is a probability measure on a certain space of events Ω and for any $\omega \in \Omega$, U_ω is a unitary operator.

1.2.4 Generators of Quantum Dynamical Semigroups

In the previous sections we have discussed the properties of a single dynamical map Λ. In order to describe the time evolution of an open system we need a one-parameter family of dynamical maps $\{\Lambda_t, t \geq 0\}$. We shall see later that generally the function $t \mapsto \Lambda_t$ does not possess simple properties and satisfies a complicated integro-differential equation.

However a large class of interesting physical phenomena may be described by approximative evolutions which fulfill the semigroup condition. The discussion of the validity of this approximation will be given in the next section.

The *quantum dynamical semigroup* (in the Schrödinger picture) is a family of linear maps $\{\Lambda_t, t \geq 0\}$ such that

A) Λ_t is a dynamical map,
B) $\Lambda_t \Lambda_s = \Lambda_{t+s}$ – semigroup condition or Markov property,
C) $\mathrm{Tr}\{(\Lambda_t \rho)A\}$ is a continuous function of t for any $\rho \in \mathcal{P}(\mathcal{H}_\mathrm{S})$ and $A \in \mathcal{B}(\mathcal{H}_\mathrm{S})$.

As a result of the mathematical theory of one-parameter contracting semigroups on Banach spaces (see Appendix A.2) there exists a densely defined linear map L, called *a generator of a semigroup*, such that

$$\frac{d}{dt}\rho_t = \mathrm{L}\rho_t \tag{32}$$

where $\rho_t = \Lambda_t \rho$; $\rho \in \{\text{domain of L}\}$.

Hence $\Lambda_t = e^{\mathrm{L}t}, t \geq 0$ where for unbounded L we use instead of a series expansion the following definition of the exponent

$$e^{\mathrm{L}t}\rho = \lim_{n\to\infty} \left(1 - \frac{t}{n}\mathrm{L}\right)^{-n} \rho \ . \tag{33}$$

Similarly for the Heisenberg dynamics $\Lambda_t^\star$ we have

$$\frac{d}{dt}A_t = \mathrm{L}^\star A_t \tag{34}$$

with $A_t = \Lambda_t^\star A$, $A \in \{\text{domain of L}^\star\}$.

The equations (32), (34) are called *quantum Markovian master equations* in the Schrödinger and the Heisenberg picture respectively (for the reviews of their properties see [6–8]).

We find now a general form of L in the case of finite-dimensional Hilbert space $\mathcal{H}_\mathrm{S}$ ($\dim \mathcal{H}_\mathrm{S} = N$). Introducing a linear basis $\{F_k\}, k = 0, 1, \ldots, N^2 - 1$ in $\mathcal{B}(\mathcal{H}_\mathrm{S})$ such that $F_0 = \mathbb{1}$ we may write a time-dependent version of (5a) as follows,

$$\Lambda_t \rho = \sum_{k,l=0}^{N^2-1} C_{kl}(t)\, F_k \rho F_l^\star \,, \tag{35}$$

where $(C_{kl}(t))$ is a positive-definite matrix.

Therefore,

$$\mathrm{L}\,\rho = \lim_{\epsilon \searrow 0} \left\{ \frac{C_{00}(\epsilon) - 1}{\epsilon}\rho + \sum_{k=0}^{N^2-1} \frac{C_{0k}(\epsilon)}{\epsilon} F_k \rho \right. \\ \left. + \rho \sum_{k=0}^{N^2-1} \frac{\overline{C}_{0k}(\epsilon)}{\epsilon} F_k^\star + \sum_{k,l=0}^{N^2-1} \frac{C_{kl}(\epsilon)}{\epsilon} F_k\, \rho\, F_l^\star \right\}$$

$$= A\,\rho + \rho\, A^\star + \sum_{k,l=0}^{N^2-1} a_{kl}\, F_k\, \rho\, F_l^\star\,, \tag{36}$$

where (a_{kl}), $k, l = 1, 2, \ldots N^2 - 1$, is a positive-definite matrix. Using the trace preserving condition $\mathrm{Tr}(\mathrm{L}\,\rho) = 0$ one obtains

$$A + A^\star = -\sum_{k,l=0}^{N^2-1} a_{kl}\, F_l^\star\, F_k\,, \tag{37}$$

leading to the first of the *standard forms of the generator* L

$$\mathrm{L}\,\rho = -i[H, \rho] + \frac{1}{2} \sum_{k,l=0}^{N^2-1} a_{kl} \left\{ [F_k\, \rho, F_l^\star] + [F_k, \rho\, F_l^\star] \right\}, \quad (a_{kl}) \geq 0\,. \tag{38}$$

Here, $H = H^\star$ is the effective Hamiltonian of the system $\mathcal{S}$. Replacing the operators $\{F_k\}, k = 1, 2, \ldots, N^2 - 1$, by their suitable linear combinations V_α one can derive the equivalent *"diagonal" standard form of* L,

$$\mathrm{L}\,\rho = -i[H, \rho] + \frac{1}{2} \sum_{\alpha} \left\{ [V_\alpha\, \rho, V_\alpha^\star] + [V_\alpha, \rho\, V_\alpha^\star] \right\}\ . \tag{39}$$

The Heisenberg generators may be written as

$$\mathrm{L}^\star \rho = i[H, A] + \frac{1}{2} \sum_{k,l=0}^{N^2-1} a_{kl} \left\{ F_l^\star [A, F_k] + [F_l^\star, A] F_k \right\}, \quad (a_{kl}) \geq 0 \tag{40}$$

$$\mathrm{L}^\star \rho = i[H, A] + \frac{1}{2} \sum_{\alpha} \left\{ V_\alpha^\star [A, V_\alpha] + [V_\alpha^\star, A] V_\alpha \right\}\ . \tag{41}$$

Gorini, Kossakowski and Sudarshan have shown that (38) defines the most general generator of a quantum dynamical semigroup for the case of a finite dimensional Hilbert space $\mathcal{H}_\mathrm{S}$ [4]. Independently Lindblad proved that (39) is the most general bounded generator for any (separable) Hilbert space if one admits countable sets of indices $\{\alpha\}$ and $\sum_\alpha V_\alpha^\star V_\alpha \in \mathcal{B}(\mathcal{H}_\mathrm{S})$ [9].

There exists no such characterization in the case of unbounded L. However there is a class of formal expressions (39) with unbounded V_α which rigorously

define quantum dynamical semigroups [10]. Moreover all known examples of L ($L^\star$) are of the standard form (38)–(41) with possibly unbounded F_k, V_α or even more singular objects like quantum fields; the sums $\sum_{k,l}$ and $\sum_\alpha$ might be replaced by integrals and a positive-definite matrix (a_{kl}) by a positive-definite integral kernel (see Sect. 2). The situation reminds of the problem of self-adjointness of the Hamiltonian operator in standard quantum mechanics. It is usually easy to check that a candidate for the Hamiltonian is symmetric but the question of essential self-adjointness is often a difficult mathematical problem. In our case one can easily see whether a proposed L or $L^\star$ is of the (generalized) standard form which is a "practical necessary condition" but to prove that it generates a one-parameter semigroup at all might be very difficult.

1.2.5 How to Construct Generators?

In principle any Markovian master equation should be derived from the underlying Hamiltonian dynamics for the total closed system using the Markovian approximation. However, in practice this is often technically impossible and therefore one needs a phenomenological prescription in order to construct generators. One may use here a close analogy between classical Pauli master equations and quantum ones.

Consider the following *Pauli master equation*

$$\frac{d}{dt}p_k(t) = \sum_{l=1}^{n}(a_{kl}\, p_l(t) - a_{lk}\, p_k(t)) \ , \qquad k = 1, 2, \dots n \ , \tag{42}$$

where $a_{kl} \geq 0$ is the *transition probability* per unit time from the state l to the state k.

We may associate with the matrix (a_{kl}) two positive maps M and $M^\star$ acting on the linear space of functions $x; x : \{1, 2, \dots, n\} \mapsto \mathbb{C}$ treated also as sequences $x = (x_1, x_2, \dots, x_n)$. Namely, we define M as

$$(\mathrm{M}x)_k = \sum_{l=1}^{n} a_{kl}\, x_l \tag{43}$$

and a dual (transposed) one

$$(\mathrm{M}^\star x)_k = \sum_{l=1}^{n} a_{lk}\, x_l \ . \tag{44}$$

The maps $\mathrm{M}, \mathrm{M}^\star$ are positive in the sense that for $x \geq 0$ (i.e. $x_k \geq 0$ for all $k = 1, 2, \dots, n$) $\mathrm{M}x, \mathrm{M}^\star x \geq 0$. The equation (42) may be written in the operator form

$$\frac{d}{dt}p(t) = \mathrm{M}p(t) - (\mathrm{M}^\star \mathbb{1}) \cdot p(t) \tag{45}$$

where

$$p(t) = (p_1(t), p_2(t), \ldots, p_n(t))$$
$$\mathbb{1} = (1, 1, \ldots, 1)$$

and

$$x \cdot y = (x_1 y_1, x_2 y_2, \ldots, x_n y_n) \tag{46}$$

We "quantize" now the equation (45) using the following correspondence principles:

1. a probability distribution p is replaced by a density matrix ρ.
2. a positive *transition map* M is replaced by a completely positive *quantum transition map* Φ.
3. a product of functions $x \cdot y$ is replaced by a symmetric product of operators $\mathrm{X} \cdot \mathrm{Y} = \frac{1}{2}\{\mathrm{X}, \mathrm{Y}\}$.

Then, adding a Hamiltonian part which is absent in the case of discrete classical systems we obtain

$$\frac{d}{dt}\rho_t = -i[H, \rho_t] + \Phi\rho_t - \frac{1}{2}\{\Phi^\star(\mathbb{1}), \rho_t\} \ . \tag{47}$$

Remembering that the completely positive maps are of the form $\Phi\,\rho = \sum_\alpha V_\alpha\,\rho\,V_\alpha^\star$ we obtain an equivalent expression for the generator (39).

Summarizing: in order to construct a quantum Markovian master equation we should find a quantum transition map Φ. It can be decomposed into *elementary transition maps* $\rho \mapsto V_\alpha\,\rho\,V_\alpha^\star$ which describe independent irreversible processes. Using phenomenological informations about the nature of such processes together with symmetry properties like the invariance with respect to symmetry groups and the detailed balance condition (see 1.3.4) one is able to guess a relevant form of Φ (see 2.3.2).

1.3 Hamiltonian Models and Markovian Approximation

1.3.1 Generalized Master Equation

Our aim is to derive an approximative Markovian master equation for the reduced dynamics of $\mathcal{S}$ using certain limiting procedures. A convenient intermediate step is the so-called generalized master equation obtained by means of the projection technique. This approach initiated by Nakajima [11], Prigogine, Resibois [12] and Zwanzig [13] was reviewed in [14]. We present now briefly its abstract version.

Let $\mathcal{B}$ be the Banach space for the total system $\mathcal{S}+\mathcal{R}$ and $\mathcal{B}_0$ its subspace associated to the open system $\mathcal{S}$. P_0 denotes projection from $\mathcal{B}$ onto $\mathcal{B}_0$ and $P_1 = \mathbb{1} - P_0$. The free dynamics is given by a group $U_t = e^{Zt}, t \in \mathbb{R}$ commuting with P_0 and the perturbed dynamics is described by a group $V_t = e^{(Z+A)t}, t \in$

$\mathbb{R}$. Introducing the following notation: $A_{ij} = P_i A P_j$, $Z_i = P_i Z = P_i Z P_i$, $i, j = 0, 1$, we define $\tilde{U}_t = e^{(Z+A_{00}+A_{11})t}$, $\tilde{U}^0_t = e^{(Z_0+A_{00})t}$. and the reduced dynamics $W_t = P_0 V_t P_0$.

Treating V_t as a perturbation of $\tilde{U}_t$ and using the second order integral equation for V_t (see Appendix A.2, (220)) one obtains the following integral equation for the reduced dynamics

$$W_t = \tilde{U}^0_t + \int_0^t ds \int_0^s du\, \tilde{U}^0_{t-s}\, A_{01}\, \tilde{U}_{s-u}\, A_{10}\, W_u \ . \tag{48}$$

Putting $\rho_t = W_t \rho$ with $\rho \in \mathcal{B}_0$ and differentiating (48) one gets a *generalized master equation*

$$\frac{d}{dt}\rho_t = (Z_0 + A_{00})\rho_t + \int_0^t G(t-s)\rho_s\, ds \tag{49}$$

with $G(s) = A_{01}\, \tilde{U}_s\, A_{10}$.

The operator-valued integral kernel $G(s)$ contain all "memory effects" in the dynamics of the open system. We expect, however, that in many cases $G(s)$ decays rapidly to zero and the equation (49) might be simplified. This kind of arguments leads to a naive *Markovian approximation* of the following form

$$\frac{d}{dt}\rho_t = \left(Z_0 + A_{00} + \int_0^t G(s)\, ds \right) \rho_t \ . \tag{50}$$

Unfortunately, the above prescription generally breaks the complete positivity and even positivity of the reduced dynamics. In the next three sections we present more refined methods of derivation which lead to quantum dynamical semigroups. Before doing this we first identify the objects used above with those introduced in previous sections. The Banach space $\mathcal{B} = \mathcal{T}(\mathcal{H}_S \otimes \mathcal{H}_R)$, and $\mathcal{B}_0 = \mathcal{T}(\mathcal{H}_S) \otimes \omega_R$ where ω_R is a fixed state of $\mathcal{R}$ commuting with the free Hamiltonian H_R. The projection P_0 is defined by the formula $P_0\gamma = (\mathrm{Tr}_R\gamma) \otimes \omega_R$ and in final expressions we identify $\mathcal{B}_0 = \mathcal{T}(\mathcal{H}_S) \otimes \omega_R$ with $\mathcal{T}(\mathcal{H}_S)$. The generator $Z = -i[H_S + H_R, \bullet]$ and the perturbation $A = -i[H_{\mathrm{int}}, \bullet]$ where H_S is the free Hamiltonian of $\mathcal{S}$ and H_{int} describes the interaction between $\mathcal{S}$ and $\mathcal{R}$. It is now obvious that W_t must be identified with the reduced dynamics (2).

1.3.2 Weak Coupling Limit

We consider now the quantum system $\mathcal{S}$ weakly interacting with the reservoir $\mathcal{R}$. It is a reasonable assumption for such systems like atoms or molecules interacting with a thermal electromagnetic field or localized spins coupled to phonons. We introduce a manifest dependence on the coupling constant λ replacing H_{int} by λH_{int}, A by λA and adding a subscript λ in all expressions from the previous section. We choose the interaction Hamiltonian of the following form

$$H_{\rm int} = \sum_{\alpha} Q_\alpha \otimes \varphi_\alpha \tag{51}$$

where $Q_\alpha = Q_\alpha^\star$ ($\varphi_\alpha = \varphi_\alpha^\star$) acts on $\mathcal{H}_{\rm S}(\mathcal{H}_{\rm R})$, and the additional condition is imposed

$$\mathrm{Tr}(\omega_{\rm R}\,\varphi_\alpha) = 0 \ . \tag{52}$$

We assume also that $H_{\rm S}$ has discrete spectrum

$$H_{\rm S} = \sum_k \epsilon_k |k\rangle\langle k| \ . \tag{53}$$

Because λ is supposed to be small we replace in (48) $\tilde{U}_t^\lambda$ by U_t and from (52) it follows that $A_{00} = 0$; $\tilde{U}_t^0 = U_t^0 = e^{Z_0 t}$, $(Z_0 = -i[H_{\rm S}, \bullet])$.

Then we go over to the interaction picture to extract some oscillating terms which might be dropped out within the weak coupling approximation. We use the fact that $U_{-t}^0 W_t^\lambda$ varies slowly for small λ so the natural time scale is given by the rescaled time parameter $\tau = \lambda^2 t$. Therefore in (48) t should be taken large and hence we obtain from (48) the approximative relation

$$\begin{aligned} U_{-t}^0 W_t^\lambda &= \mathbb{1} + \lambda^2 \int_0^t ds \int_0^s du\, U_{-s}^0 A_{01} U_{s-u} A_{10} U_u^0 (U_{-u}^0 W_u^\lambda) \\ &= \mathbb{1} + \lambda^2 \int_0^t ds\, K(s)(U_{-s} W_s^\lambda) \ , \end{aligned} \tag{54}$$

where

$$K(s) = U_{-s}^0 K\, U_s^0 \ , \tag{55}$$

and

$$K = \int_0^\infty A_{01} U_t A_{10}\, dt \ . \tag{56}$$

As noticed by Davies [15,16] and explicitely shown by Dümcke and Spohn [17] the map K, given in a manifest form by

$$K\rho = -\sum_{\alpha\beta} \int_0^\infty dt\ \mathrm{Tr}_{\rm R} \left\{ [Q_\alpha \otimes \varphi_\alpha, [Q_\beta(t) \otimes \varphi_\beta(t), \rho \otimes \omega_{\rm R}]] \right\} \ , \tag{57}$$

does not generate a quantum dynamical semigroup (except for some trivial cases).

Writing $Q_\alpha(t) = e^{-iH_{\rm S}t} Q_\alpha e^{iH_{\rm S}t}$ as

$$Q_\alpha(t) = \sum_\omega Q_\omega^\alpha\, e^{-i\omega t} \ , \tag{58}$$

where $\{\omega\}$ is a set of energy differences $\{\epsilon_k - \epsilon_l\}$ (see (8)) and

$$\begin{aligned} Q_\omega^\alpha &= \sum_{\epsilon_k - \epsilon_l = \omega} |k\rangle\langle k \mid Q_\alpha \mid l\rangle\langle l| \ , \\ Q_{-\omega}^\alpha &= Q_\omega^{\alpha\star} \ , \end{aligned} \tag{59}$$

we may extract from $K(s)$ the oscillating terms $\propto e^{i(\omega+\omega')s}$ $(\omega \neq -\omega')$ which give a negligible contribution to the integral (7) for sufficiently small λ.

Therefore $K(s)$ may be replaced by a time independent map $K^\sharp$ defined by the following *averaging procedure* [15,16]

$$K^\sharp = \lim_{a\to\infty} \frac{1}{a} \int_0^a U^0_{-s} K U^0_s \, ds \ . \tag{60}$$

The manifest form of $K^\sharp$ is now

$$K^\sharp \rho = -i[H', \rho] + \frac{1}{2} \sum_{\alpha,\beta} \sum_{\omega} h_{\alpha\beta}(\omega) \left\{ [Q^\alpha_\omega \, \rho, Q^{\beta\star}_\omega] + [Q^\alpha_\omega, \rho \, Q^{\beta\star}_\omega] \right\} \ , \tag{61}$$

with

$$H' = \sum_{\alpha,\beta} \sum_{\omega} S_{\alpha\beta}(\omega) \, Q^{\alpha\star}_\omega Q^\beta_\omega \ , \tag{62}$$

$$\int_0^\infty e^{i\omega t} \mathrm{Tr}(\omega_\mathrm{R} \, \varphi_\alpha(t) \varphi_\beta) = \frac{1}{2} h_{\alpha\beta}(\omega) + i S_{\alpha\beta}(\omega) \ , \tag{63}$$

where for all ω $(h_{\alpha\beta}(\omega))$ is a positive matrix and $(S_{\alpha\beta}(\omega))$ is hermitian (see Appendix A.3). Therefore $H' = H'^\star$ and $K^\sharp$ is of standard form (38). Moreover, from (60) it follows that $U^0_t K^\sharp = K^\sharp U^0_t$ and W^λ_t may be approximated for a sufficiently small λ by the solution of the following Markovian master equation

$$\frac{d}{dt} \rho_t = -i[H_\mathrm{S}, \rho_t] + \lambda^2 K^\sharp \rho_t \ , \tag{64}$$

with $K^\sharp$ given by (61)–(63).

We comment now some implicit assumptions used in the above derivation which are rigorously discussed by Davies [15, 16]. The transformation of integral equation (9) is justified if the correlation functions $f_{\alpha\beta}(t) = \mathrm{Tr}(\omega_\mathrm{R} \varphi_\alpha(t) \varphi_\beta)$ are at least integrable (strictly $\int_0^\infty |f_{\alpha\beta}(t)|(1+t)^\epsilon dt < \infty$ for certain $\epsilon > 0$). Moreover similar decay conditions must be imposed on higher order correlation functions in order to prove that in (48) $\tilde{U}_t \equiv \tilde{U}^\lambda_t$ may be replaced by U_t. This cannot be done for a system $\mathcal{R}$ in a finite volume because of *Poincaré recurrences*.

Therefore as models for reservoirs we choose such systems like quantum fields in infinite space and with ω_R being the vacuum state or ideal quantum gas in the thermodynamic limit. In the rigorous derivation of (64) [15, 16] one assumes that λ may be chosen so small that the relaxation of the open system $\mathcal{S}$ is slow comparing with all oscillations $e^{i(\omega+\omega')t}$; $\omega' \neq \omega$. However, for concrete physical examples this might be not true and hence the use of $K^\sharp$ not justified. The problem may be solved at least for some case if we write H_S as $H^0_\mathrm{S} + H^1_\mathrm{S}$, $[H^0_\mathrm{S}, H^1_\mathrm{S}] = 0$ where for H^0_S all "small" terms $\omega + \omega'$ vanish and H^1_S may be treated as a weak perturbation. Then one can apply the above procedure of derivation of $K^\sharp$ with H_S replaced by H^0_S and finally add H^1_S to the total effective Hamiltonian of $\mathcal{S}$. Some rigorous results concerning the above problem may be found in [18].

1.3.3 Low Density Limit

A model discussed in the following section consists of the quantum system $\mathcal{S}$ with the Hamiltonian $H_{\rm S}$ given by (53) immersed in an ideal gas at low density. Such models are used for instance in the theory of collisional broadening of spectral lines [19]. The rigorous analysis of the Markovian approximation for this model was performed by Dümke [20]. Here we present a heuristic derivation, but the final result coincides with that of [20].

We begin with an analysis of the scattering process involving the system $\mathcal{S}$ and a single particle of the gas. The Hamiltonian of such a system is given by

$$H = H_{\rm S} + H_{\rm P} + H_{\rm int} \ , \tag{65}$$

with the Hamiltonian of the particle

$$H_{\rm P} = \int d^3\boldsymbol{p}\ E_{\boldsymbol{p}} |\boldsymbol{p}\rangle\langle\boldsymbol{p}| \ , \tag{66}$$

where $\langle \boldsymbol{p} \mid \boldsymbol{p}\rangle = \delta^3(\boldsymbol{p}-\boldsymbol{p}')$, $\boldsymbol{p}$ – momentum vector, $E_{\boldsymbol{p}}$ – kinetic energy .

The scattering process is described by the Moeller wave operators

$$\Omega_{\pm}\Psi = \lim_{t\to\pm\infty} e^{-iHt}e^{i(H_{\rm S}+H_{\rm P})t}\Psi \ , \tag{67}$$
$$\Psi \in \mathcal{H}_{\rm S}\otimes\mathcal{H}_{\rm P} \ .$$

By $\Gamma_{\pm}$ we denote the Moeller maps acting on $\mathcal{T}(\mathcal{H}_{\rm S}\otimes\mathcal{H}_{\rm P})$,

$$\Gamma_{\pm}\gamma = \Omega_{\pm}\gamma\Omega_{\pm}^{\star} \ ; \quad \gamma \in \mathcal{T}(\mathcal{H}_{\rm S}\otimes\mathcal{H}_{\rm P}) \ . \tag{68}$$

Defining the following one-parameter groups on $\mathcal{T}(\mathcal{H}_{\rm S}\otimes\mathcal{H}_{\rm P})$,

$$V_t^0\gamma = e^{-i(H_{\rm S}+H_{\rm P})t}\gamma e^{i(H_{\rm S}+H_{\rm P})t} \ , \tag{69}$$
$$V_t\gamma = e^{-iHt}\gamma e^{iHt} \ , \tag{70}$$

and the perturbation

$$\mathrm{L}_{\rm int}\gamma = -i[H_{\rm int},\gamma] \ , \tag{71}$$

we may write for $t \gg \tau_{\rm coll}$ ($\tau_{\rm coll}$ – duration of collision)

$$V_{-t}^0 V_t = \mathbb{1} + \int_0^t V_{-s}^0 \mathrm{L}_{\rm int} V_s \, ds \sim \mathbb{1} + \int_0^t V_{-s}^0 \left(\mathrm{L}_{\rm int}\Gamma_+\right) V_s^0 \, ds \ . \tag{72}$$

Taking as a reference state on $\mathcal{H}_{\rm P}$ the following density matrix normalized to 1 in a volume L^3,

$$\sigma_L = \frac{1}{L^3}\int d^3\boldsymbol{p}\, G(\boldsymbol{p})|\boldsymbol{p}\rangle\langle\boldsymbol{p}| \equiv \frac{1}{L^3}\sigma \ ,$$

with $G(\boldsymbol{p})$ being a probability distribution of momenta we obtain the following reduced dynamics in the interaction picture,

$$\tilde{\Lambda}_t^{(1)}\rho = \rho + \frac{1}{L^3}\int_0^t K(s)\rho\, ds \ , \tag{73}$$

where

$$K(s) = U_{-s}^0 K U_s^0 \ , \qquad U_t^0\rho = e^{-iH_{\rm S}t}\rho\, e^{iH_{\rm S}t} \ , \tag{74}$$

and

$$K\rho = {\rm Tr}_{\rm P}\left({\rm L}_{\rm int}\Gamma_+\rho\otimes\sigma\right) \ . \tag{75}$$

As one may expect in order to obtain a proper Markovian master equation directly from (73)–(75) K should be a generator of a quantum dynamical semigroup. This is however not the case although K given by (75) is often used in the literature [19]. To obtain a proper equation we use again the averaging procedure (60) which is justified here because we are interested in the long time behavior of $\mathcal{S}$ with natural time scale $\tau = \nu t$ for sufficiently small densities ν of the gas. Hence we may write

$$\tilde{\Lambda}_t^{(1)}\rho = \rho + \frac{t}{L^3}K^\sharp\rho \ , \tag{76}$$

where the compact form of $K^\sharp$ may be obtained using the unitarity of Ω_+ and its relations to the T-matrix defined as

$$T = H_{\rm int}\Omega_+ \ . \tag{77}$$

After straightforward calculations one obtains [20]

$$\begin{aligned} K^\sharp\rho = -i[H',\rho] + \pi\sum_\omega \int d^3\boldsymbol{p}\int d^3\boldsymbol{p}'\, G(\boldsymbol{p})\,\delta(E_{\boldsymbol{p}'} - E_{\boldsymbol{p}} + \omega) \\ \{[T_\omega(\boldsymbol{p}',\boldsymbol{p})\rho, T_\omega^\star(\boldsymbol{p}',\boldsymbol{p})] + [T_\omega(\boldsymbol{p}',\boldsymbol{p}), \rho T_\omega^\star(\boldsymbol{p}',\boldsymbol{p})]\} \ , \end{aligned} \tag{78}$$

where

$$H' = \sum_{\epsilon_k=\epsilon_l}\int d^3\boldsymbol{p}\, G(\boldsymbol{p})\left\{\langle k,\boldsymbol{p}\mid T\mid l,\boldsymbol{p}\rangle + \langle l,\boldsymbol{p}\mid T^\star\mid k,\boldsymbol{p}\rangle\right\}|k\rangle\langle l| \ , \tag{79}$$

and

$$T_\omega(\boldsymbol{p}',\boldsymbol{p}) = \sum_{\epsilon_k-\epsilon_l=\omega}\langle k,\boldsymbol{p}'\mid T\mid l,\boldsymbol{p}\rangle|k\rangle\langle l| \ . \tag{80}$$

Obviously $K^\sharp$ is of (generalized) standard form (39).

Now we are able to formulate the final result. Suppose that there are N particles in volume L^3. For a low density $\nu = N/L^3$ the collisions of $\mathcal{S}$ with different particles are statistically independent events. It follows that the total change of ρ /in the interaction picture/ may be written as

$$\tilde{\Lambda}_t^{(N)}\rho = \left(\tilde{\Lambda}_t^{(1)}\right)^N\rho = \left(1 + \frac{\nu t}{N}K^\sharp\right)^N\rho \ . \tag{81}$$

Hence for $N \to \infty$, $L \to \infty$, $N/L^3 = \nu$ we obtain

$$\tilde{\Lambda}_t^{(\infty)} \rho = e^{\nu K^\sharp t} \rho \ . \tag{82}$$

Because $K^\sharp$ commutes with U_t^0 we may write the Markovian master equation in the Schrödinger picture as follows,

$$\frac{d}{dt}\rho_t = -i[H_{\rm S}, \rho_t] + \nu K^\sharp \rho_t \ , \tag{83}$$

with $K^\sharp$ given by (78)–(80).

1.3.4 Heat Bath, Detailed Balance and Return to Equilibrium

In both previous sections we have assumed that the reference state $\omega_{\rm R}$ of the reservoir $\mathcal{R}$ was a certain density matrix invariant with respect to the reservoir's dynamics. Now we assume that $\mathcal{R}$ is a *heat bath* at the inverse temperature $\beta = \frac{1}{kT}$. In the case of weak coupling limit it implies the additional relation (see Appendix A.3)

$$h_{\alpha\beta}(-\omega) = e^{-\beta\omega} h_{\beta\alpha}(\omega) \ , \tag{84}$$

and for the low density approximation

$$G(\boldsymbol{p}) = e^{-\beta E_{\boldsymbol{p}}} \Big/ \int d^3\boldsymbol{p}\, e^{-\beta E_{\boldsymbol{p}}} \ . \tag{85}$$

In both cases the obtained generators (61)–(64) and (78)–(83) satisfy a quantum detailed balance condition with respect to the Gibbs state

$$\rho_\beta = e^{-\beta H_{\rm S}} \big/ {\rm Tr} e^{-\beta H_{\rm S}} \ . \tag{86}$$

This condition may be formulated as follows.

Let L be a generator of a quantum dynamical semigroup written as

$$\mathrm{L} = -i[H_{\rm eff}, \bullet] + \mathrm{L_D} \ . \tag{87}$$

We say that L satisfies a *quantum detailed balance condition* with respect to the stationary state $\tilde{\rho} > 0$ if [21, 22]

$$[H_{\rm eff}, \tilde{\rho}] = 0 \tag{88}$$

and

$$(\mathrm{L_D^\star} A, B) = (A, \mathrm{L_D^\star} B) \ , \tag{89}$$

with $(A, B) = {\rm Tr}(\tilde{\rho}\, A^\star B)$ and all $A, B \in \{\text{domain } \mathrm{L}^\star\}$. For $\tilde{\rho} = \rho_\beta$ we may give an example of $\mathrm{L_D}$ satisfying (89):

$$\mathrm{L_D}\,\rho = \frac{1}{2}\sum_{\omega\geq 0}\{[V_\omega\,\rho, V_\omega^\star] + [V_\omega, \rho\,V_\omega^\star] + e^{-\beta\omega}\,[V_\omega^\star\rho, V_\omega] + e^{-\beta\omega}\,[V_\omega^\star, \rho\,V_\omega]\}\ , \tag{90}$$

where $e^{iH_\mathrm{S}t}V_\omega e^{-iH_\mathrm{S}t} = e^{-i\omega t}V_\omega$.

The most general form of the detailed balance generator with respect to ρ_β (for $\dim\mathcal{H}_\mathrm{S} < \infty$) may be written as

$$\mathrm{L} = -i[H_\mathrm{eff}, \bullet] + \sum_\alpha \left(\mathrm{or}\ \int P(d\alpha)\right)\mathrm{L}_\mathrm{D}^{(\alpha)}\ , \tag{91}$$

with $[H_\mathrm{eff}, H_\mathrm{S}] = 0$; $\mathrm{L}_\mathrm{D}^{(\alpha)}$ given by (90) and $P(\cdot)$ a positive measure.

We leave it to the reader to check that (61)–(64) and (78)–(83) are of the form (90), (91) under the conditions (84), (85) and (a) and (b) in (97). The Gibbs state ρ_β is a stationary state for L given by (90), (91). The question arises under what conditions the system *returns to equilibrium* for any initial state, i.e.,

$$\lim_{t\to\infty} e^{\mathrm{L}t}\rho = \rho_\beta \tag{92}$$

for all $\rho \in \mathcal{P}(\mathcal{H}_\mathrm{S})$.

The answer is rather simple in this case [23, 24].

From (89) it follows that $\mathrm{L}_\mathrm{D}^\star$ is a self-adjoint operator in the Hilbert space of operators with the scalar product $(A, B) = \mathrm{Tr}(\rho_\beta A^\star B)$. Hence (92) is equivalent to the fact that the only eigenvector of $\mathrm{L}_\mathrm{D}^\star$ to the eigenvalue 0 is $c\cdot\mathbb{1}$. This is true if and only if the equality

$$(X, \mathrm{L}_\mathrm{D}^\star X) = -\sum_\alpha\left(\mathrm{or}\ \int P(d\alpha)\right) \times \sum_{\omega\geq 0}\left\{\mathrm{Tr}\left(\rho_\beta\,[V_\omega^{(\alpha)}, X]^\star[V_\omega^{(\alpha)}, X]\right) + e^{-\beta\omega}\,\mathrm{Tr}\left(\rho_\beta\,[V_\omega^{(\alpha)\star}, X]^\star[V_\omega^{(\alpha)\star}, X]\right)\right\} = 0 \tag{93}$$

implies $X = c\cdot\mathbb{1}$.

Therefore, the condition (92) is equivalent to the following one:

$$\text{if}\ \ [V_\omega^{(\alpha)}, X] = [V_\omega^{(\alpha)\star}, X] = 0 \tag{94}$$

for all $\omega \geq 0$ and α, then $X = c\mathbb{1}$.

The extensive discussion of stationary states and ergodic properties of quantum dynamical semigroups may be found in [23–25].

The generators derived in Subsubsects. 1.3.2, 1.3.3 possess an interesting property. Namely if the spectrum of H_S is non degenerated then the diagonal and off-diagonal matrix elements of ρ_t in the energy representation *evolve independently* and the time evolution of diagonal ones is governed by the

Pauli master equation (42). The transition probabilities in the case of the weak coupling limit may be computed from the Fermi golden rule and in the case of the low density approximation are given by

$$a_{kl} = 2\pi\nu \int d^3\boldsymbol{p} \int d^3\boldsymbol{p}'\, G(\boldsymbol{p}) \times \delta\left\{(E_{\boldsymbol{p}'} + \epsilon_k) - (E_{\boldsymbol{p}} + \epsilon_l)\right\} \left|T_{kl}(\boldsymbol{p}', \boldsymbol{p})\right|^2 \tag{95}$$

If $\mathcal{R}$ is a heat bath, one may expect that the transition probabilities satisfy a *classical detailed balance condition*

$$a_{kl}\, e^{-\beta\omega_l} = a_{lk}\, e^{-\beta\omega_k} \ . \tag{96}$$

This is always true for the weak coupling limit but for the low density limit one of the following additional conditions must be fulfilled:

$$\begin{aligned} &(a) \quad T_{kl}(\boldsymbol{p}', \boldsymbol{p}) = T_{lk}(-\boldsymbol{p}, -\boldsymbol{p}'),\ E_{\boldsymbol{p}} = E_{-\boldsymbol{p}} \text{ – micro reversibility,} \\ &(b) \quad T_{kl}(\boldsymbol{p}', \boldsymbol{p}) = \overline{T}_{lk}(\boldsymbol{p}, \boldsymbol{p}') \text{ – hermiticity .} \end{aligned} \tag{97}$$

The latter is always satisfied in Born approximation.

1.3.5 Singular Coupling Limit

For the weak coupling or low density approximation the motion due to the dissipation is slow in comparison with the free motion of $\mathcal{S}$. Due to this fact we could neglect some oscillating terms in the equations of motion to obtain a proper Markovian master equation which depends strongly on the form of H_{S}. Then it is possible to describe properly the return to equilibrium for the systems coupled to a heat bath. However, there exists examples of quantum open systems strongly driven by some external macroscopic devices with asymptotic states far from equilibrium (e.g. laser systems) [26]. For such systems it is often justified to use the third method of derivation of Markovian master equation the so-called *singular coupling limit* [26–28]. By rescaling of the free Hamiltonian for the reservoir, $H_{\mathrm{R}} \to \epsilon^{-2} H_{\mathrm{R}}$ ($\epsilon \searrow 0$) we accelerate the decay of correlation in $\mathcal{R}$. In order to obtain a nonzero effect we rescale also the interaction Hamiltonian $H_{\mathrm{int}} \to \epsilon^{-1} H_{\mathrm{int}}$. Hence for $\epsilon \searrow 0$ the leading term in the integral equation (48) reads

$$W_t^{\epsilon} = U_t^0 + \frac{1}{\epsilon^2} \int_0^t ds\, U_{t-s}^0 \int_0^s du\, A_{01} U_u^{\mathrm{R},\epsilon} A_{10} W_{s-u}^{\epsilon} \ , \tag{98}$$

with $U_t^{\mathrm{R},\epsilon} = e^{-\frac{i}{\epsilon^2}[H_{\mathrm{R}}, \bullet]t}$ and $A = -i[H_{\mathrm{int}}, \bullet]$, $H_{\mathrm{int}} = \sum_\alpha Q_\alpha \otimes \varphi_\alpha$.

Changing variables $u \to \epsilon^2 \tau$ and putting $\epsilon \searrow 0$ we obtain finally the Markovian master equation

$$\frac{d}{dt}\rho_t = -i[H_{\mathrm{S}}, \rho_t] + K\rho_t \ , \tag{99}$$

with

$$K\rho = -\mathrm{Tr}_{\mathrm{R}} \int_0^\infty \left[H_{\mathrm{int}}, [e^{-iH_{\mathrm{R}}t} H_{\mathrm{int}}\, e^{iH_{\mathrm{R}}t}, \rho \otimes \omega_{\mathrm{R}}]\right] dt \ . \tag{100}$$

Using the properties of the correlation functions (Appendix A.3) one can transform (100) into a standard form (38) ($Q_\alpha = Q_\alpha^\star$),

$$K\rho = -[H', \rho] + \frac{1}{2} \sum_{\alpha,\beta} a_{\alpha\beta} \left\{[Q_\alpha, \rho\, Q_\beta] + [Q_\alpha \rho, Q_\beta]\right\} \ . \tag{101}$$

Here, $H' = \sum_{\alpha,\beta} S_{\alpha\beta} Q_\beta Q_\alpha$,

$$\int_0^\infty \mathrm{Tr}(\omega_{\mathrm{R}}\, \varphi_\alpha(t) \varphi_\beta) dt = \frac{1}{2} a_{\alpha\beta} + i S_{\alpha\beta} \ , \tag{102}$$

where $(a_{\alpha\beta})$ – a positive matrix, $S_{\alpha\beta} = \overline{S}_{\beta\alpha}$.

Finally, one should mention about the derivations of Markovian master equations without any approximations or limiting procedures. In the mathematical language it is a problem of *dilations of quantum dynamical semigroups* (see for example [29–31] and many references therein). There exists a number of such dilations from very abstract to more explicit and physical ones. For all of them the reservoirs are certain extreme idealizations of real systems with unbounded from below Hamiltonians and very singular couplings between $\mathcal{R}$ and $\mathcal{S}$. Some recently obtained dilations provide an equivalent description of Markovian open quantum systems in terms of certain Langevin – type *stochastic differential equations* which might be useful for applications too.

1.4 Extensions of the Formalism

1.4.1 Nonconservative Dynamical Semigroups

There are situations in which not a whole Hilbert space $\mathcal{H}_{\mathrm{S}}$ of the open system is of interest for us. The relevant pure states generate a linear subspace $\mathcal{H}_{\mathrm{S}}^0 \subset \mathcal{H}_{\mathrm{S}}$ with orthogonal projection $\mathit{\Pi} : \mathcal{H}_{\mathrm{S}} \to \mathcal{H}_{\mathrm{S}}^0$. The interesting part of the time dependent density matrix is given now by the formula

$$\sigma_t = T_t\, \sigma = \mathit{\Pi} \left\{\mathrm{Tr}_{\mathrm{R}} \left(U_t\, \sigma \otimes \omega_{\mathrm{R}} U_t^\star\right)\right\} \mathit{\Pi} \ , \tag{103}$$

where $\sigma \in \mathcal{T}(\mathcal{H}_{\mathrm{S}})$, $\sigma \geq 0$, $\sigma = \mathit{\Pi}\sigma\mathit{\Pi}$, $t \geq 0$, $U_t = e^{-iH_{\mathrm{tot}}t}$. T_t may be called a *nonconservative dynamical map* because $\mathrm{Tr} T_t\, \sigma \leq \mathrm{Tr}\sigma$. Obviously, the dual map $T_t^\star$ is completely positive but the unity preserving condition (8b) is replaced now by

$$T_t^\star \mathbb{1} \leq \mathbb{1} \ . \tag{104}$$

Imposing on $\{T_t, t \geq 0\}$ a semigroup condition one obtains from (88) the standard form of the *nonconservative quantum Markovian master equation*

$$\frac{d}{dt}\sigma_t = A\,\sigma_t + \sigma_t A^\star + \sum_\alpha V_\alpha \sigma_t V_\alpha^\star \ , \tag{105}$$

with $\sigma_t \in \mathcal{T}(\mathcal{H}_{\rm S}^0)$.

The operators A, V_α act on $\mathcal{H}_{\rm S}^0$ and satisfy

$$A + A^\star + \sum_\alpha V_\alpha^\star V_\alpha \ \leq \ 0 \ . \tag{106}$$

It follows that A may be written as

$$A = -iH_{\rm eff} - \frac{1}{2}\sum_\alpha V_\alpha^\star V_\alpha - B \ , \tag{107}$$

where $H_{\rm eff} = H_{\rm eff}^\star$ is an effective Hamiltonian and $B \geq 0$ may be called *optical potential*. As a possible application of such nonconservative semigroups one can mention a description of heavy-ion dissipative collisions including different channels of reaction [32].

1.4.2 Time-dependent Generators

The external conditions which influence an open system may vary in time. A natural extension of the Markovian master equation to this case involves *time-dependent generators*. We may write

$$\frac{d}{dt}\rho_t = {\rm L}_t\,\rho_t \tag{108}$$

where for all $t \geq 0$ ${\rm L}_t$ is a generator of a quantum dynamical semigroup. Under certain technical conditions the solution of (108) exists and may be written in terms of the two-parameter family of dynamical maps $\Lambda_{t,s}$, $t \geq s \geq 0$, which satisfies the relations

$$\rho_t = \Lambda_{t,s}\,\rho_s \ , \tag{109}$$

$$\Lambda_{t,r}\,\Lambda_{r,s} = \Lambda_{t,s} \ , \quad t \geq r \geq s \ , \tag{110}$$

$$\Lambda_{t,s} = \mathbf{T}\exp\int_s^t {\rm L}_\tau d\tau \tag{111}$$

with $\mathbf{T}$ – a chronological product.

The derivation of (108) from the underlying microscopic model is not an easy problem even if the temporal change of the external conditions is entirely due to the time-dependent perturbation of the Hamiltonian; $H_{\rm S} \mapsto H_{\rm S}(t) = H_{\rm S} + H_{\rm ext}(t)$ [33]. The reason of this difficulty is the appearance of an additional time scale associated with $H_{\rm ext}(t)$. Only if $H_{\rm ext}(t)$ is slowly varying with respect to the relaxation of $\mathcal{S}$ the final result is simple; ${\rm L}_t$ may be given by (61)–(64) calculated with $H_{\rm S}$ replaced by $H_{\rm S}(t)$ [34]. In more complicated situations it remains to use a phenomenological approach as presented in the lecture of Lendi.

1.4.3 Nonlinear Quantum Dynamical Semigroups

Nonlinear kinetic equations are commonly used in classical statistical mechanics. We mention here the Boltzmann equation, the Vlasov equation and the Landau equation which describe the dynamics of many-body systems in terms of the time-dependent probability distribution on the phase space of a single particle. All these equations are rigorous consequences of the microscopic Hamiltonian dynamics in the low density, the mean-field and the weak coupling limit respectively (see a review [8] and references therein). One may expect that in quantum theory the nonlinear equations for a single particle density matrix ρ_t might be used as a reasonable approximation describing the dynamics of many-body systems isolated or interacting with reservoirs. A well known example of such equation is the time-dependent Hartree equation [35] for many-body isolated systems. Its extension including linear dissipative terms was studied in [8]. Here we present some results of the paper [36] where the general theory of nonlinear quantum master equation was outlined and illustrated by a number of examples with nonlinear dissipative terms.

The general form of a nonlinear quantum master equation may be postulated as follows,

$$\frac{d}{dt}\rho_t = \mathrm{L}[\rho_t]\,\rho_t \ , \quad \rho_0 = \rho \ , \quad t \geq 0 \ , \tag{112}$$

where, for any $\sigma \in \mathcal{P}(\mathcal{H})$, $\mathrm{L}[\sigma]$ is a generator of a quantum dynamical semigroup. Under certain technical conditions on the function $\sigma \mapsto \mathrm{L}[\sigma]$ one can prove that (112) has a unique solution $\rho_t = \Phi_t(\rho)$ where $\{\Phi_t; t \geq 0\}$ is a one-parameter family of nonlinear maps on $\mathcal{P}(\mathcal{H})$ which satisfy the semigroup condition

$$\Phi_t(\Phi_s(\rho)) = \Phi_{t+s}(\rho) \ . \tag{113}$$

The above properties of $\{\Phi_t; t \geq 0\}$ follow immediately from its construction in terms of the following limiting procedure.

For a given partition $0 = t_0 < t_1 < \cdots < t_{n+1} = T$ of the interval $[0, T]$ such that $t_{k+1} - t_k \leq \Delta$, we define $\Phi_t^{(n,\Delta)}, t \in [0, T]$ by the recursive relation

$$\begin{gathered} \Phi_t^{(n,\Delta)}(\rho) = \rho \quad \text{for} \quad t = 0 \ , \\ \Phi_t^{(n,\Delta)}(\rho) = e^{\mathrm{L}[\Phi_{t_k}^{(n,\Delta)}(\rho)](t-t_k)} \Phi_{t_k}^{(n,\Delta)}(\rho) \ , \\ \text{for} \quad t \in [t_k, t_{k+1}] \ . \end{gathered} \tag{114}$$

Now, for any $t \in [0, T]$ we define

$$\rho_t = \Phi_t(\rho) = \lim_{\substack{n\to\infty \\ \Delta\to 0}} \Phi_t^{(n,\Delta)}(\rho) \ . \tag{115}$$

In the next two sections we briefly discuss two physically interesting examples of nonlinear quantum dynamical semigroups.

1.4.4 Discrete Quantum Boltzmann Equation

The first example of the nonlinear quantum master equation may be called *discrete quantum Boltzmann equation*. We present here a purely phenomenological justification of such equations but a suitable microscopic model might be constructed as well [36]. Consider N identical molecules with an internal structure which is described by a pure point spectrum Hamiltonian h. We assume that due to collisions of molecules the energy of internal excitations may be transferred from one molecule to another without being lost. Using the analogy with the classical Boltzmann equation one may propose the following equation of motion for the density matrix ρ_t describing the internal state of a single molecule,

$$\frac{d}{dt}\rho_t = -i[h,\rho_t] + \mathrm{Tr}_2\{K\rho_t\otimes\rho_t\} \tag{116}$$

Here, K denotes the following map acting on $\mathcal{T}(\mathcal{H}^{(1)}\otimes\mathcal{H}^{(2)})$ ($\mathcal{H}^{(1)},\mathcal{H}^{(2)}$ – the Hilbert spaces of the first and second molecule respectively),

$$K\gamma = \frac{1}{2}\sum_\alpha \{[T_\alpha\gamma, T_\alpha^\star] + [T_\alpha, \gamma T_\alpha^\star]\} \ , \tag{117}$$

with $\{T_\alpha\}$ – "transition matrices" describing the transfer of energy between molecules. The energy conservation implies

$$[T_\alpha, h^{(1)} + h^{(2)}] = 0 \ , \tag{118}$$

and some kind of "microreversibility" is supposed,

$$T_\alpha^\star\, T_\alpha = T_\alpha\, T_\alpha^\star \ . \tag{119}$$

Moreover, $\{T_\alpha\}$ are invariant with respect to the permutations of molecules. It is easy to check that (116) may be written in form (112) with $\mathrm{L}[\sigma]\rho = \mathrm{Tr}_2\{K\rho\otimes\sigma\}$.

The solutions of (116) possess the following properties which justify the name "quantum Boltzmann equation":

1) The energy per molecule $E_t = \mathrm{Tr}(\rho_t\, h)$ is conserved,

$$\frac{d}{dt}E_t = 0 \ . \tag{120}$$

2) The H-theorem is valid,

$$\frac{d}{dt}S(\rho_t) \geq 0 \ . \tag{121}$$

3) Gibbs states $\rho_\beta = e^{-\beta h}/\mathrm{Tr}e^{-\beta h}$, $\beta\in\mathbb{R}$ are stationary solutions of (116).

The properties 1), 3) are direct consequences of (118), (119), and the property 2) follows from the fact that due to (119) the semigroup e^{Kt} acting on $\mathcal{T}(\mathcal{H}^{(1)}\otimes\mathcal{H}^{(2)})$ preserves the infinite temperature state and hence by the remark at the end of Subsubsect. 1.2.3 increases the entropy.

1.4.5 Nonlinear Schrödinger Equation

The underlying microscopic model for the present example may be constructed as follows. We consider a system of N identical particles interacting with the reservoir $\mathcal{R}$ by means of the mean-field coupling. Hence the total Hamiltonian of the system is given by

$$H = \sum_{j=1}^{N} h^{(j)} + H_{\mathrm{R}} + \lambda \sum_{j=1}^{N} \sum_{\nu} Q_{\nu}^{(j)} \otimes \varphi_{\nu} \tag{122}$$

where $h^{(j)}$ is a single particle Hamiltonian, H_{R} – the Hamiltonian of $\mathcal{R}$, $Q_{\nu}^{(j)} = Q_{\nu}^{(j)\star}$ is a single particle observable and $\varphi_{\nu} = \varphi_{\nu}^{\star}$ is an operator acting on $\mathcal{H}_{\mathrm{R}}$.

The very structure of the generator of the quantum dynamical semigroup obtained from (122) is the same for the weak coupling and singular coupling limit and is given by the following expression,

$$\begin{aligned} \frac{d}{dt}\rho_t^{(N)} = &-i\left[\sum_{k=1}^{N} h^{(k)} + \frac{\lambda^2}{2}\sum_{k,l=1}^{N} U^{(k,l)}, \rho_t^{(N)}\right] \\ &+\frac{\lambda^2}{2}\sum_{\alpha}\sum_{k,l=1}^{N}\left\{[V_{\alpha}^{(k)}\rho_t^{(N)}, V_{\alpha}^{(l)\star}] + [V_{\alpha}^{(k)}, \rho_t^{(N)} V_{\alpha}^{(l)\star}]\right\} \end{aligned} \tag{123}$$

Here, $\rho_t^{(N)}$ is the N-particle density matrix, $U^{(k,l)},\ k \neq l$ describe two-particle interaction, $V_{\alpha}^{(k)}$ is a single-particle operator. The details of $V_{\alpha}^{(k)}$ and $U^{(k,l)}$ depend on the method of derivation, the form of the Hamiltonian (122) and the state of $\mathcal{R}$ and are irrelevant for the further discussion. The reduction of the N-particle dynamics to a single-particle one may be done by means of the so-called *mean-field limit*. It consists of replacing the coupling constant λ by $\lambda'/\sqrt{N}$ and putting as an initial state in (123) the product state $\underset{N}{\otimes}\rho$. Then one can show that in the limit $N \to \infty$ the product states evolve into the product states $\underset{N}{\otimes}\rho_t$ (up to the terms of order $N^{-1/2}$) such that ρ_t satisfies the following nonlinear equation of motion written again in terms of the physical coupling constant λ,

$$\frac{d}{dt}\rho_t = -i[(h + NU_{\mathrm{H}}[\rho_t] + NU_{\mathrm{D}}[\rho_t]), \rho_t] \ . \tag{124}$$

Here,

$$U_{\mathrm{H}}[\rho_t] = \lambda^2 \mathrm{Tr}_2\left\{U^{(1,2)} \mathbb{1} \otimes \rho\right\} \tag{125}$$

is the usual *Hartree potential* and

$$U_{\mathrm{D}}[\rho_t] = \frac{i}{2}\lambda^2 \sum_{\alpha}\{\mathrm{Tr}(V_{\alpha}^{\star}\rho)\, V_{\alpha} - \mathrm{Tr}(V_{\alpha}\rho)V_{\alpha}^{\star}\} \tag{126}$$

is a state-dependent "potential" describing *collective dissipative processes*.

Putting $\rho = |\psi\rangle\langle\psi|$ one obtains the *nonlinear dissipative Schrödinger equation* for ψ_t,

$$i\frac{d}{dt}\psi_t = h\psi_t + \lambda^2 N\langle\psi_t \mid U^{(1,2)} \mid \psi_t\rangle\psi_t + \frac{i}{2}\lambda^2 N\sum_\alpha \left(\langle\psi_t \mid V_\alpha^\star \mid \psi_t\rangle V_\alpha\psi_t - \langle\psi_t \mid V_\alpha \mid \psi_t\rangle V_\alpha^\star\psi_t\right) \ . \quad (127)$$

In the next chapter we shall apply the equation (127) to the model of superradiance.

1.5 A System of N Two-level Atoms

1.5.1 The Hamiltonian of the System

In this section we would like to illustrate the general theory presented in the previous sections by the example of N two-level atoms interacting with an electromagnetic field at a thermal equilibrium. This model was studied by many authors (see for example [37,38] and references therein) mainly for the zero-temperature case without discussion of the complete positivity.

The two-level atoms are located at fixed positions $\boldsymbol{r}_j$, $j = 1, 2, \ldots, N$. By S_j^α, $\alpha = 1, 2, 3$ we denote the spin - $\frac{1}{2}$ matrices associated with the j'th atom and $S_j^\pm = S_j^1 \pm iS_j^2$. The total Hamiltonian of the system which consists of N atoms and an electromagnetic field confined in a finite volume L^3 can be written as ($\hbar \equiv c \equiv 1$)

$$H = H_{\rm at}^{(N)} + H_{\rm rad}^L + H_{\rm int}^L \ , \quad (128)$$

where

$$H_{\rm at}^{(N)} = \omega\sum_{j=1}^N S_j^3 \ , \quad (129)$$

$$H_{\rm rad}^L = \sum_{\nu=1}^2\sum_{\boldsymbol{k}} |\boldsymbol{k}|\, a_{\boldsymbol{k},\nu}^\dagger a_{\boldsymbol{k},\nu} \ , \quad (130)$$

with

$$[a_{\boldsymbol{k},\nu}, a_{\boldsymbol{k}',\nu'}^\dagger] = \delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\nu\nu'},$$

and

$$\{\boldsymbol{k}\} = \left\{\left(\frac{2\pi n_1}{L}, \frac{2\pi n_2}{L}, \frac{2\pi n_3}{L}a\right), n_1, n_2, n_3 = 0, \pm1, \pm2, \ldots\right\} \ .$$

The interaction Hamiltonian is expressed in the electric dipole approximation,

$$H_{\rm int}^L = \sum_{j=1}^N \boldsymbol{\mathcal{D}}_j \otimes \boldsymbol{E}_{\rm reg}(\boldsymbol{r}_j) \tag{131}$$

where $\boldsymbol{\mathcal{D}}_j = 2\,\boldsymbol{d}\,S_j^1$ is an atomic electric dipole operator and $\boldsymbol{E}_{\rm reg}$ is a regularized electric field operator given by the formula

$$\boldsymbol{E}_{\rm reg} = i\sum_{\nu=1}^2 \sum_{\boldsymbol{k}\le\mathcal{K}} \left(\frac{2\pi|\boldsymbol{k}|}{L^3}\right)^{1/2} \boldsymbol{e}_{\boldsymbol{k},\nu} \left\{ e^{i\boldsymbol{k}\cdot\boldsymbol{r}} a_{\boldsymbol{k},\nu} - e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} a_{\boldsymbol{k},\nu}^\dagger \right\} , \tag{132}$$

with $\boldsymbol{e}_{\boldsymbol{k},\nu}$ – a unit polarization vector and $\mathcal{K}$ – an ultraviolet cut-off which is necessary for the intermediate calculations but will be eliminated in final formulas.

1.5.2 The Markovian Master Equation

The interaction Hamiltonian may be written in the following form,

$$H_{\rm int}^L = \sum_{j=1}^N \left(S_j^- + S_J^+\right) \otimes \varphi_j^L \ . \tag{133}$$

We apply now the weak coupling method (see Subsubsect. 1.3.2) to derive the Markovian master equation for the atomic system. The first step in this procedure is the evaluation of the correlation functions for a Gibbs state ω_β^L and taking the thermodynamic limit.

We obtain

$$\begin{aligned} f_{mn}(t) &= \lim_{L\to\infty} {\rm Tr}(\omega_\beta^L \varphi_m^L(t)\,\varphi_n^L) \\ &= \frac{1}{4\pi}\sum_{\nu=1}^2 \int_{|\boldsymbol{k}|\le\mathcal{K}} d^3\boldsymbol{k}\ |\boldsymbol{k}|(\boldsymbol{d}_m\boldsymbol{e}_{\boldsymbol{k},\nu})(\boldsymbol{d}_n\boldsymbol{e}_{\boldsymbol{k},\nu}) e^{i\boldsymbol{k}(\boldsymbol{r}_m-\boldsymbol{r}_n)} \\ &\quad \times \left\{ e^{-i|\boldsymbol{k}|t}(n_\beta(|\boldsymbol{k}|)+1) + e^{i|\boldsymbol{k}|t} n_\beta(|\boldsymbol{k}|) \right\} , \end{aligned} \tag{134}$$

with $n_\beta(x) = (e^{\beta x}-1)^{-1}$.

Using the identity $\int_0^\infty e^{ixt}dt = \pi\delta(x) + i\mathcal{P}\left(\frac{1}{x}\right)$ and changing the order of integration (that is possible because of the introduced cut-off $\mathcal{K}$) we obtain for $0<\omega<\mathcal{K}$

$$\int_0^\infty f_{mn}(t) e^{i\omega t}dt = \frac{1}{2}h_{mn}(\omega) + iS_{mn}^{\mathcal{K}}(\omega) \ , \tag{135}$$

where

$$\begin{aligned} h_{mn}(\omega) &= \frac{1}{2\pi}\sum_{\nu=1}^2 \int d^3\boldsymbol{k}\, e^{i\boldsymbol{k}(\boldsymbol{r}_m-\boldsymbol{r}_n)} \{|\boldsymbol{k}|(\boldsymbol{d}_m\boldsymbol{e}_{\boldsymbol{k},\nu}) \\ &\quad \times(\boldsymbol{d}_n\boldsymbol{e}_{\boldsymbol{k},\nu})(n_\beta(|\boldsymbol{k}|)+1)\,\delta(|\boldsymbol{k}|-\omega) \ , \end{aligned} \tag{136}$$

and $S^{\mathcal{K}}_{mn}(\omega)$ is a cut-off-dependent matrix given by

$$S^{\mathcal{K}}_{mn}(\omega) = -\frac{1}{2\pi}\sum_{\nu=1}^{2}\int_{|\boldsymbol{k}|\leq\mathcal{K}} d^3\boldsymbol{k}\, e^{i\boldsymbol{k}(\boldsymbol{r}_m-\boldsymbol{r}_n)}|\boldsymbol{k}|(\boldsymbol{d}_m\boldsymbol{e}_{\boldsymbol{k},\nu}) \times(\boldsymbol{d}_n\boldsymbol{e}_{\boldsymbol{k},\nu})\,\mathcal{P}\left\{\frac{n_\beta(|\boldsymbol{k}|)+1}{\omega-|\boldsymbol{k}|}+\frac{n_\beta(|\boldsymbol{k}|)}{\omega+|\boldsymbol{k}|}\right\}\ . \tag{137}$$

The matrix $(h_{mn}(\omega))$ is real and, as expected, positive-semidefinite. $S^{\mathcal{K}}_{mn}(\omega)$ is real and symmetric (see Appendix A.3). Both matrices are functions of the dipole vectors $\boldsymbol{d}_m, \boldsymbol{d}_n$ and the vectors $(\boldsymbol{r}_m - \boldsymbol{r}_n)$.

In the following we shall use the notation

$$\begin{aligned} &h_{mn}(\omega) = a_{mn}\ , \quad (a_{mn}) \geq 0\ , \\ &S^{\mathcal{K}}_{mn}(\omega) + S^{\mathcal{K}}_{mn}(-\omega) = \Omega^{\mathcal{K}}_{mn}\ . \end{aligned} \tag{138}$$

We remember that $(\Omega^{\mathcal{K}}_{mn})$ determines the Hamiltonian correction to $H^{(N)}_{\mathrm{at}}$. From (137) it follows that for $\mathcal{K}\to\infty$, Ω_{mn} is singular at the point $\boldsymbol{r}_m = \boldsymbol{r}_n$. Therefore, we obtain an infinite contribution to any free atom Hamiltonian $h^{(j)} = \omega S^3_j$. The usual procedure of removing it is the renormalization which consists in adding to $h^{(j)}$ a suitable $\mathcal{K}$-dependent counterterm.

The form of $\Omega_{mn} = \lim_{\mathcal{K}\to\infty}\Omega_{mn}$ $(\boldsymbol{r}_m \neq \boldsymbol{r}_n)$ may be found only approximately. Detailed analysis shows that the associated Hamiltonian $H'^{(N)} = \sum_{m\neq n}\Omega_{mn}S^+_mS^-_n$ can be interpreted as the dipole-dipole Van der Waals interaction between atoms.

The manifest form of a_{mn} can be easily calculated for the case of parallel dipoles $\boldsymbol{d}_m = \boldsymbol{d}$, $m = 1, 2, \ldots, N$.

Then,

$$a_{mn} = \frac{4}{3}\boldsymbol{d}^2\omega^3(n_\beta(\omega)+1)\left\{j_0(\xi_{mn}) + P_2(\cos\Theta_{mn})j_2(\xi_{mn})\right\}\ , \tag{139}$$

in terms of Bessel-functions

$$\begin{aligned} j_0(x) &= \frac{1}{x}\sin x\ , \\ j_2(x) &= \left(\frac{3}{x^3}-\frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x\ , \end{aligned} \tag{140}$$

and the Legendre-polynomial

$$P_2(\varphi) = \frac{1}{2}(3\varphi^2 - 1)\ . \tag{141}$$

Here,

$$\xi_{mn} = \omega|\boldsymbol{r}_m - \boldsymbol{r}_n|\ , \quad \cos\Theta_{mn} = \frac{\boldsymbol{d}(\boldsymbol{r}_m-\boldsymbol{r}_n)}{|\boldsymbol{d}||\boldsymbol{r}_m-\boldsymbol{r}_n|}\ . \tag{142}$$

The final form of the Markovian master equation for the N-atomic density matrix $\rho_t^{(N)}$ reads

$$\frac{d}{dt}\rho_t^{(N)} = -i\omega \sum_{m=1}^{N} \left[S_m^3, \rho_t^{(N)}\right] - i \sum_{m\neq n=1}^{N} \Omega_{mn} \left[S_m^+ S_n^-, \rho_t^{(N)}\right]$$
$$+\frac{1}{2} \sum_{m,n=1}^{N} a_{mn} \left\{ \left[S_m^- \rho_t^{(N)}, S_n^+\right] + \left[S_m^-, \rho_t^{(N)} S_n^+\right] \right.$$
$$\left. +e^{-\beta\omega} \left[S_m^+ \rho_t^{(N)}, S_n^-\right] + e^{-\beta\omega} \left[S_m^+, \rho_t^{(N)} S_n^-\right] \right\} \tag{143}$$

1.5.3 Return to Equilibrium and Superradiance

As a consequence of the general theory (143) satisfies the quantum detailed balance condition with respect to the Gibbs state $\rho_\beta^{(N)} = e^{-\beta H_{\rm at}^{(N)}}/{\rm Tr} e^{-\beta H_{\rm at}^{(N)}}$.

The question of return to equilibrium is not trivial in general. We discuss first the simplest case

$$a_{mn} = \gamma\, \delta_{mn}\ , \quad \gamma > 0 \tag{144}$$

This is a good approximation if the distances between atoms are much longer than the wave length $\lambda = \frac{2\pi}{\omega}$. We see now immediately that the condition (93) is fulfilled and hence (91) holds.

We assume now that (a_{mn}) satisfies the following condition:

the matrix (a_{mn}) is *strictly positive*;

$$(a_{mn}) > 0\ , \quad \text{with the lowest eigenvalue } \epsilon > 0\ . \tag{145}$$

Then, the dissipative part of the generator defined by (143) may be written as

$$\mathrm{L}_D = \mathrm{L}'_D + \mathrm{L}^\epsilon_D\ , \tag{146}$$

where L'_D is given by (143) with a_{mn} replaced by $a'_{mn} = a_{mn} - \epsilon\delta_{mn}$ and L^ϵ_D is obtained putting $a_{mn} = \epsilon\, \delta_{mn}$.

According to the results of Subsubsect. 1.3.4 - $\mathrm{L}^\star_D$, - ${\mathrm{L}'}^\star{}_D$ and - L^ϵ_D are positive operators on the Hilbert space $\mathcal{B}(\mathcal{H}^{(N)})$ with a scalar product $(A,B)_\beta = {\rm Tr}(\rho_\beta^{(N)} A^\star B)$. Hence if $\mathrm{L}^\star_D X = 0$ then $\mathrm{L}^{\epsilon\star}_D X = 0$, too. Because, as stated above, $\mathrm{L}^{\epsilon\star}_D X = 0$ if and only if $X = c\mathbb{1}$, then (145) implies that our system returns to the equilibrium.

However, if ϵ is very small then the relaxation to $\rho_\beta^{(N)}$ may be very slow and one observes the transient non-ergodic behavior of the system which evolves towards a quasi-stationary state depending on its initial state. The examples of such type of behavior called subradiance or limited superradiance were recently studied both theoretically and experimentally [38–40] mainly for multilevel atoms.

We discuss now a simple theoretical model which describes at least qualitatively the subradiance and superradiance phenomena (for a review see [38]). Putting $a_{mn} = \delta$ for all $m, n = 1, 2, \ldots, N$ and $\Omega_{mn} = 0$ one obtains the following generator of a quantum dynamical semigroup,

$$\begin{aligned} \mathrm{L}\,\rho^{(N)} = -i\omega \left[S_N^3, \rho^{(N)}\right] + \frac{\delta}{2} \Big\{ \left[S_N^- \rho^{(N)}, S_N^+\right] + \left[S_N^-, \rho^{(N)} S_N^+\right] \\ + e^{-\beta\omega} \left[S_N^+ \rho^{(N)}, S_N^-\right] + e^{-\beta\omega} \left[S_N^+, \rho^{(N)} S_N^-\right] \Big\} \ , \end{aligned} \tag{147}$$

with $S_N^\alpha = \sum_{j=1}^N S_j^\alpha$.

The subspace of operators X satisfying

$$[S_N^\alpha, X] = 0 \ , \quad \alpha = +, -, 3 \tag{148}$$

is not trivial [41]. It contains for example projectors on the subspace of N-atomic states with a given symmetry with respect to permutations of atoms. Therefore the probability of finding the system in a state of a given symmetry is a constant of motion. This explains the origin of subradiance phenomenon, i.e., the energy trapping due to a quantum interference between atoms. The generator (147) is of a mean-field type as studied in the Subsubsect. 1.4.5. The associated nonlinear Schrödinger equation (127) is of the following form,

$$i\frac{d}{dt}\psi_t = \omega S^3 \psi_t - i\frac{\delta' N}{2} \left\{ \langle \psi_t \mid S^+ \mid \psi_t \rangle S^- \psi_t - \langle \psi_t \mid S^- \mid \psi_t \rangle S^+ \psi_t \right\} \ , \tag{149}$$

with $\delta' = \delta \left(1 - e^{-\beta\omega}\right)$.

Introducing the parameterization

$$\psi_t = \begin{pmatrix} \sqrt{p_t}\, e^{i\Theta_t} \\ \sqrt{1-p_t}\, e^{i\Theta'_t} \end{pmatrix} \ , \quad p_t \in [0,1] \ , \quad \Theta_t \, , \, \Theta'_t \in \mathbb{R} \ , \tag{150}$$

one obtains from (149)

$$\begin{aligned} \frac{d}{dt}\Theta_t = \frac{d}{dt}\Theta'_t = 0 \ , \\ \frac{dp_t}{dt} = -\delta' N (1-p_t) p_t \ , \end{aligned} \tag{151}$$

with the solution

$$\begin{aligned} \Theta_t = \Theta_0 \ , \quad \Theta'_t = \Theta'_0 \\ p_t = \left(e^{\delta' N (t - t_D)} + 1\right)^{-1} \ , \\ t_D = \frac{1}{\delta' N} \ln\left(\frac{p_0}{1-p_0}\right) \ . \end{aligned} \tag{152}$$

The radiated energy

$$I(t) = -N\omega \frac{d}{dt} p_t = \frac{\omega\, \delta' N^2}{2} \cosh^{-2} \left\{ \frac{1}{2} N \delta'(t - t_D) \right\} \tag{153}$$

shows an N^2-dependence and a bell-shape typical for superradiance.

The equation (149), written explicitely in terms of matrix elements of $\rho_t = |\psi_t\rangle\langle\psi_t|$, is well known [38] but the derivations are usually based on different arguments then those used in Subsubsect. 1.4.5.

2 Quantum Dynamical Semigroups for Unstable Particles

2.1 Introduction

This section of the notes is devoted to the presentation of a special class of quantum dynamical semigroups the, so-called quasi-free completely positive semigroups. Despite of their mathematical simplicity due to the fact that they are exactly soluble the range of their possible applications is rather wide. It includes all processes which can be formally described in terms of decomposition and production of noninteracting particles or quasi-particles which can be treated at least approximately as bosons or fermions. We give a few examples of such phenomena:

1. Decay of elementary particles and light nuclei if the interaction among them can be neglected.
2. Linear dissipation and pumping in open quantum systems with quadratic Hamiltonians.
3. Propagation of quantized electromagnetic waves in absorbing and radiating media in the absence of nonlinear effects.
4. Transition between a set of excited electronic states and a large number of low lying states under the assumption that only a small fraction of electrons is being excited and the transition accompany the emission and absorption of energy quanta (photons, phonons, etc.).

We begin with an analysis of the linearly damped and pumped harmonic oscillator which provides the simplest example of bosonic quasi-free dynamical semigroup 2.2. Then in Subsubsects. 2.3.2–2.3.3 the generators are constructed which describe unstable bosons or fermions and the simplified single-particle formalism is introduced following the results of references [41–43]. The independently developed theory of quasi-free completely positive maps and semigroups [44, 45] provides the exact solutions of the Markovian master equations for unstable particles 2.3.4. The derivation of such Markovian master equations from the underlying Hamiltonian dynamics is discussed in Subsubsect. 2.3.5 for the Lee-type nonrelativistic and non-local field theories [41–43]. Finally a phenomenological model of relativistic unstable particles is studied [46].

2.2 Damped and Pumped Quantum Harmonic Oscillator

2.2.1 Derivation of the Markovian Master Equation

Consider the phonon picture of the quantum harmonic oscillator. The Hamiltonian may be written as

$$H_{\rm osc} = \omega\, a^\dagger a \ , \tag{154}$$

where the annihilation and creation operators fulfill the commutation rule

$$[a, a^\dagger] = 1 \ . \tag{155}$$

The eigenstates $\{|n\rangle;\ n = 0, 1, 2, \ldots\}$ of $H_{\rm osc}$ satisfy

$$a^\dagger a|n\rangle = n|n\rangle \tag{156}$$

and are interpreted as n-phonon states.

We assume now that the harmonic oscillator interacts with a reservoir. The effect of the interaction is a "friction force" which decreases the energy of the oscillator and a pumping "Langevin force" increasing the energy. In the phonon language it is described by the decay and production of phonons. According to the discussion in Subsubsect. 1.2.5 these two processes might be represented by two transition maps Φ_1 and Φ_2.

We assume that

$$\Phi_1(|n\rangle\langle n|) = C_n^1|n-1\rangle\langle n-1| \tag{157}$$

$$\Phi_2(|n\rangle\langle n|) = C_n^2|n+1\rangle\langle n+1| \tag{158}$$

The simplest choice of Φ_1, Φ_2 satisfying (157)–(158) is the following,

$$\Phi_1\rho \ = \ \gamma\, a\, \rho\, a^\dagger \ , \quad \gamma \geq 0 \tag{159}$$

$$\Phi_2\rho \ = \ \delta\, a^\dagger\, \rho\, a \ , \quad \delta \geq 0 \tag{160}$$

which leads to the well-known Markovian master equation

$$\frac{d}{dt}\rho_t = -i\omega[a^\dagger a, \rho_t] + \frac{1}{2}\gamma\left\{[a\,\rho_t, a^\dagger] + [a, \rho_t\, a^\dagger]\right\} + \frac{1}{2}\delta\left\{[a^\dagger\rho_t, a] + [a^\dagger, \rho_t\, a]\right\} \ . \tag{161}$$

The above derivation was purely phenomenological. One may construct, of course, Hamiltonian models of the harmonic oscillator coupled to the reservoir $\mathcal{R}$ and apply for example the weak coupling limit 1.3.2 [47]. The most general interaction Hamiltonian which leads to (161) must be linear in the operators $a, a^\dagger$.

2.2.2 Birth and Death Process, Kinetic Equation

Comparing (161) with (89) under the assumption $\delta < \gamma$ we see that the generator appearing in (161) satisfies a quantum detailed balance condition with respect to the stationary state $\rho_\beta = e^{-\beta\omega a^\dagger a}/\mathrm{Tr}e^{-\beta\omega a^\dagger a}$ with $\beta = \frac{1}{\omega}\ln(\gamma/\delta)$. Moreover according to the condition (93) the system returns to ρ_β for any initial state ρ. As mentioned in Subsubsect. 1.3.4 the diagonal elements of the density matrix ρ_t in the phonon number representation denoted by $p_n(t)$ evolve independently from off-diagonal ones. Their evolution is governed by the following master equation describing birth and death process,

$$\frac{d}{dt}p_n(t) = \gamma(n+1)\,p_{n+1}(t) + \delta\,n\,p_{n-1}(t) \\ -[\gamma n + \delta(n+1)]\,p_n(t) \qquad n = 0, 1, 2, \ldots \tag{162}$$

One can find also the closed equation for the mean number of phonons $\bar{n}_t = \mathrm{Tr}(\rho_t\, a^\dagger a)$,

$$\frac{d}{dt}\,\overline{n}_t = \mathrm{Tr}\big((\mathrm{L}\,\rho_t)\,a^\dagger a\big) = \mathrm{Tr}\,\big(\rho_t\,\mathrm{L}^\star a^\dagger a\big) \tag{163}$$

Using the explicit form of $\mathrm{L}^\star$ and the commutation relation one obtains the kinetic equation

$$\frac{d}{dt}\overline{n}_t = -(\gamma-\delta)\,\overline{n}_t + \delta\ . \tag{164}$$

2.2.3 Explicit Solutions

The model of the damped and pumped oscillator given by (161) is exactly soluble. This fact may be expressed in many equivalent ways but we discuss only two of them.

For any complex number α we define the unitary *Weyl operator*

$$W(\alpha) = \exp\frac{i}{\sqrt{2}}(\alpha a + \overline{\alpha}a^\dagger)\ . \tag{165}$$

Weyl operators satisfy the relations

$$W(\alpha)\,W(\beta) = W(\alpha+\beta)\exp\frac{1}{4}(\overline{\alpha}\,\beta - \alpha\,\overline{\beta})\ , \tag{166}$$

$$W(\alpha)\,aW^\star(\alpha) = a - \frac{i}{\sqrt{2}}\overline{\alpha}\ , \\ W(\alpha)\,a^\dagger W^\star(\alpha) = a^\dagger + \frac{i}{\sqrt{2}}\alpha\ . \tag{167}$$

Define now the following map acting on Weyl operators [48],

$$\Lambda_t^\star W(\alpha) = \exp\left\{-\frac{|\alpha|^2}{4}\frac{\gamma}{\gamma-\delta}\left(1-e^{-(\gamma-\delta)t}\right)\right\}W(\alpha_t)\ , \\ \text{where} \qquad \alpha_t = \exp\left\{-(i\omega+\frac{1}{2}(\gamma-\delta))t\right\}\alpha, \quad t\geq 0\ . \tag{168}$$

Using (166) and (167) one can differentiate the expression (168) with respect to t and show that

$$\frac{d}{dt}\Lambda_t^\star W(\alpha) = \mathrm{L}^\star \Lambda_t^\star W(\alpha) \ , \tag{169}$$

where $\mathrm{L}^\star$ is a Heisenberg generator dual to the generator defined by (161).

Hence $\Lambda_t^\star$ given by (168) is the Heisenberg picture version of the quantum dynamical semigroup governed by (161). Another representation of the solution is given in terms of the ordered products $a^{\dagger m}a^n$.

We define the map $\Lambda_t^\star$, $t \geq 0$, as follows,

$$\begin{aligned} \Lambda_t^\star \mathbb{1} &= \mathbb{1} \ , \\ \Lambda_t^\star a^{\dagger m} a^n &= \sum_{r=0}^{\min(m,n)} \frac{m!n!}{(m-r)!(n-r)!r!} \left[\frac{\delta}{\gamma-\delta}\left(1-e^{-(\gamma-\delta)t}\right)\right]^r \\ &\quad \left(e^{(i\omega-\frac{1}{2}(\gamma-\delta))t}a^\dagger\right)^{(m-r)} \left(e^{(-i\omega-\frac{1}{2}(\gamma-\delta))t}a\right)^{(n-r)} \ . \end{aligned} \tag{170}$$

Again taking the time derivative of (170) one can explicitely show the equivalence of (168) and (170).

There exists also other representations of the discussed semigroup. One can mention here coherent states representations (see [48] and references therein) explicit forms of Λ_t as integral kernels in position or momentum representation [49], the description of Λ_t in terms of Markov processes on groups [50]. The most suitable form for a rigorous mathematical analysis is (168) which involves bounded operators only.

2.3 Models of Unstable Particles

2.3.1 Fock Spaces and Quantum Fields

The harmonic oscillator is the simplest model of a many-boson system with a trivial one-dimensional single-particle Hilbert space $\mathcal{H}_1 = \mathbb{C}$. Now we generalize the presented description of decay and production processes to the case of indistinguishable particles /bosons or fermions/ with arbitrary $\mathcal{H}_1$. We treat bosons and fermions on the same footing and in all expressions with double sign $(\pm)$, the sign $(+)$ refers to bosons and $(-)$ to fermions.

The single particle Hilbert space $\mathcal{H}_1$ is represented as a L^2 space of wave functions $\xi \mapsto \psi(\xi)$ where $\xi = (x, \sigma)$. Here x represents continuous variables and σ discrete ones. The scalar product is given by

$$\langle \psi \mid \varphi \rangle = \int d\xi \ \bar{\psi}(\xi)\varphi(\xi) \ , \tag{171}$$

where $\int d\xi \equiv \sum_\sigma \int dx$.

The n-particle Hilbert space is defined as

$$\mathcal{H}_n = \Gamma^{(\pm)} \left\{ \underset{n}{\otimes} \mathcal{H}_1 \right\} \ , \tag{172}$$

where $\Gamma^{(\pm)}$ is a projection on the symmetric $(+)$ or antisymmetric $(-)$ subspace. The elements of $\mathcal{H}_n$ are denoted by $\psi_n(\xi_1, \xi_2, \ldots, \xi_n)$, and we put $\mathcal{H}_0 = \mathbb{C}$. The system under consideration is a many-body system with varying number of particles and the suitable Hilbert space is a Fock space $\mathcal{F}$ defined as an orthogonal sum

$$\mathcal{F} = \overset{\infty}{\underset{n=0}{\oplus}} \mathcal{H}_n \ . \tag{173}$$

We shall use the notation

$$\Psi \in \mathcal{F} \ ; \quad \Psi = (\psi_0, \psi_1, \ldots) \ , \quad \psi_n \in \mathcal{H}_n \ , \quad \psi_n \equiv (\Psi)_n \ .$$

Let $f, g \in \mathcal{H}_1$; then the associated annihilation and creation operators are defined as follows

$$\begin{aligned} (a[f]\,\Psi)_n(\xi_1, \ldots, \xi_n) &= (n+1)^{1/2} \int d\xi\, \bar{f}(\xi)\, \psi_{n+1}(\xi, \xi_1, \ldots, \xi_n) \ , \\ (a^\dagger[g]\,\Psi)_n(\xi_1, \ldots, \xi_n) &= (n)^{-1/2} \sum_{j=1}^{n} (\pm 1)^j g(\xi_j)\, \psi_{n-1}(\xi_1, \ldots, \xi_{j-1}, \xi_{j+1}, \ldots, \xi_n), \end{aligned} \tag{174}$$

and satisfy the canonical commutation or anticommutation relations

$$\begin{aligned} [a[f], a[g]]_\pm &= \left[a^\dagger[f], a^\dagger[g]\right]_\pm = 0 \\ \left[a[f], a^\dagger[g]\right]_\pm &= \langle f \mid g \rangle \end{aligned} \tag{175}$$

Here $[A, B]_+ \equiv [A, B] = AB - BA$, $[A, B]_- \equiv \{A, B\} = AB + BA$.

We shall use also the quantum fields $a(\xi)$, $a^\dagger(\xi)$ being operator-valued distributions and defined by the following expressions,

$$a[f] = \int d\xi\, \bar{f}(\xi)\, a(\xi) \ , \quad a^\dagger[g] = \int d\xi\, g(\xi)\, a^\dagger(\xi) \ . \tag{176}$$

The CCR or CAR in terms of quantum fields have the following form

$$\begin{aligned} [a(\xi), a(\xi')]_\pm &= [a^\dagger(\xi), a^\dagger(\xi')]_\pm = 0 \ , \\ [a(\xi), a^\dagger(\xi')]_\pm &= \delta(\xi - \xi'), \quad \delta(\xi - \xi') = \delta_{\sigma\sigma'}\delta(x - x') \ . \end{aligned} \tag{177}$$

Using quantum fields one can construct all observables of our system (for fermions one takes always "even functions" of quantum fields). The important class of them consists of single-particle observables which represent additive physical quantities like kinetic energy, momentum components, number of particles etc.. All of them may be written as

$$A_{\mathrm{F}} = \int d\xi \int d\xi' A_1(\xi \mid \xi')\, a^\dagger(\xi)\, a(\xi') \ , \tag{178}$$

where $A_1(\xi \mid \xi')$ is an integral kernel (generally a distribution) representing an operator A_1 acting on $\mathcal{H}_1$ as follows,

$$(A_1\psi)(\xi) = \int d\xi' A_1(\xi \mid \xi')\,\psi(\xi') \ . \tag{179}$$

The states of the system are described by density matrices $\rho \in \mathcal{P}(\mathcal{F})$ on Fock space. Very often we are interested in the expectation values of additive observables only. In these cases we may use a simplified description of a many-body system in terms of a reduced single-particle density matrix $\rho^{(1)}$. It is a trace-class positive operator acting on $\mathcal{H}_1$ and defined by the relation

$$\mathrm{Tr}(\rho\, A_{\mathrm{F}}) = \mathrm{Tr}(\rho^{(1)} A_1) \ . \tag{180}$$

Putting $A_1 = \mathbb{1}$ we obtain the normalization condition

$$\mathrm{Tr}\rho^{(1)} = \mathrm{Tr}\left(\rho \int d\xi\, a^\dagger(\xi)\, a(\xi)\right) \ , = \overline{N} \tag{181}$$

where $\overline{N}$ is a mean number of particles in the state ρ. The single particle density matrix $\rho^{(1)}$ may be represented as an integral kernel

$$\rho^{(1)}(\xi \mid \xi') = \mathrm{Tr}(\rho\, a^\dagger(\xi')\, a(\xi)) \ . \tag{182}$$

2.3.2 Construction of Markovian Master Equation

We construct now using phenomenological arguments the generator of a quantum dynamical semigroup which describes the decay and creation processes of unstable bosons or fermions. We assume the existence of two orthonormal sets of vectors in $\mathcal{H}_1$ denoted by $\{\varphi_k\}$ and $\{\psi_m\}$ which represent the independent decay and production modes, respectively. Then, similarly to the case of the harmonic oscillator we may define the transition map Φ as the following sum,

$$\Phi = \sum_k \Phi_1^{(k)} + \sum_m \Phi_2^{(m)} \ , \tag{183}$$

with

$$\begin{aligned} \Phi_1^{(k)}\rho &= \gamma_k\, a[\phi_k]\, \rho\, a^\dagger\,[\phi_k] \ , \\ \Phi_2^{(m)}\rho &= \delta_m\, a^\dagger\,[\psi_m]\, \rho\, a\,[\psi_m] \ . \end{aligned} \tag{184}$$

As a consequence, we obtain the following master equation in the Schrödinger picture,

$$\begin{aligned} \frac{d}{dt}\rho_t = -i[H,\rho_t] &+ \frac{1}{2}\sum_k \gamma_k \left\{ \left[a[\varphi_k]\,\rho_t, a^\dagger[\varphi_k]\right] \right. \\ &\left. + \left[a[\varphi_k], \rho_t\, a^\dagger[\varphi_k]\right] \right\} + \frac{1}{2}\sum_m \delta_m \left\{ \left[a^\dagger[\psi_m]\,\rho_t, a[\psi_m]\right] \right. \\ &\left. + \left[a^\dagger[\psi_m], \rho_t\, a[\psi_m]\right] \right\} \ . \end{aligned} \tag{185}$$

Defining the *decay operator* Γ as

$$\Gamma = \sum_k \gamma_k |\varphi_k\rangle\langle\varphi_k| \ , \tag{186}$$

and the *production operator* Δ

$$\Delta = \sum_m \delta_m |\psi_m\rangle\langle\psi_m| \ , \tag{187}$$

with integral kernels $\Gamma(\xi \mid \xi')$, $\Delta(\xi \mid \xi')$ respectively, we obtain an equivalent form of (185),

$$\begin{aligned}\frac{d}{dt}\rho_t = -i[H,\rho_t] + \frac{1}{2}\int d\xi \int d\xi' \big\{ \Gamma(\xi \mid \xi') \big([a(\xi)\rho_t, a^\dagger(\xi')] \\ + [a(\xi), \rho_t\, a^\dagger(\xi')] \big) + \Delta(\xi \mid \xi') \big([a^\dagger(\xi)\rho_t, a(\xi')] \\ + [a^\dagger(\xi), \rho_t\, a(\xi')] \big) \big\} \ .\end{aligned} \tag{188}$$

This representation may be used for positive operators Γ and Δ with continuous spectrum also.

2.3.3 Single-particle Description

For a harmonic oscillator it was possible to obtain a closed kinetic equation for the mean number of particles. The analogical simplified description of unstable particles in terms of a single-particle density matrix $\rho_t^{(1)}$ exists also. We consider a model of noninteracting particles, i.e., $H = H_{\rm F}$ where $H_{\rm F}$ is given by a single-particle Hamiltonian H_1 according to (178).

Defining now $\rho_t^{(1)}$ by (182) and using (188) one obtains a closed equation for $\rho_t^{(1)}$,

$$\frac{d}{dt}\rho_t^{(1)} = -i[H_1, \rho_t^{(1)}] - \frac{1}{2}\Big\{ (\Gamma - (\pm)\Delta), \rho_t^{(1)} \Big\} + \Delta \ . \tag{189}$$

One immediately finds the solution of (189) as

$$\rho_t^{(1)} = T_t\, \rho_0^{(1)} T_t^\star + \int_0^t T_s\, \Delta\, T_s^\star ds \tag{190}$$

where $T_t = \exp\big\{ \big[-iH_1 - \frac{1}{2}(\Gamma - (\pm)\Delta) \big]\, t \big\}$. The equation (189) finds applications in quantum optics as the so-called *Lamb equation* (see the lecture by Lendi).

In the absence of production processes $\Delta = 0$ and for $\rho_0^{(1)} = |\psi_0\rangle\langle\psi_0|$, (166) leads to

$$\rho_t^{(1)} = |\psi_t\rangle\langle\psi_t| \ , \quad \psi_t = e^{(-iH_1 - \frac{1}{2}\Gamma)t}\psi_0 \ . \tag{191}$$

We recover the usual phenomenological description of unstable particles in terms of a "complex Hamiltonian" $H - \frac{i}{2}\Gamma$. Obviously, for interacting particles the equation of motion for $\rho_t^{(1)}$ is not closed and a whole BBKGY hierarchy is involved. However, even in this case one may use (189) with H_1 replaced by the non-linear Hartree-Fock Hamiltonian as a reasonable approximation.

2.3.4 Explicit Solutions

We restrict ourselves to the case of noninteracting particles, i.e., $H = H_{\rm F}$. As suggested by the example of the harmonic oscillator the explicit representation of the dynamics governed by (188) may be constructed using the single-particle contracting semigroup T_t. Indeed, let us define for all $t \geq 0$ the Heisenberg map $\Lambda_t^\star$ on the set of ordered products of creation and annihilation operators (in the fermionic case we take $m = n$) by

$$\Lambda_t^\star \mathbb{1} = \mathbb{1} \ ,$$

$$\begin{aligned} &\Lambda_t^\star \left(a^\dagger[f_1] \cdots a^\dagger[f_m] a[g_1] \cdots a[g_n] \right) \\ &= \sum_P \epsilon^{(\pm)} \, (\text{perm, det}) \, \{ \langle f_{j_k} \mid Q_t \mid g_{i_l} \rangle \} \, a^\dagger[T_t^\dagger f_{\alpha_1}] \cdots \\ &\quad \cdots a^\dagger[T_t^\dagger f_{\alpha_{m-r}}] a[T_t^\dagger g_{\beta_1}] \cdots a[T_t^\dagger g_{\beta_{n-r}}] \ . \end{aligned} \tag{192}$$

The sum is taken over all partitions $\{(j_1, \ldots, j_r)(\alpha_1, \ldots, \alpha_{m-r})\}$, $\{(i_1, \ldots, i_r)(\beta_1, \ldots, \beta_{n-r})\}$ of $\{1, 2, \ldots, m\}, \{1, 2, \ldots, n\}$ such that $j_1 < j_2 < \cdots < j_r$, $\alpha_1 < \alpha_2, \cdots, \alpha_{m-r}$, $i_1 < i_2 < \cdots < i_r$, $\beta_1 < \beta_2, \cdots, \beta_{n-r}$; $\epsilon^+ = 1$, ϵ^- is a product of signatures of permutations $\{1, 2, \ldots, m\} \to \{j_1, \ldots, j_r, \alpha_1, \ldots, \alpha_{m-r}\}$, $\{1, 2, \ldots, n\} \to \{i_1, \ldots, i_r, \beta_1, \ldots, \beta_{n-r}\}$; a permanent is taken for bosons, a determinant for fermions;

$$Q_t = \int_0^t T_s \, \Delta \, T_s^\star ds \ . \tag{193}$$

For bosons the creation and annihilation operators are unbounded. Hence, for mathematical reasons it is more convenient to define the action of $\Lambda_t^\star$ on Weyl operators

$$W(f) = \exp \frac{i}{\sqrt{2}} \{ a[f] + a^\dagger[f] \} \ . \tag{194}$$

The definition equivalent to (192) for the bosonic case is the following,

$$\Lambda_t^\star W(f) = \exp \left\{ -\frac{1}{4} \langle f \mid R_t \mid f \rangle \right\} W(T_t^\star f) \tag{195}$$

where

$$R_t = \int_0^t T_s \Gamma \, T_s^\star ds \ . \tag{196}$$

Again, like for the harmonic oscillator the equivalence of (195) or (192) with the time-evolution governed by (188) (with $H = H_{\rm F}$) may be checked by differentiation of (195), (192) with respect to t and use of CCR or CAR.

The formulas (195) and (192) for bosons and fermions, respectively, may be treated as rigorous definitions of the quantum dynamical semigroup

$\{\Lambda_t^\star, t \geq 0\}$. Such semigroups are the so-called quasi-free completely positive semigroups on CCR and CAR algebras studied extensively in references [44, 45]. To explain this notion we remind first of the definition of a quasi free state. These states defined on algebras of observables constructed from boson or fermion fields are quantum analogons of Gaussian probability distributions. Namely, denoting by $\omega(A)$ the mean value of an observable A in a state ω one may define a *quasi-free state* by the following conditions,

$$\omega(a^\sharp(\xi_1)\dots a^\sharp(\xi_{2n+1})) = 0 \ ,$$
$$\omega(a^\sharp(\xi_1)\dots a^\sharp(\xi_{2n})) = \sum_P (\pm 1)^{\chi(P)} \prod_{k=1}^{n} \omega(a^\sharp(\xi_{2k-1}) a^\sharp(\xi_{2k})) \ ,$$
$$n = 0, 1, 2, \dots \tag{197}$$

Here, the sum is taken over all partitions P of $\{1, 2, \dots, 2n\}$ into pairs $\{j_{2k-1}, j_{2k}\}$, $k = 1, 2, \dots, n$, such that $j_{2k-1} < j_{2k}$ and $\chi(P)$ is the parity of the permutation $\{1, 2, \dots, 2n\} \to \{j_1, j_2, \dots, j_{2n}\}$. The symbol $a^\sharp$ denotes a or $a^\dagger$. The above definition makes sense for the states given by density matrices i.e. $\omega(A) = \mathrm{Tr}(\omega A)$ and those obtained in the thermodynamic limit, i.e., $\omega(A) = \lim_{L\to\infty} \mathrm{Tr}(\omega^L A)$. In addition, we restrict ourselves to the quasi-free states ω which are invariant with respect to the gauge transformation $a(\cdot) \mapsto e^{i\varphi} a(\cdot)$, $a^\dagger(\cdot) \mapsto e^{i\varphi} a^\dagger(\cdot)$. They are uniquely determined by the single-particle density matrices $\sigma \geq 0$ (not necessarily trace-class) such that

$$\omega = \omega_\sigma \quad , \quad \omega_\sigma(a^\dagger(\xi') a(\xi)) = \sigma(\xi \mid \xi') \ . \tag{198}$$

The *quasi-free quantum dynamical semigroups* are those which transform quasi-free states into quasi-free states i.e.

$$\Lambda_t \, \omega_\sigma = \omega_{\sigma_t} \ . \tag{199}$$

A straightforward calculation shows that for our model described by (188) (with $H = H_{\mathrm{F}}$) (199) holds with σ_t being the solution of the equation (189) with the initial condition $\sigma_0 = \sigma$.

We close this section presenting a simple application of the above results [46]. We consider unstable bosons with a Hamiltonian $H_1 = \sum_k \epsilon_k |\varphi_k\rangle\langle\varphi_k|$, decay modes $\{\varphi\}$ and decay rates γ_k. The production of particles is negligible. We would like to compute the time evolution of the probability distribution of the number of particles $P_t(N = m), m = 0, 1, 2, \dots$. The related characteristic function $f_t(s) = \sum_{m=0}^{\infty} P_t(N = m) e^{ism}$ may be written as

$$f_t(s) = \mathrm{Tr}\left(\rho \, \Lambda_t^\star e^{isN}\right) \ , \tag{200}$$

with $N = \sum_k a_k^\dagger a_k$, $a_k \equiv a[\varphi_k]$.

Using the identity

$$\exp\left\{ i \sum_k \nu_k \, a_k^\dagger a_k \right\} = \sum_{m=0}^{\infty} \sum_{k_1,\dots,k_m} \prod_{j=1}^{m} \frac{e^{i\nu_{k_j}} - 1}{m!} \prod_{j=1}^{m} a_{k_j}^\dagger \prod_{j=1}^{m} a_{k_j} \ , \tag{201}$$

the equation (192) which for $\Delta = 0$ takes the form

$$\Lambda_t^\star \left(a^\dagger[f_1]\cdots a^\dagger[f_m]a[g_1]\cdots a[g_n]\right) \tag{202}$$

$$= a^\dagger[T_t^\star f_1]\cdots a^\dagger[T_t^\star f_m]a[T_t^\star g_1]\cdots a[T_t^\star g_n] \tag{203}$$

and the fact that

$$T_t^\star \varphi_k = \exp\left\{(i\epsilon_k - \frac{1}{2}\gamma_k)t\right\}\varphi_k \tag{204}$$

one obtains

$$\Lambda_t^\star \left(e^{isN}\right) = \sum_{m=0}^{\infty}\sum_{k_1,\ldots,k_m}\prod_{j=1}^{m}\frac{e^{i\gamma_k}(e^{is}-1)}{m!}\prod_{j=1}^{m}a_{k_j}^\dagger\prod_{j=1}^{m}a_{k_j}$$

$$= \exp\left\{i\sum_k \mu_k^t(s)\, a_k^\dagger a_k\right\} \tag{205}$$

where $\mu_k^t(s) = \ln\left(1 + e^{-\gamma_k t}(e^{is}-1)\right)$.

Hence it is possible to calculate $f_t(s)$ for a number of initial states. For example, if $\rho = |k;n\rangle\langle k;n|$ with $|k;n\rangle = (n!)^{-1/2}(a_k^\dagger)^n|0\rangle$, $|0\rangle$ – the vacuum state, then

$$f_t(s) = [\eta + (1-\eta)e^{is}]^n \tag{206}$$

is a characteristic function of the binomial probability distribution $P_t(N = m) = \binom{n}{m}(1-\eta)^m\eta^{n-m}$. Here, $\eta = 1 - e^{-\gamma_k t}$ is the probability of decay in the time interval $[0,t]$. One remarks the statistical independence of decay processes described by the binomial distribution of order n for the n-particle initial state.

2.3.5 Hamiltonian Models of Unstable Particles

In this section we want to comment briefly on the possible derivation of previously studied dynamical semigroups from Hamiltonian field-theoretical models [41–43]. We discuss for simplicity the following decomposition and production process

$$A \rightleftharpoons B + C \tag{207}$$

For mathematical reasons we assume that the unstable particles are confined by a potential or a box such that the free single-particle Hamiltonian has a pure point spectrum $\{\epsilon_k\}$ but the decay products move freely in a whole space. Due to the well-known problems with relativistic, local field theory we use the nonrelativistic, non-local Lee-type interaction Hamiltonians. The Fock spaces and quantum fields are denoted as follows

$$\begin{array}{llllll} \mathrm{A}\ ; & \mathcal{F}_\mathrm{A}\ , & a_k\ , & a_k^\dagger\ , & & \\ \mathrm{B}\ ; & \mathcal{F}_\mathrm{B}\ , & b(\xi)\ , & b^\dagger(\xi)\ , & \xi = (\boldsymbol{p},\sigma)\ , \boldsymbol{p}\in\mathbb{R}^3\ , \\ \mathrm{C}\ ; & \mathcal{F}_\mathrm{C}\ , & c(\eta)\ , & c^\dagger(\eta)\ , & \eta = (\boldsymbol{q},\chi)\ , \boldsymbol{q}\in\mathbb{R}^3\ , \end{array}$$

where for decay products we use the momentum representation.

The total Hamiltonian is given by

$$H = H_{\rm A} + H_{\rm B} + H_{\rm C} + \lambda H_{\rm int} \ ,$$

where

$$\begin{aligned} H_{\rm A} &= \sum_k \epsilon_k \, a_k^\dagger a_k \ , \\ H_{\rm B} &= \int d\xi \, \epsilon_{\rm B}(\xi) \, b^\dagger(\xi) b(\xi) \ , \\ H_{\rm C} &= \int d\eta \, \epsilon_{\rm C}(\eta) \, c^\dagger(\eta) c(\eta) \ , \qquad (208) \\ H_{\rm int} &= \sum_k \int d\xi \int d\eta \left\{ g(k,\xi,\eta) \, a_k \, b^\dagger(\xi) \, c^\dagger(\eta) + h.c. \right\} \ , \qquad (209) \end{aligned}$$

with $g(k,\xi,\eta)$ – a regular form factor.

The decay products are treated as a reservoir $\mathcal{R}$. The reference state of $\mathcal{R}$ is given by $\omega_{\rm R} = \omega_{\rm B} \otimes \omega_{\rm C}$ where $\omega_{\rm B}$, $\omega_{\rm C}$ are quasi-free states fixed by the two-point correlation functions

$$\begin{aligned} \omega_{\rm B}(b^\dagger(\xi) b(\xi')) &= n_{\rm B}(\xi) \, \delta(\xi - \xi') \\ \omega_{\rm C}(c^\dagger(\eta) c(\eta')) &= n_{\rm C}(\eta) \, \delta(\eta - \eta') \qquad (210) \end{aligned}$$

where $n_{\rm B}(\xi)$, $n_{\rm C}(\eta)$ are the probability distributions of particles in momentum space multiplied by the density of particles.

Under certain technical conditions on the form factor $g(k,\xi,\eta)$ it is possible to apply the rigorous weak coupling limit to obtain the Markovian master equation (185) with $a[\varphi_k] = a[\psi_k] = a_k$, $H = \sum_k \epsilon_k{}' a_k^\dagger a_k$ where $\epsilon_k{}'$ is a renormalized energy containing corrections of order λ^2.

The decay and production constants are, as usually for the weak coupling limit, equal to those calculated by the Fermi golden rule and given by

$$\begin{aligned} \gamma_k &= 2\pi\lambda^2 \int d\xi \int d\eta \, (1 \pm n_{\rm B}(\xi))(1 \pm n_{\rm C}(\eta)) \\ &\quad \times |g(k,\xi,\eta)|^2 \, \delta(\epsilon_{\rm B}(\xi) + \epsilon_{\rm C}(\eta) - \epsilon_k) \ , \qquad (211) \\ \delta_k &= 2\pi\lambda^2 \int d\xi \int d\eta \, n_{\rm B}(\xi) \, n_{\rm C}(\eta) \, |g(k,\xi,\eta)|^2 \\ &\quad \times \delta(\epsilon_{\rm B}(\xi) + \epsilon_{\rm C}(\eta) - \epsilon_k) \ . \end{aligned}$$

In order to obtain a more general form of the generator with different decay and production modes one may use the singular coupling limit as discussed in Subsubsect. 1.3.5. It is still an open problem to find clear physical conditions deciding whether the weak coupling or singular coupling limit gives better approximation to the exact dynamics of the open system. One should mention also that the generalization of the above scheme to a larger number of decay products and many channels of reaction is straightforward.

2.3.6 Relativistic Unstable Particles

The most fundamental examples of unstable physical systems are unstable elementary particles. The proper description of them might be possible within the framework of relativistic quantum field theory. However, because of well-known difficulties concerning the rigorous formulation of such theories we restrict ourselves to the phenomenological approach presented in [46]. We would like to describe a system of relativistic noninteracting particles characterized besides the usual parameters as mass, spin etc. by the decay constant $\gamma = \frac{1}{m\tau}$ where τ is a decay time, m – a rest mass ($\hbar \equiv c \equiv 1$).

The mathematical framework is the following. $\mathcal{F}$ denotes the Fock space over a single-particle Hilbert space $\mathcal{H}_1$. The kinematics of the system is described by the unitary representation $U(\bullet)$ of the Poincaré group $\mathcal{P}$ acting on $\mathcal{H}_1$. $\mathcal{P}$ consists of all pairs (a, L) with $a \in \mathbb{R}^4$ and $\mathrm{L} \in \mathcal{L}$ the proper orthochronous Lorentz group and acts as a transformation group

$$x \mapsto (a, \mathrm{L})x = \mathrm{L}x + a \tag{212}$$

on the Minkowski space $\mathbb{R}^4$ equipped with a scalar product

$$x \cdot y = x_0 y_0 - \boldsymbol{xy} \ . \tag{213}$$

The representation $U(\bullet)$ on $\mathcal{H}_1$ induces a unitary representation $V(\bullet)$ on the Fock space satisfying the relation

$$V(a, \mathrm{L})\, a^\sharp[f] V^\star(a, \mathrm{L}) = a^\sharp[U(a, \mathrm{L})f] \ . \tag{214}$$

The irreversible and Markovian dynamics (in the Heisenberg picture) of a non-relativistic system may be treated as a representation of the semigroup $\mathbb{R}^+ = \{t; t \in \mathbb{R}, t \geq 0\}$ into the semigroup of a completely positive unity preserving maps on the algebra of observables : $\mathbb{R}^+ \ni t \mapsto \Lambda_t^\star$. In the relativistic theory one should replace the absolute future $\mathbb{R}^+$ by the future cone $\mathbb{F} = \{a \in \mathbb{R}^4, a_0 \geq 0, a^2 \geq 0\}$. Therefore we describe the dynamics of unstable particles by the representation of the future cone $\mathbb{F}$ into the quasi-free completely positive identity preserving maps on the algebra of observables $\mathcal{A} \subseteq \mathcal{B}(\mathcal{F})$, i.e., there exists a family $\{\Lambda_a^\star, a \in \mathbb{F}\}$ satisfying the following conditions:

1) for any $a \in \mathbb{F}$, $\Lambda_a^\star$ is a quasi-free completely positive map on $\mathcal{A}$
2) $\Lambda_a^\star \mathbb{1} = \mathbb{1}$, for all $a \in \mathbb{F}$
3) for all $a, b \in \mathbb{F}$, $\Lambda_a^\star \Lambda_b^\star = \Lambda_{a+b}^\star$ – semigroup property
4) for all $(a, \mathrm{L}) \in \mathcal{P}$, $b \in \mathbb{F}$ and $A \in \mathcal{A}$,
   $V^\star(a, \mathrm{L}) \{\Lambda_b^\star [V(a, \mathrm{L}) A\, V^\star(a, \mathrm{L})]\} V(a, \mathrm{L}) = \Lambda_{\mathrm{L}b}^\star A$
   - relativistic covariance.

The above conditions reflect the physical assumptions of irreversibility, statistical independence, exponential character and relativistic invariance of decay processes.

Taking into account that the vacuum state $|0\rangle$ should be invariant with respect to Λ_a, i.e., $\langle 0 \mid \Lambda_a^\star A \mid 0\rangle = \langle 0 \mid A \mid 0\rangle$ one proves that $\Lambda_a^\star$ is defined by the expression (203) with $\{T_t, t \in \mathbb{R}^+\}$ replaced by $\{T_a, a \in \mathbb{F}\}$ satisfying the following conditions:

a) for all $a \in \mathbb{F}$, T_a is a linear contraction on $\mathcal{H}_1$ ($\|T_a\| \leq 1$)
b) for all $a, b \in \mathbb{F}$, $\quad T_a T_b = T_{a+b}$
c) $U(a, L)\, T_b\, U^\star(a, \mathrm{L}) = T_{\mathrm{L}b}$

For bosons one can use the definition of $\Lambda_a^\star$ in terms of Weyl operators,

$$\Lambda_a^\star W(f) = \exp\left\{-\frac{1}{4}\langle f \mid 1 - T_a T_a^\star \mid f\rangle\right\} W(T_a^\star f)\ . \tag{215}$$

The contraction semigroup $\{T_a; a \in \mathbb{F}\}$ provides the usual single-particle description of a relativistic unstable particle [51].

We discuss now briefly the case of massive spin zero particles. The Hilbert space $\mathcal{H}_1$ is isomorphic to $L^2(\mathbb{R}^4, d\mu_m)$ with the usual Lorentz invariant measure $d\mu_m = \delta(p^2 - m^2)\Theta(p_0)d^4p$ on the hyperboloid of positive energy with mass m. Then the form of T_a is uniquely determined (up to the units of the parameter a) by the conditions a), b), c) and may be written as

$$(T_a\varphi)(p) = e^{(i-\frac{\gamma}{2})a\cdot p}\varphi(p)\ , \tag{216}$$

where γ is a decay constant and the units of a are chosen in such a way that for $\gamma \to 0+$, $T_a \to U(a, \mathbb{1})$. The relativistic semigroup $\Lambda_a^\star$ may be written in exponential form,

$$\Lambda_a^\star = e^{a\cdot \mathrm{L}^\star}\ , \tag{217}$$

where $\mathrm{L}^\star$ is a four-vector which consists of four maps acting on A and is formally given by the following expression,

$$\begin{aligned}\mathrm{L}^\star A = \int & d\mu_m(p)\, p \left\{ i[a^\dagger(p)a(p), A] \right. \\ & \left. + \frac{\gamma}{2}\left(a^\dagger(p)[A, a(p)] + [a^\dagger(p), A]a(p)\right)\right\}\ ,\end{aligned} \tag{218}$$

where $a(p), a^\dagger(p)$ are quantum fields in the momentum representation.

For higher spin particles with possible additional internal degrees of freedom the more complicated matrix representations T_a of $\mathbb{F}$ may appear but all essential features of the above construction remain valid.

Appendix

A.1 Banach Spaces $\mathcal{B}(\mathcal{H})$ and $\mathcal{T}(\mathcal{H})$

$\mathcal{H}$ denotes a complex separable Hilbert space with a scalar product $\langle \Phi \mid \Psi\rangle$ and a norm $\|\Psi\| = (\langle \Psi \mid \Psi\rangle)^{1/2}$. A linear operator A acting on $\mathcal{H}$ is *bounded*

if $\sup_{\|\Psi\|\leq 1}\|A\Psi\| < \infty$. The set of all bounded operators equipped with a *norm* $\|A\|_\infty = \sup_{\|\Psi\|\leq 1}\|A\Psi\|$ is a Banach space $\mathcal{B}(\mathcal{H})$. $\mathcal{B}(\mathcal{H})$ is an *algebra* with respect to the composition of operators and with an *involution* $\star$ (adjoint operation) satisfying

$$\langle A^\star\psi \mid \varphi\rangle = \langle \psi \mid A\varphi\rangle \ ,$$
$$(AB)^\star = B^\star A^\star \ , \quad (A^\star)^\star = A \ , \quad (\alpha A + \beta B)^\star = \overline{\alpha}A^\star + \overline{\beta}B^\star \ ,$$
$$\|A^\star A\|_\infty = \|A\|_\infty^2 = \|A^\star\|_\infty^2 \ .$$

An operator $A \in \mathcal{B}(\mathcal{H})$ is *self-adjoint* if $A = A^\star$ and *positive* ($A \geq 0$) if $\langle\psi \mid A\psi\rangle \geq 0$ for all $\psi \in \mathcal{H}$. For any $B \geq 0$ there exists a *square root operator* $B^{1/2} \geq 0$ such that $B^{1/2}B^{1/2} = B$ and if $BA = AB$ then $B^{1/2}A = AB^{1/2}$.

Let $A \in \mathcal{B}(\mathcal{H})$. We define a *trace of* A as a number (if it exists)

$$\mathrm{Tr} = \sum_{n=1}^{\infty}\langle\varphi_n \mid A\varphi_n\rangle \ ,$$

where $\{\varphi_n\}$ is a orthonormal basis in $\mathcal{H}$. TrA (if it exists) is independent of a choice of $\{\varphi_n\}$. An operator $\sigma \in \mathcal{B}(\mathcal{H})$ is called *trace class* if $\mathrm{Tr}(\sigma^\star\sigma)^{1/2}$ exists.

The set of all trace class operators $\mathcal{T}(\mathcal{H})$ is a Banach space with a *trace norm* $\|\sigma\|_1 = \mathrm{Tr}(\sigma^\star\sigma)^{1/2}$. If $\sigma = \sigma^\star \in \mathcal{T}(\mathcal{H})$, then there exists a spectral representation $\sigma = \sum_{n=1}^{\infty}\lambda_n|\varphi_n\rangle\langle\varphi_n|$ where $\langle\varphi_n \mid \varphi_m\rangle = \delta_{nm}$ and $\mathrm{Tr}\sigma = \sum_{n=1}^{\infty}\lambda_n$, $\|\sigma\|_1 = \sum_{n=1}^{\infty}|\lambda_n|$.

If $\sigma \in \mathcal{T}(\mathcal{H})$, $A \in \mathcal{B}(\mathcal{H})$ then $\sigma A, A\sigma \in \mathcal{T}(\mathcal{H})$ and $|\mathrm{Tr}(\sigma A)| \leq \|\sigma\|_1\|A\|_\infty$.

For a fixed $A \in \mathcal{B}(\mathcal{H})$ we define a linear and bounded functional f_A on $\mathcal{T}(\mathcal{H})$ such that

$$f_A(\sigma) = \mathrm{Tr}(\sigma A) \ .$$

All linear and bounded functionals on $\mathcal{T}(\mathcal{H})$ form a Banach space $\mathcal{T}(\mathcal{H})^\star$ (*dual space*) with a norm $\|f\| = \sup_{\|\sigma\|_1\leq 1}|f(\sigma)|$. Any functional $f \in \mathcal{T}(\mathcal{H})^\star$ is equal to a certain f_A and $\|f\| = \|A\|_\infty$. Hence the two Banach spaces $\mathcal{B}(\mathcal{H})$ and $\mathcal{T}(\mathcal{H})^\star$ are isomorphic and isometric. It follows that for any linear and bounded map Λ on $\mathcal{T}(\mathcal{H})$ there exists a *dual map* $\Lambda^\star$ on $\mathcal{B}(\mathcal{H})$ such that

$$\mathrm{Tr}\,[(\Lambda\sigma)A] = \mathrm{Tr}(\sigma\Lambda^\star A) \ ,$$

for all $\sigma \in \mathcal{T}(\mathcal{H})$ and $A \in \mathcal{B}(\mathcal{H})$.

A.2 One-parameter Semigroups

A *one-parameter semigroup* on a Banach space $\mathcal{X}$ is a family $\{T_t, t \geq 0\}$ of bounded linear operators on $\mathcal{X}$ satisfying the following conditions:

$$\text{a) } T_0 = \mathbb{1} \ , \quad \text{b) } T_tT_s = T_{t+s} \ , \quad t, s \geq 0 \ .$$

A one-parameter semigroup is *norm continuous* if $\lim_{t\searrow 0}\|T_t - \mathbb{1}\|_\infty = 0$, *strongly continuous* if $\lim_{t\searrow 0}\|T_t x - x\| = 0$ for all $x \in \mathcal{X}$ and *weakly continuous* if $\lim_{t\searrow 0}|f(T_t\, x) - f(x)| = 0$ for all $x \in \mathcal{X}$ and all linear and bounded functionals $f \in \mathcal{X}^\star$ (dual space).

For one-parameter semigroups weak continuity is equivalent to strong continuity and implies the existence of constants M, α such that $\|T_t\| \leq Me^{\alpha t}$ for all $t \geq 0$.

A (infinitesimal) *generator* Z of a one-parameter strongly continuous semigroup is defined by

$$\lim_{t\to 0+}\frac{1}{t}\|T_t\, x - x - t\,\mathrm{Z}\, x\| = 0 \qquad \text{for } x \in \mathrm{dom}(\mathrm{Z})\ .$$

The subspace dom(Z) is dense in $\mathcal{X}$ and invariant under T_t. Moreover $T_t\,\mathrm{Z}\, x = \mathrm{Z}\, T_t\, x$ for $x \in \mathrm{dom}(\mathrm{Z})$. Z is a *closed operator*, i.e., if $x_n \in \mathrm{dom}(\mathrm{Z})$ and $\lim_{n\to\infty}\|x_n - x\| = \lim_{n\to\infty}\|\mathrm{Z}\, x_n - y\| = 0$ then $x \in \mathrm{dom}(\mathrm{Z})$ and $\mathrm{Z}x = y$.

$\{T_t, t \geq 0\}$ is norm continuous if and only if its generator is bounded and hence $T_t = e^{\mathrm{Z}t} = \sum_{n=0}^{\infty}\frac{t^n}{n!}\mathrm{Z}^n$. $\{T_t^\star, t \geq 0\}$ denotes a *dual one-parameter semigroup* defined on $\mathcal{X}^\star$ as $(T_t^\star f)(x) = f(T_t x)$ for any $f \in \mathcal{X}^\star$ and $x \in \mathcal{X}$. The dual generator $\mathrm{Z}^\star$ is given by

$$\lim_{t\to 0+}\frac{1}{t}\|T_t^\star f - f - t\,\mathrm{Z}^\star f\| = 0 \qquad f \in \mathrm{dom}(\mathrm{Z}^\star)\ .$$

$T_t^\star$ is uniquely determined by $\mathrm{Z}^\star$ and $\mathrm{dom}(\mathrm{Z}^\star)$ is dense in $\mathcal{X}^\star$ in the $\star$-weak topology, i.e., for any $f \in \mathcal{X}^\star$ there exists a sequence $f_n \in \mathrm{dom}(\mathrm{Z}^\star)$ such that for any $x \in \mathcal{X}$ $\lim_{n\to\infty}|f_n(x) - f(x)| = 0$.

A one-parameter *contraction semigroup* is defined as a one-parameter strongly continuous semigroup $\{T_t, t \geq 0\}$ such that $\|T_t\| \leq 1$. The following statements are equivalent:

a) Z is a generator of a contraction semigroup
b) Z is a densely defined closed operator on $\mathcal{X}$ such that for all $\lambda > 0$ $(\lambda - \mathrm{Z})^{-1}$ is a bounded operator and

$$\|(\lambda - \mathrm{Z})^{-1}\| \leq \lambda^{-1}\ .$$

The exponential form of the contraction semigroup $T_t = e^{\mathrm{Z}t}$ is meaningful in the sense: $\lim_{n\to\infty}\|T_t\, x - (\mathbb{1} - \frac{t}{n}\mathrm{Z})^{-n}x\| = 0$. A one parameter semigroup on $\mathcal{T}(\mathcal{H})$ which satisfies:

a) $\mathrm{Tr}(T_t\,\rho) = \mathrm{Tr}\rho$
b) if $\rho \geq 0$ then $T_t\,\rho \geq 0$,

is a contraction semigroup. If Z is a generator of a contraction semigroup $\{T_t, t \geq 0\}$ and $A \in \mathcal{B}(\mathcal{X})$ then $\mathrm{Z} + A$ generates a one parameter strongly continuous semigroup $\{S_t, t \geq 0\}$ such that

$$\|S_t\| \leq e^{\|A\|t}\ .$$

The following integral equations are satisfied:

$$S_t\, x = T_t\, x + \int_0^t ds\, T_{t-s} A\, S_s\, x \ , \tag{219}$$

$$S_t\, x = T_t\, x + \int_0^t ds\, T_{t-s} A\, T_s\, x + \int_0^t ds \int_0^s dr\, T_{t-s} A\, T_{s-r} A\, S_r\, x \ . \tag{220}$$

A.3 Quantum Correlation Functions

Let $U_t = e^{-iHt}$ be a one-parameter unitary group on the Hilbert space $\mathcal{H}$ and ω a density matrix commuting with U_t, i.e., $[\omega, U_t] = 0$. We shall use the notation $A_t = U_t^\star A\, U_t$, $\omega(A) = \mathrm{Tr}(\omega A)$ for an operator A acting on $\mathcal{H}$.

The relation holds

$$\omega(A_t B) = \omega(A_{t+\tau} B_\tau) = \overline{\omega(B_{-t}^\star A^\star)} \ . \tag{221}$$

A function $F(t) = \omega(A_t^\star A)$ is of *positive type* i.e. for any sequence $t_1, \ldots, t_n$, the matrix $a_{kl} = F(t_k - t_l)$, $k = 1, 2, \ldots, n$, is positive.

By Bochner's theorem the Fourier transform $\hat{F}(x) = \int_{-\infty}^{\infty} e^{ixt} F(t)\, dt$ *is positive*, $\hat{F}(x) \geq 0$.

It follows that for any sequence of operators $A^k, k = 1, 2, \ldots, m$, and any $x \in \mathbb{R}$ the matrix

$$\hat{F}_{kl}(x) = \int_{-\infty}^{\infty} e^{ixt} \omega(A_t^{k\star} A^l) dt \qquad \text{is positive} \ ,$$

$$\left[\hat{F}_{kl}(x)\right] \geq 0 \ . \tag{222}$$

The following equality holds:

$$\int_0^\infty e^{ixt} \omega(A_t^{k\star} A^l) dt = \frac{1}{2} \hat{F}_{kl}(x) + i S_{kl}(x) \ , \quad \text{where } S_{kl}(x) = \bar{S}_{lk}(x) \ . \tag{223}$$

The above results remain true in the thermodynamic limit.

Let $F_{AB}(t) = \omega(A_t B)$. By $F_{AB}(z)$ we denote the analytical continuation of $F_{AB}(t)$ into a strip $\{z; z \in \mathbb{C}, \mathrm{Im}\, z \in (-\beta, 0]\}$.

We say that the state ω satisfies a *KMS* condition if

$$F_{AB}(-t) = F_{BA}(t - i\beta) \tag{224}$$

for a dense set of operators A, B.

The KMS-condition is satisfied if and only if $\omega = e^{-\beta H}/\mathrm{Tr} e^{-\beta H}$ (for systems in a finite volume).

The KMS-condition holds for equilibrium states in the thermodynamic limit.

Let ω_β satisfy (224), then $\hat{F}_{kl}(x)$ given by (222) fulfills the relation

$$\hat{F}_{kl}(-x) = e^{-\beta x} \hat{F}_{-l-k}(x) \ , \tag{225}$$

where we use the convention $A^{-k} \equiv (A^k)^\star$.

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N-Level Systems and Applications to Spectroscopy

Karl Lendi

1 Introduction

The main motivation of these lecture notes is to provide an easier access to the useful results of completely positive quantum dynamical semigroups of N-level systems for all those who are interested in practical applications and to work out some particular details which may be useful for the interpretation of experiments.

It is certainly clear from the preceding lectures that the quantum theory of open systems in the Markovian limit is based on mathematically rigorous concepts which, for the whole time-evolution, fully respect the basic laws of quantum mechanics, in particular, the von Neumann conditions of hermiticity, trace-preservation and positivity of any density operator. The results of this theory are not only of mathematical beauty but also of extraordinary practical accessibility and, therefore, it would seem natural to formulate any practical calculation by starting from the general structure of so-called quantum Markovian master equations [1–3] as obtained from the semigroup generators. However, according to the literature this has not been the way of handling the problems in the past. Although it seems to be generally recognized now that density operators instead of wave functions should be used whenever relaxation and dissipation are physically important, the question of what kind of dynamical equations should be chosen has not attracted wide and serious attention. In many cases one is satisfied with some phenomenological attempts to introduce relaxation constants just in order to account for the result of one specific experiment. Some serious inconsistencies such as, e.g., unbounded solutions or negative or even imaginary probabilities [4–7] may then be a consequence. On the other hand, it must be mentioned that many remarkable and successful approaches have been in use mainly in the fields of laser theory [8] and general quantum optics [9–11] but without explicitly using complete positivity arguments. Furthermore, the wide fields of optical and magnetic resonance spectroscopy are dominated by the famous Bloch equations [12, 13] that, as must be expected, have the correct structure

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and can be derived from a very special and simple generator of a completely positive quantum dynamical semigroup [14]. Thus, it will certainly be desirable to explore more general Bloch-like equations for the description of more sophisticated experiments and the only safe grounds to derive such equations is the above-mentioned theory. Therefore, a good part of the lecture will be devoted to this problem.

2 General Structure of Quantum Markovian Master Equations for N-level Systems

2.1 The Kossakowski-Generator of Infinitesimal Time-evolution

The states at time t of any open system $\mathcal{S}$ considered in the following will be described by a hermitian $(N \times N)$-matrix $\rho(t)$. The time evolution from an initial state $\rho(0) \xrightarrow{\Lambda_t} \rho(t)$ is given by a completely positive semigroup Λ_t which preserves hermiticity, trace and positivity for ρ for $0 \leq t < \infty$ where $t = \infty$ may also be included for completely relaxing semigroups (see Subsect. 2.5). In terms of the infinitesimal generator L of $\Lambda_t = \exp(\mathrm{L}t)$ a quantum Markovian master equation reads

$$\dot{\rho}(t) = \mathrm{L}\rho(t) \ , \tag{1}$$

where L is time-independent. ρ acts on a complex vector space $\mathcal{H} = \mathbb{C}^{(N)}$ of dimension N, the finite-dimensional Hilbert space associated to $\mathcal{S}$, and L is a linear transformation in the set $\mathfrak{A}$ of all $(N \times N)$-density matrices which is also a complex vector space $\mathfrak{A} = \mathbb{C}^{(N^2)}$ of dimension N^2. It will be of importance in the following sections that due to hermiticity and trace-normalization of ρ the time-evolution can be described entirely in terms of a real vector in a vector space $\mathbb{R}^{(M)}$ of dimension $M = N^2 - 1$.

In a series of papers [14–16] Kossakowski has analyzed the detailed mathematical structure of the generator L which can be written in final normal form as

$$\mathrm{L}\rho(t) = -i[H, \rho(t)] + \frac{1}{2} \sum_{i,k=1}^{N^2-1} a_{ik} \left([F_i, \rho(t) F_k^\star] + [F_i \rho(t), F_k^\star] \right) \ . \tag{2}$$

Here $H = H^\star$ is the Hamiltonian describing the reversible dynamics of the open quantum system but including possible effects due to the surroundings. For uniqueness reasons of the decomposition into Hamiltonian and non-Hamiltonian parts one postulates

$$\mathrm{Tr}(H) = 0 \ . \tag{3}$$

The set $\{F_i | i = 1, 2, \ldots, M = N^2 - 1\} = \{F_i\}_1^M$ contains M $(N \times N)$-matrices with the particular properties,

$$\mathrm{Tr}(F_i) = 0 \ , \quad \mathrm{Tr}(F_i F_k^\star) = \delta_{ik} \ , \quad \forall i,k \ , \tag{4}$$

and is called a complete orthonormal matrix set. Finally, all physically important information pertaining to the irreversible dynamics is contained in the complex $(M \times M)$-matrix $A = \{a_{ik}\}_1^M$ satisfying

$$A \geq 0 \ . \tag{5}$$

It is thus hermitian. The matrix elements a_{ik} will have the meaning of lifetimes, longitudinal or transverse relaxation times and equilibrium parameters such as stationary polarization or magnetization. As a basic consequence of Kossakowski's structure theorem (2) all these parameters are not independent among each other but restricted by some inequalities to be extracted from (5).

It must be remarked that at this stage of the theory no rules are yet known about the calculation of the a_{ik}'s from first principles although this is possible either by analyzing the analogy to the results obtained in the weak or singular coupling limits [17–20]. We will come back to this problem later. For the moment being we assume that the a_{ik}'s are given either from phenomenological considerations or, else, from calculations and continue exploring the general structure of master equations.

2.2 Positive-semidefiniteness of the Relaxation Matrix

All inequalities among relaxation parameters can be deduced from this property of A, and it is certainly worthwhile to recall some useful theorems. Note again that writing down master equations by introducing relaxation on purely phenomenological grounds, as is frequently done for interpretations of experiments, would require a careful discussion of their exact solutions in order to obtain the same information as from the analysis of positive-semidefiniteness of A. However, exact solutions are not known in most cases which manifests clearly the power of this structure theorem.

The hermitian matrix A on $\mathbb{C}^{(M)}$ is called positive-semidefinite if the associated quadratic form $q(A)$ is positive-semidefinite, i.e.,

$$q(A) = \sum_{i,k=1}^{M} a_{ik} \bar{x}_i x_k \geq 0 \ , \quad \forall \underline{x} \in \mathbb{C}^{(M)} \ . \tag{6}$$

Denote the set of eigenvalues of A by $\{\mu_i\}$. Then, the following conditions are satisfied [21, 22]:

$$\mu_i \geq 0 \ , \qquad \forall i \ , \tag{7}$$

$$a_{ii} \geq 0 \ , \qquad \forall i \ , \tag{8}$$

$$B_l \geq 0 \ , \qquad 1 < l < M \ , \tag{9}$$

where B_l is any leading submatrix of order l obtained by deleting a number of rows, not necessarily of consecutive indices, and the corresponding columns.

One of the most frequently used inequalities is then obtained by considering $l = 2$ and using (7), with the result

$$|a_{ik}|^2 \leq a_{ii}a_{kk} \ , \quad \forall i \neq k \ . \tag{10}$$

To test commonly used phenomenological master equations on their positivity the criterion of strict diagonal dominance may be useful, that is

$$a_{ii} > \sum_{k \neq i}^{M} |a_{ik}| \ , \quad \forall i \ . \tag{11}$$

This condition is sufficient but not necessary and implies positive-definiteness. Finally, we consider a two-level system for which $M = N^2 - 1 = 3$. From the characteristic polynomial, Vieta's root theorem and (7) one finds the inequalities

$$a_{11}a_{22} + a_{11}a_{33} + a_{22}a_{33} \geq |a_{12}|^2 + |a_{13}|^2 + |a_{23}|^2 \ , \tag{12}$$

$$a_{11}a_{22}a_{33} + 2\mathrm{Re}\ (a_{12}a_{23}a_{31}) \geq |a_{12}|^2 a_{33} + |a_{13}|^2 a_{22} + |a_{23}|^2 a_{11} \ . \tag{13}$$

Introducing a real vector $\underline{z} = \{z_1, z_2, z_3\}^T$ with components defined by

$$\begin{aligned} z_1 &= |a_{12}|/(3a_{11}a_{22})^{1/2} \ , \\ z_2 &= |a_{13}|/(3a_{11}a_{33})^{1/2} \ , \\ z_3 &= |a_{23}|/(3a_{22}a_{33})^{1/2} \ , \end{aligned} \tag{14}$$

the upper bound is given by

$$\|\underline{z}\|^2 \leq 1 \ . \tag{15}$$

It will be shown later that the norm $\|\underline{z}\|$ is a combined global measure of coherence and of the existence of a non-trivial, stationary final state if coherence is defined to be due to the coupling between diagonal and off-diagonal elements of the density matrix in the differential equations.

2.3 Complete Orthonormal Matrix Sets

Whenever a concrete realization of the set $\{F_i\}_1^M$ of M matrices of dimension N with the properties (4) is needed for calculations a particularly convenient choice is offered by the infinitesimal generators of SU(N) [23–25].

Any transformation $\mathfrak{U} \in \mathrm{SU}(N)$ is determined by $M = N^2 - 1$ independent real parameters $\underline{\vartheta} = (\vartheta_1, \vartheta_2, \ldots, \vartheta_M)^T$ and can be written as

$$\mathfrak{U}(\underline{\vartheta}) = e^{iX(\underline{\vartheta})} \ , \qquad \vartheta_k \in \mathbb{R} \ , \quad \forall k \ , \text{with} \tag{16}$$

$$\mathfrak{U}^\star(\underline{\vartheta}) = \mathfrak{U}^{-1}(\underline{\vartheta}) \longrightarrow X^\star(\underline{\vartheta}) = X(\underline{\vartheta}) \ , \tag{17}$$

$$\det\{\mathfrak{U}(\underline{\vartheta})\} = 1 \longrightarrow \mathrm{Tr}\{X(\underline{\vartheta})\} = 0 \ . \tag{18}$$

Furthermore, set $\mathfrak{U}(\underline{0}) = \mathbb{1}$ and define $F_k = F_k^\star$ by

$$F_k = -i\frac{\partial}{\partial\vartheta_k}\mathfrak{U}(\underline{\vartheta})\bigg|_{\underline{\vartheta}=0} \quad . \tag{19}$$

Then, since any traceless hermitian matrix is also determined by M real parameters, $X(\underline{\vartheta})$ can directly be decomposed into

$$X(\underline{\vartheta}) = \sum_{k=1}^{M} \vartheta_k F_k \ . \tag{20}$$

Thus, the F_i's form a complete basis in a real M-dimensional vector space $\mathbb{R}^{(M)}$ where an inner product is naturally defined for any two elements $X(\underline{\vartheta})$ and $X(\underline{\eta})$ by

$$(\underline{\vartheta}\cdot\underline{\eta}) \equiv \mathrm{Tr}\{X(\underline{\vartheta})X(\underline{\eta})\} = \sum_{i,k=1}^{M} \vartheta_i\eta_k \ \mathrm{Tr}(F_iF_k) \ . \tag{21}$$

Note that the elements of $\mathbb{R}^{(M)}$ may be thought of as being either traceless hermitian matrices or, equivalently, numerical vectors. In order to regain the ordinary Euclidean scalar product $(\underline{\vartheta}\cdot\underline{\eta}) = \sum_i \vartheta_i\eta_i$ one can evidently apply a Schmidt-like orthonormalization procedure to the sequence $\{F_i\}$. It is in this sense then that one speaks of an orthonormalized matrix set with $\mathrm{Tr}(F_iF_k) = \delta_{ik}$, and (20) is an orthogonal decomposition where

$$\vartheta_k = \mathrm{Tr}(X(\underline{\vartheta})F_k) \ . \tag{22}$$

From now on we assume orthonormality of the generators $\{F_i\}$. Since they form a Lie algebra and any anticommutator of two hermitian matrices is again a hermitian matrix the two following relations hold,

$$[F_i, F_k] = i\sum_{l=1}^{M} f_{ikl}F_l \ , \tag{23}$$

$$\{F_i, F_k\} = \frac{2}{N}F_0\,\delta_{ik} + \sum_{l=1}^{M} d_{ikl}F_l \ , \tag{24}$$

with $f_{ikl}, d_{ikl} \in \mathbb{R}, \forall i,k,l$. F_0 is the (unnormalized) unit matrix, $\{\cdot,\cdot\}$ is an anticommutator and $\{f_{ikl}\}$ are the completely antisymmetric and $\{d_{ikl}\}$ the completely symmetric (with respect to interchange of any pair of indices) structure constants of the Lie algebra.

In analogy to the Pauli matrices, the generators of SU(2), a simple systematic construction of the F_i-matrices for arbitrary N is given as follows. Consider the $(N\times N)$-matrices $P^{(i,k)}$ whose elements $p_{\mu\nu}^{(i,k)}$ are defined by

$$p_{\mu\nu}^{(i,k)} = \delta_{\mu i}\,\delta_{\nu k} \ , \quad (i,k,\mu,\nu = 1,2,\ldots,N) \ , \tag{25}$$

i.e., all elements are zero except for one. For $i \neq k$ there are $N(N-1)$ such matrices from which the same number of traceless matrices is constructed by the linear combinations

$$S^{(i,k)} = \frac{1}{\sqrt{2}} \left(P^{(i,k)} + P^{(k,i)} \right) \ , \quad i < k \ , \tag{26}$$

$$J^{(i,k)} = \frac{-i}{\sqrt{2}} \left(P^{(i,k)} - P^{(k,i)} \right) \ , \quad i < k \ . \tag{27}$$

With the projectors $P^{(i,i)}$ one finally constructs $N-1$ further matrices which are real, diagonal and traceless by the prescription

$$D^{(l)} = \frac{1}{\sqrt{l(l+1)}} \left\{ \sum_{k=1}^{l} P^{(k,k)} - l P^{(l+1,l+1)} \right\} \ , \quad (l = 1, 2, \ldots, N-1) \ . \tag{28}$$

In total we have $M = N^2 - 1$ new matrices. It follows from (25) that

$$\mathrm{Tr} \left(P^{(i,k)} P^{(m,n)} \right) = \delta_{in} \delta_{km} \ , \tag{29}$$

and thus, the new set $\mathcal{M} = \{S^{(i,k)}, J^{(i,k)}, D^{(l)}\}$ is orthonormalized with respect to the trace and complete. Consequently, we can identify $\mathcal{M}$ with $\{F_i\}_1^M$ and have herewith chosen a particular representation which fixes also the values of the structure constants. Most practical calculations concern problems with $N = 2, 3, 4$ for which the corresponding matrices and structure constants are listed in Appendix A.1.

From the above it is clear that the second, dissipative part of (2) is a quadratic form independent of the chosen representation. Let's rewrite it as

$$\mathrm{L_D} \bullet = \frac{1}{2} \sum_{i,k=1}^{M} a_{ik} \left([F_i, \bullet F_k] + [F_i \bullet, F_k] \right) \tag{30}$$

and introduce the matrix-valued vectors $\underline{F} = (F_1, F_2, \ldots, F_M)^T$ and $\underline{W} = (W_1, W_2, \ldots, W_M)^T$ related by $\underline{W} = S\underline{F}$ such that the transformed relaxation matrix is $A \to \tilde{A} = SAS^\star$. Since A is positive-semidefinite S can be chosen to diagonalize it with eigenvalues $\{\lambda_i\}$, $(\lambda_i \geq 0, \ \forall i)$. Next define a new vector $\underline{V}$ by

$$\underline{V} = \left(\sqrt{\lambda_1} W_1, \sqrt{\lambda_2} W_2, \ldots, \sqrt{\lambda_M} W_M \right)^T \tag{31}$$

to obtain (30) in the diagonal form

$$\mathrm{L_D} \bullet = \frac{1}{2} \sum_{i=1}^{M} \left([V_i, \bullet V_i] + [V_i \bullet, V_i] \right) \ , \tag{32}$$

a representation also proposed by Lindblad [26] even for infinite dimension and frequently used in Alicki's lectures. If the V_i's are not hermitian the second factor in the commutators in (32) must be replaced by $V_i^\star$. For our purposes we prefer the original Kossakowski-normal form (2).

2.4 Coherence-vector Formulation

The aim of this section is to transform the original master equation, which is a complex matrix equation, into an inhomogeneous linear vector equation in a real vector space, i.e.,

$$\dot{\rho}(t) = \mathrm{L}\rho(t) \;\rightarrow\; \dot{\underline{v}}(t) = G\,\underline{v}(t) + \underline{k}\ . \tag{33}$$

Taking advantage of the results in Subsect. 2.3 this is straightforward. Choose again a complete orthonormal matrix set $\{F_i\}_1^M$ with

$$F_i = F_i^\star\ , \quad \mathrm{Tr}(F_i) = 0\ , \quad \mathrm{Tr}(F_i F_k) = \delta_{ik}\ . \tag{34}$$

Any density operator can be represented by an orthogonal decomposition similar to (20) but the coefficients are time-dependent. Thus,

$$\rho(t) = \frac{1}{N}F_0 + \sum_{i=1}^{M} v_i(t) F_i\ , \tag{35}$$

where the M real-valued functions

$$v_i(t) = \mathrm{Tr}(\rho(t) F_i) \tag{36}$$

are again taken to be components of a so-called coherence-vector

$$\underline{v}(t) = (v_1(t), v_2(t), \ldots, v_M(t))^T \in \mathbb{R}^{(M)}\ . \tag{37}$$

In the course of time-evolution $\underline{v}(t)$ will undergo some kind of rotation in $\mathbb{R}^{(M)}$ and its length may shrink or dilate. Whereas rotation is due to the Hamiltonian as well as the non-Hamiltonian terms in L the change of length is exclusively caused by non-Hamiltonian contributions. Before commenting more on this geometrical picture we work out some details of the differential equation for $\underline{v}(t)$ in (33).

We separate

$$\mathrm{L} = \mathrm{L_H} + \mathrm{L_D}\ , \tag{38}$$

$$\mathrm{L_H}\,\rho = -i[H, \rho]\ , \tag{39}$$

$$\mathrm{L_D}\,\rho = \frac{1}{2}\sum_{i,k=1}^{M} a_{ik}(2\,F_i\,\rho\,F_k - \rho\,F_k F_i - F_k F_i\,\rho)\ , \tag{40}$$

and, correspondingly,

$$G = Q + R\ , \tag{41}$$

such that

$$\mathrm{L_H}\,\rho \rightarrow Q\,\underline{v}\ , \qquad \mathrm{L_D}\,\rho \rightarrow R\,\underline{v} + \underline{k}\ . \tag{42}$$

Consider first the case $\mathrm{L_D}\rho = 0$ ($A = 0$), i.e., the dynamics is Hamiltonian and given by $\dot{\underline{v}} = Q\,\underline{v}$ or, e.g.,

$$\dot{v}_s = \mathrm{Tr}\,(\dot{\rho}(t)F_s) = -i\ \mathrm{Tr}\,([H,\rho(t)]\,F_s)\ . \tag{43}$$

Remembering (3) H can be decomposed into

$$H = \sum_{n=1}^{M} h_n F_n\ , \quad h_n \in \mathbb{R}\ , \tag{44}$$

and, thus,

$$\dot{v}_s = \sum_{m=1}^{M} q_{sm} v_m\ , \quad q_{sm} = \sum_{n=1}^{M} h_n f_{nms}\ . \tag{45}$$

Evidently, the antisymmetry of f_{nms} is transferred to $q_{sm} = -q_{ms}$ and we have

$$Q = -Q^T\ , \tag{46}$$

This skew-symmetry of Q has the consequence that

$$\|\underline{v}(t)\| = \text{const.}\ , \quad \forall t\ , \tag{47}$$

which follows from $\frac{\partial}{\partial t}\|\underline{v}(t)\|^2 = \big(\underline{v}(t)\cdot\{Q+Q^T\}\underline{v}(t)\big)$ and, thus, provides an important constant of motion. It is for this reason that for classical dynamical systems the original nonlinear equations are transformed, whenever possible, to the above quantum-like linear structure by constructing a Lax-pair [27,28].

Consider next the opposite case, $\mathrm{L_H}\,\rho = 0$ $(H = 0)$. In order to evaluate $\dot{\rho} = \mathrm{L}\,\rho$ or, equivalently, $\dot{v}_s = \mathrm{Tr}(\mathrm{L_D}\,\rho\,F_s)$ we use, as a consequence of (23) and (24),

$$F_m F_n = \frac{1}{N} F_0\,\delta_{mn} + \frac{i}{2}\sum_{l=1}^{M} \bar{z}_{mnl}\,F_l\ , \tag{48}$$

where the complex structure constants are defined by

$$z_{mnl} = f_{mnl} + i d_{mnl}\ , \tag{49}$$

and find for the elements of R and $\underline{k}$ the formulas

$$r_{sm} = -\frac{1}{4}\sum_{i,k,l=1}^{M} a_{ik}\,(z_{ilm}f_{kls} + \bar{z}_{klm}f_{ils})\ , \tag{50}$$

$$k_s = \frac{i}{N}\sum_{i,k=1}^{M} a_{ik} f_{iks}\ . \tag{51}$$

That all these quantities are real follows from the Lie structure and the hermiticity of A. In fact, writing

$$a_{ik} = \mathrm{Re}(a_{ik}) + i\ \mathrm{Im}(a_{ik}) \tag{52}$$

and collecting terms yields the real forms

$$r_{sm} = -\frac{1}{4} \sum_{\substack{i,k,l=1 \\ (i \le k)}}^{M} (2 - \delta_{ik}) \mathrm{Re}(a_{ik}) \{ f_{ils} f_{klm} + f_{kls} f_{ilm} \}$$

$$+ \frac{1}{2} \sum_{\substack{i,k,l=1 \\ (i<k)}}^{M} \mathrm{Im}(a_{ik}) \{ f_{kls}\, d_{ilm} - f_{ils}\, d_{klm} \} \ , \tag{53}$$

$$k_s = -\frac{2}{N} \sum_{\substack{i,k,l=1 \\ (i<k)}}^{M} \mathrm{Im}(a_{ik}) f_{iks} \ . \tag{54}$$

From the above relations the symmetry properties of the real relaxation matrix R are obvious. The wide belief that any R should be symmetric is not true in general, but the following statements are true.

$$i) \quad R = R^T \qquad \text{if } A = A^T \ , \quad 3 \le N < \infty \ , \tag{55}$$

$$ii) \quad R = R^T \qquad \text{for arbitrary } A \text{ and } N = 2 \ . \tag{56}$$

The last statement follows from the fact that only for the Lie algebra of SU(2) the symmetric structure constants vanish (Appendix A.1). For all other cases R is unsymmetric.

The final problem concerns the solution of (33), a coupled system of M linear inhomogeneous first-order differential equations. We sketch only briefly the standard procedure [29] for $\det(G) \neq 0$ and G diagonalizable with real eigenvalues. The general case will be treated in the following Section. Now, we are looking for a solution in the form

$$\underline{v}(t) = \underline{v}^{(0)}(t) + \underline{v}^{(\infty)} \ , \tag{57}$$

with given initial condition $\underline{v}(0)$ and, thus,

$$\underline{v}^{(0)}(0) = \underline{v}(0) - \underline{v}^{(\infty)} \ . \tag{58}$$

The solution of the homogeneous part is

$$\underline{v}^{(0)}(t) = \sum_{k=1}^{M} s_k \, e^{\lambda_k t} \underline{x}^{(k)} \ , \tag{59}$$

where $\lambda_k \le 0$ and $\underline{x}^{(k)}$ are solutions of the time-independent eigenvalue problem

$$G \, \underline{x}^{(k)} = \lambda_k \, \underline{x}^{(k)} \ , \tag{60}$$

and the coefficient vector $\underline{s} = (s_1, s_2, \ldots, s_M)^T$ is obtained from the homogenous initial condition by inversion,

$$\underline{s} = Y^{-1} \underline{v}^{(0)}(0) \ , \tag{61}$$

where the i-th column of the matrix Y is $\underline{x}^{(i)}$. If $\underline{k} \neq 0$ there exists a non-trivial stationary state given by

$$\underline{v}^{(\infty)} = -G^{-1}\underline{k} \tag{62}$$

and, due to the form of (59), it can only be reached by $\lim_{t\to\infty} \underline{v}(t) = \underline{v}^{(\infty)}$. We will come back to this point in the next Section. Returning, in conclusion, to the geometrical picture associated with time-evolution in terms of $\underline{v}(t) \in \mathbb{R}^{(M)}$ the following is worth mentioning. In terms of the Frobenius-norm $\|\rho(t)\|$ and (35) one obtains

$$\|\rho(t)\|^2 = \mathrm{Tr}\{\rho^2(t)\} = \frac{1}{N} + \sum_{k=1}^{M} v_k^2(t) \ . \tag{63}$$

Recall that for $R \neq 0$ the constant of motion (47) is lost, and denote for brevity the time-dependent length by $\eta(t)$,

$$\eta^2(t) = \|\underline{v}(t)\|^2 = \sum_{k=1}^{M} v_k^2(t) \ . \tag{64}$$

Thus, $\eta(t)$ is bounded by the spectral condition imposed on $\rho(t)$ by positivity and trace normalization. In fact, if the spectrum of ρ is denoted by $\sigma[\rho] = \{p_i\}_1^N$, one has

$$0 \leq p_i \leq 1 \quad \forall i \ , \tag{65}$$

and this implies the two limiting cases

$$\|\rho(t)\|_{\min} = \frac{1}{\sqrt{N}} \ , \quad \|\rho(t)\|_{\max} = 1 \ , \tag{66}$$

referring to the central state or the pure states, respectively, such that there are the bounds

$$0 \leq \eta(t) \leq \left(1 - \frac{1}{N}\right)^{1/2} \ , \quad t \geq 0 \ . \tag{67}$$

This, in turn, sets important restrictions on the complex spectrum of G,

$$\sigma[G] = \{\lambda_k = \mu_k + i\nu_k\}_1^M \ , \quad \mu_k, \nu_k \in \mathbb{R} \ , \tag{68}$$

since it follows immediately from (57) and (59) that for normalized eigenvectors $\{\underline{x}^{(k)}\}$, one has

$$\eta(t) \leq \sum_{k=1}^{M} |s_k| e^{\mu_k t} + \|\underline{v}^{(\infty)}\| \ . \tag{69}$$

It will become clear in the next Subsect. 2.5 that this type of estimate holds for general G. Since (67) and (69) are satisfied for any initial condition we have proven that

$$A = A^\star \geq 0 \rightarrow \mu_k(A) \leq 0 \ , \quad \forall \lambda_k \in \sigma[G] \ . \tag{70}$$

Consider now a sphere in N dimensions with radius $r_N = (1 - 1/N)^{1/2}$. In the course of time-evolution the point of the vector $\underline{v}(t)$ may describe some trajectory through the inner of the enclosed volume including the origin as well as the surface. In fact, for $R = 0$, i.e., purely reversible (Hamiltonian) dynamics the trajectory is strictly on the surface with radius $\eta(0)$. For a more general case, it may start, for instance, at a certain point on the surface and pass, after some time, exactly through the origin, hereafter returning again to some point on the surface.

This would be the case for spontaneous emission of a two-level atom which starts in the excited state and falls back to the ground state by emission of a photon. The (2×2)-density matrix is [9]

$$\rho(t) = \frac{1}{2} F_0 + v_3(t) F_3 \ , \quad v_1 = v_2 = 0 \ , \tag{71}$$

with

$$v_3(t) = \frac{1}{\sqrt{2}} \left(2\, e^{-2\gamma t} - 1 \right) \ , \tag{72}$$

where F_0 is the unit and $\sqrt{2} F_3$ the diagonal Pauli matrix. Time-evolution transforms diagonal into diagonal states and is, of course, completely positive. Note that $\mathrm{Tr}\{\rho^2(t)\} \neq \mathrm{Tr}\{\rho(t)\} = 1$ except for $t = 0$ or $t = \infty$, and $\eta(t_0) = 0$ for $t_0 = (1/2\gamma) \ln 2$, $(2\gamma)^{-1}$ being the lifetime.

In summary, if η depends upon time there is irreversible behavior involved but the details of the functional dependence may be complicated and one should not expect to find a very useful connection to quantities like "degree of mixture" [30] or von Neumann entropy. Besides this, the usefulness of the coherence vector concept should have become clear from the foregoing considerations.

2.5 Relaxing Semigroups

It is generally of interest to know whether for a given generator L there exists a time-independent final destination state $\rho^{(\infty)}$. This may be a stationary state far from equilibrium or a thermodynamic equilibrium state.

By definition, a semigroup $\Lambda_t = \exp(Lt)$ is called relaxing iff

$$\lim_{t \to \infty} \rho(t) = \rho^{(\infty)} \ . \tag{73}$$

This raises questions concerning existence, uniqueness and particular properties of $\rho^{(\infty)}$ as related to properties of L and, possibly, initial conditions $\rho(0)$. The most prominent and widely used situation is given if $\rho^{(\infty)}$ is unique and

$$\lim_{t \to \infty} \rho(t) = \rho^{(\infty)} \ , \quad \forall \rho(0) \ . \tag{74}$$

In this case the semigroup Λ_t is said to be uniquely or "genuinely" relaxing. Note that (74) is equivalent to $\dot{\rho} = 0$, thus, $\mathrm{L}\,\rho^{(\infty)} = 0$, a consequence of the procedure outlined in the preceding Subsect. 2.4. One can say, too, that $\rho^{(\infty)}$ is a fixed point of the mapping Λ_t because of

$$\Lambda_t\,\rho^{(\infty)} = \rho^{(\infty)}\ . \tag{75}$$

A theorem which guarantees complete relaxation in the sense of (74) in terms of a spectral property of the original relaxation matrix A has been derived by Spohn [31]. It states that

$$2\,d_0 < N\ , \tag{76}$$

where d_0 is the multiplicity of the eigenvalue zero of A. This condition is sufficient but not always necessary as will be shown later for two-level systems.

In order to better understand the details of the asymptotic behavior of $\rho(t)$, also for cases other than those defined by (74), we give an analysis in terms of the coherence vector formulation and classify all possibilities for the admitted bounded solutions of

$$\dot{\underline{v}}(t) = G\,\underline{v}(t) + \underline{k}\ . \tag{77}$$

Since this requires standard algebraic methods [22] only definitions and results will be quoted [32].

As mentioned earlier, G is of no definite symmetry in general and may not be completely diagonalizable in $\mathbb{R}^{(M)}$. If there are degenerate eigenvalues λ_k of multiplicity d_k the corresponding subspace is denoted by $\mathbb{R}^{(d_k)}_{[\lambda_k]} \subset \mathbb{R}^{(M)}$ and, if G is non-diagonalizable in this subspace, the associated Jordan-block is $J^{(d_k)}_{[\lambda_k]}$. The spectrum (68) is then conveniently decomposed into three subsets,

$$\sigma[G] = \sigma^{(n)} \cup \sigma^{(J)} \cup \sigma^{(0)}\ , \tag{78}$$

$$\sigma^{(n)} = \{\lambda_k\}_1^K\ ; \qquad \begin{array}{l}\mu_k \le 0, \nu_k \text{ arbitrary} (\nu_k \neq 0 \text{ for } \mu_k = 0);\\ \text{if } \lambda_{k'} = \lambda_{k"} = \ldots (d_{k'} - \text{fold}),\\ G \text{ diagonalizable in } \mathbb{R}^{(d_{k'})}_{[\lambda_{k'}]}\end{array} \tag{79}$$

$$\sigma^{(J)} = \{\lambda_l\}_{K+1}^L\ ; \qquad \begin{array}{l}\mu_l < 0, \nu_l \text{ arbitrary};\\ \text{only degenerate eigenvalues } \lambda_{l'}\ (d_{l'} - \text{fold}) \text{ with}\\ \text{associated Jordan-block} J^{(d_{l'})}_{[\lambda_{l'}]},\\ \text{non-diagonalizable.}\end{array} \tag{80}$$

$$\sigma^{(0)} = \{\lambda_m\}_{L+1}^M\ ; \qquad \begin{array}{l}\lambda_m = 0\ ;\\ G \text{ diagonalizable in } \mathbb{R}^{((M-L-1)}_{[0]}\ .\end{array} \tag{81}$$

Note that this defines the necessary and sufficient form of $\sigma[G]$ in order to guarantee a time-independent state $\rho^{(\infty)}$. Of course, there are exceptions to

(78) for $\mu_k = 0$ which will be discussed later. Now, the solution $\underline{v}^{(0)}(t)$ of the homogenous part of (77),

$$\dot{\underline{v}}^{(0)}(t) = G\,\underline{v}^{(0)}(t)\ , \tag{82}$$

has the general representation

$$\begin{aligned}\underline{v}^{(0)}(t) = &\sum_{\substack{k=1\\ \lambda_k\in\sigma^{(n)}}}^{K} s_k\, e^{\lambda_k t}\underline{x}^{(k)} \\ &+ \sum_{\substack{l=(K+1)\\ \lambda_l\in\sigma^{(J)}}}^{(L)} e^{\lambda_l t}\left\{\sum_{q=1}^{d_l} s_q\,\underline{p}_q^{(l)}(t)\right\} + \sum_{\substack{m=(L+1)\\ \lambda_m\in\sigma^{(0)}}}^{M} s_m\,\underline{x}^{(m)}\ ,\end{aligned} \tag{83}$$

where the special summation $l = (K+1)$ until (L) in the second summand means that l runs only over the starting indices of all subsequences belonging to different degenerate eigenvalues. The vector

$$\underline{s} = (s_1, s_2, \ldots, s_M)^T \tag{84}$$

contains the initial condition. The components of the vectors $\underline{p}_q^{(l)}(t)$ are polynomials in t at most of degree $(q-1)$ generated by

$$\underline{p}_q^{(l)}(t) = \sum_{n=0}^{q-1} \frac{t^n}{n!}\,(G - \lambda_l \mathbb{1}_M)^n\,\underline{y}_q^{(l)}\ , \tag{85}$$

where the constant vector $\underline{y}_q^{(l)}$ is a solution of

$$(G - \lambda_l \mathbb{1}_M)^q\,\underline{y}_q^{(l)} = 0\ . \tag{86}$$

A simple example of a matrix G with a Jordan-block is worked out for a two-level system in [32] for illustration.

Next, we write a solution of (77) as

$$\underline{v}(t) = \underline{v}^{(0)}(t) + \underline{v}^{(1)} \tag{87}$$

and look for a particular solution $\underline{v}^{(1)}$ satisfying

$$G\,\underline{v}^{(1)} + \underline{k} = 0\ . \tag{88}$$

Three cases must then be distinguished ($\underline{k} \neq 0$). First, for $\sigma[G] = \sigma^{(n)} \cup \sigma^{(J)}$ one has $\det(G) \neq 0$ and, therefore, the unique solution independent of any initial conditions is (62) and we identify

$$\underline{v}^{(1)} \equiv \underline{v}^{(\infty)} = -G^{-1}\underline{k} \ , \tag{89}$$

in this case.

Second, for general $\sigma[G]$ as in (78), $\det(G) = 0$ and (88) has no solution at all if $\underline{k}$ is incompatible with G. As a consequence, (77) has no solution either.

Third, if $\underline{k} \equiv \underline{k}^{(c)}$ is compatible and the deficiency index of G is $\Delta = M - r(G)$ where r is the rank then the equation $G\underline{v}^{(1)} + \underline{k}^{(c)} = 0$ has a Δ-parametric set of solutions (infinitely many). Note that this means that, in contrast to the first case, every given initial condition determines a corresponding final state in a unique way. This is guaranteed by the fact that Y^{-1} as in (61) always exists because, by construction, the columns of Y are the M linearly independent solutions of (82) for $t = 0$. As a quintessence the commonly used technique to determine the stationary solutions by setting all derivatives equal to zero fails in this case since $\underline{v}^{(\infty)} \neq \underline{v}^{(1)}$, but

$$\underline{v}^{(\infty)} = \lim_{t\to\infty} \underline{v}^{(0)}(t) + \underline{v}^{(1)} \ . \tag{90}$$

Finally, we mention the exceptions to (78) concerning complex conjugated pairs of eigenvalues in $\sigma^{(n)}$ with real part equal to zero. Recall that for any pair $\{\lambda_k, \lambda_{k+1}\} \in \sigma^{(n)}$ with $\lambda_k = \bar{\lambda}_{k+1}$ the corresponding two summands in (83) can be written as [29]

$$\begin{aligned} e^{\mu_k t} \Big\{ & s_k(\underline{w}_1^{(k)} \cos(\nu_k t) - \underline{w}_2^{(k)} \sin(\nu_k t)) \\ & + s_{k+1}(\underline{w}_1^{(k)} \sin(\nu_k t) + \underline{w}_2^{(k)} \cos(\nu_k t)) \Big\} \ , \end{aligned} \tag{91}$$

where the vector $\underline{w}^{(k)} = \underline{w}_1^{(k)} + i\underline{w}_2^{(k)}$ is a complex-valued solution of $G\,\underline{w}^{(k)} = \lambda_k\,\underline{w}^{(k)}$. Obviously, for $\mu_k = 0$ the limit for $t \to \infty$ does not exist. Thus, the general situation may yield some components of $\underline{v}^{(0)}(t)$ with existing limit and the others without limit. In this case, the semigroup is called "partially relaxing" and one can write, for large $t > T$,

$$\rho^{(T)}(t) \cong \rho^{(r)} + \rho^{(p)}(t) \ , \tag{92}$$

where

$$\rho^{(r)} = \lim_{t\to\infty} \Big\{ \rho(t) - \rho^{(p)}(t) \Big\} \ , \tag{93}$$

$\rho^{(p)}(t)$ being the purely periodic undamped part of $\rho(t)$. Similar considerations as above may be found in [33–37].

Since stationary states are of central importance for entropy production in irreversible processes we will continue related discussions in an extra Sect. 8 lateron.

3 Two-level Systems: Generalized Magnetic or Optical Bloch-equations

3.1 Details of the Full Relaxation Equations for Static External Fields

By analogy to notational conventions in magnetic resonance we write the general time-independent Hamiltonian as

$$H = \frac{1}{2}\begin{pmatrix} \omega_0 & \omega_1 + i\omega_2 \\ \omega_1 - i\omega_2 & -\omega_0 \end{pmatrix} , \tag{94}$$

and, according to (44) and Appendix A.1,

$$h_1 = \frac{\omega_1}{\sqrt{2}} , \qquad h_2 = -\frac{\omega_2}{\sqrt{2}} , \qquad h_3 = \frac{\omega_0}{\sqrt{2}} . \tag{95}$$

To avoid too many indices the relaxation-matrix A is conveniently parameterized by

$$A = \begin{pmatrix} \frac{1}{2}(\gamma_1 + \gamma_2 - \gamma_3) & \alpha + i\nu & \beta + i\mu \\ \alpha - i\nu & \frac{1}{2}(\gamma_1 + \gamma_3 - \gamma_2) & \delta + i\lambda \\ \beta - i\mu & \delta - i\lambda & \frac{1}{2}(\gamma_2 + \gamma_3 - \gamma_1) \end{pmatrix} , \tag{96}$$

and the "Bloch-vector" $\underline{v}$ has components

$$\underline{v} = (u, v, w)^T , \tag{97}$$

where

$$u = \mathrm{Tr}(F_1\,\rho) = \sqrt{2}\,\mathrm{Re}(\rho_{12}) , \tag{98}$$

$$v = \mathrm{Tr}(F_2\,\rho) = -\sqrt{2}\,\mathrm{Im}(\rho_{12}) , \tag{99}$$

$$w = \mathrm{Tr}(F_3\,\rho) = \frac{1}{\sqrt{2}}(\rho_{11} - \rho_{22}) . \tag{100}$$

With these definitions one gets for $G = Q + R$ from (45)

$$Q = \begin{pmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{pmatrix} , \tag{101}$$

from (53)

$$R = \begin{pmatrix} -\gamma_3 & \alpha & \beta \\ \alpha & -\gamma_2 & \delta \\ \beta & \delta & -\gamma_1 \end{pmatrix} , \tag{102}$$

and for $\underline{k}$ from (54),

$$\underline{k} = -\sqrt{2}(\lambda, -\mu, \nu)^T . \tag{103}$$

Thus, the most general master equation compatible with complete positivity of time-evolution is equivalent to the three coupled differential equations

$$\dot{u} = -\gamma_3 u + (\alpha - \omega_0)v + (\beta - \omega_2)w - \sqrt{2}\lambda \ , \tag{104}$$

$$\dot{v} = (\alpha + \omega_0)u - \gamma_2 v + (\delta - \omega_1)w + \sqrt{2}\mu \ , \tag{105}$$

$$\dot{w} = (\beta + \omega_2)u + (\delta + \omega_1)v - \gamma_1 w - \sqrt{2}\nu \ . \tag{106}$$

In addition, the positive-semidefiniteness of A imposes, according to Subsect. 2.2, the following restrictions on the induced relaxation parameters:

$$0 \leq \gamma_i \leq \gamma_k + \gamma_l \ , \qquad (i,k,l) \text{ a permutation of } (1,2,3) \ , \tag{107}$$

$$4(\alpha^2 + \nu^2) \leq \gamma_1^2 - (\gamma_2 - \gamma_3)^2 \ , \tag{108}$$

$$4(\beta^2 + \mu^2) \leq \gamma_2^2 - (\gamma_1 - \gamma_3)^2 \ , \tag{109}$$

$$4(\delta^2 + \lambda^2) \leq \gamma_3^2 - (\gamma_1 - \gamma_2)^2 \ , \tag{110}$$

$$\begin{aligned} 16(\alpha\beta\delta + \alpha\lambda\mu + \delta\mu\nu) + 4\gamma_1(\alpha^2 + \nu^2) + 4\gamma_2(\beta^2 + \mu^2) + 4\gamma_3(\delta^2 + \lambda^2) \\ + \gamma_1^2(\gamma_2 + \gamma_3) + \gamma_2^2(\gamma_1 + \gamma_3) + \gamma_3^2(\gamma_1 + \gamma_2) \geq \\ 16\beta\lambda\nu + 4\gamma_1(\beta^2 + \delta^2 + \lambda^2 + \mu^2) \\ + 4\gamma_2(\alpha^2 + \delta^2 + \lambda^2 + \nu^2) + 4\gamma_3(\alpha^2 + \beta^2 + \mu^2 + \nu^2) \\ + 2\gamma_1\gamma_2\gamma_3 + \gamma_1^3 + \gamma_2^3 + \gamma_3^3 \ . \end{aligned} \tag{111}$$

Note that equations similar to (104)–(106) can be obtained for externally applied alternating fields but this more delicate discussion is postponed to the next section.

It is certainly urgent to show that a very special case of (104)–(106) yields the old familiar Bloch equations in a static field for the (normalized) magnetization $\underline{M} = (M_x, M_y, M_z)^T$ and, correspondingly, $M_x = u$, $M_y = v$, $M_z = w$. We set

$$\omega_1 = \omega_2 = 0 \ , \quad \alpha = \beta = \delta = \lambda = \mu = 0 \ , \tag{112}$$

and rename

$$\frac{1}{T_1} \equiv \gamma_1 \ , \quad \frac{1}{T_2} \equiv \gamma_2 = \gamma_3 \ , \quad \frac{M_0}{T_1} \equiv -\sqrt{2}\nu \ , \tag{113}$$

to obtain

$$\begin{aligned} \dot{M}_x &= -\frac{M_x}{T_2} - \omega_0 M_y \ , \\ \dot{M}_y &= \omega_0 M_x - \frac{M_y}{T_2} \ , \\ \dot{M}_z &= -\frac{1}{T_1}(M_z - M_0) \ , \end{aligned} \tag{114}$$

where $M_0 \leq 1/\sqrt{2}$ (see (67)) is the stationary z-magnetization, and T_1 and T_2 the longitudinal and transverse relaxation times correlated by

$$T_1 \geq \frac{1}{2} T_2 \ , \tag{115}$$

as obtained from (107) and (113). To trace back the details of the generator L_{D} in (30) and (32) for this simple case one observes that A is given by

$$A = \begin{pmatrix} \frac{1}{2T_1} & -i\frac{M_0}{\sqrt{2}T_1} & 0 \\ +i\frac{M_0}{\sqrt{2}T_1} & \frac{1}{2T_1} & 0 \\ 0 & 0 & \frac{1}{T_2} - \frac{1}{2T_1} \end{pmatrix} \ , \tag{116}$$

with eigenvalues

$$\lambda_{1,2} = \frac{1}{2T_1}(1 \pm \sqrt{2} M_0) \ , \quad \lambda_3 = \frac{1}{T_2} - \frac{1}{2T_1} \ , \tag{117}$$

and eigenvectors (rows of S)

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i & 0 \\ 1 & -i & 0 \\ 0 & 0 & \sqrt{2} \end{pmatrix} \ , \tag{118}$$

such that from $\underline{W} = S\underline{F}$ and (31) one obtains [47] the form (32) for non-hermitian $\underline{V}$, explicitely given in terms of the unnormalized Pauli matrices by

$$\begin{aligned} V_1 &= \sqrt{\frac{\lambda_1}{2}}(\sigma_1 + i\sigma_2) \ , \\ V_2 &= -\sqrt{\frac{\lambda_2}{2}}(\sigma_1 - i\sigma_2) \ , \\ V_3 &= \sqrt{\lambda_3}\, \sigma_3 \ . \end{aligned} \tag{119}$$

It may come as a surprise that the theory of quantum Markovian master equations provides such general equations that even after the many restrictions in (112) one still obtains a result that is of such a wide applicability that it covers almost all experimental situations as is well-known for the Bloch-equations. This suggests exploring the physical implications of the more general cases.

For the moment being we return to the general solutions of $\dot{\underline{v}} = G\,\underline{v} + \underline{k}$ outlined in Appendix A.2 and discuss some of their properties. If the determinant D of the evolution matrix G, given by

$$\begin{aligned} D = &-2\alpha\omega_1\omega_2 + 2\beta\omega_0\omega_1 - 2\delta\omega_0\omega_2 + 2\alpha\beta\delta \\ &-\gamma_1\gamma_2\gamma_3 + \gamma_1(\alpha^2 - \omega_0^2) + \gamma_2(\beta^2 - \omega_2^2) + \gamma_3(\delta^2 - \omega_1^2) \ , \end{aligned} \tag{120}$$

is not zero there exists a unique stationary solution $\underline{v}^{(\infty)} = (u_\infty, v_\infty, w_\infty)^T$ with components

$$\begin{aligned} u_\infty = \frac{\sqrt{2}}{D} \big\{ &\lambda[\gamma_1\gamma_2 + \omega_1^2 - \delta^2] - \mu[\gamma_1(\alpha - \omega_0) + (\delta + \omega_1)(\beta - \omega_2)] \\ &+\nu[(\alpha - \omega_0)(\delta - \omega_1) + \gamma_2(\beta - \omega_2)] \big\} \ , \end{aligned} \tag{121}$$

$$v_\infty = \frac{\sqrt{2}}{D}\left\{\lambda[\gamma_1(\alpha+\omega_0)+(\delta-\omega_1)(\beta+\omega_2)]-\mu[\gamma_1\gamma_3+\omega_2^2-\beta^2]\right.$$
$$\left.+\nu[\gamma_3(\delta-\omega_1)+(\alpha+\omega_0)(\beta-\omega_2)]\right\}\ , \tag{122}$$

$$w_\infty = \frac{\sqrt{2}}{D}\left\{\lambda[\gamma_2(\beta+\omega_2)+(\alpha+\omega_0)(\delta+\omega_1)-\mu[\gamma_3(\delta+\omega_1)\right.$$
$$\left.+(\alpha-\omega_0)(\beta+\omega_2)]+\nu[\gamma_2\gamma_3+\omega_0^2-\alpha^2]\right\}\ . \tag{123}$$

The approach to $\underline{v}^{(\infty)}$ is smooth multi-exponential for a discriminant $d \leq 0$ in (363) but exponentially damped oscillatory for $d > 0$. Purely reversible dynamics is easily recovered from (367) by setting all relaxation parameters equal to zero which yields the oscillation frequencies $\pm(\omega_0^2+\omega_1^2+\omega_2^2)^{1/2}$ corresponding to the diagonalized Hamiltonian (94).

3.2 Alternating External Fields and Constant Relaxation

The most general effect of an alternating external field will show up in a time-dependent Hamiltonian as well as in modified relaxation parameters that may become dependent upon strength and frequency of the field since the latter acts not only on the open system but equally well on the reservoir. A rigorous derivation within a Markovian approximation seems almost impossible but phenomenological experience has shown that, in numerous cases, such a description may be quite adequate. An attempt to treat this complicated situation under certain restrictions will be presented in Sect. 6. The following treatment applies to relatively weak fields and the only time-dependence of the generator L is introduced through the Hamiltonian resulting also in a time-dependent matrix G_t in the coherence-vector picture. In place of (94) we choose a real H in the form

$$H(t) = \frac{1}{2}\begin{pmatrix} \omega_0 & 2\omega_1\cos(\omega t) \\ 2\omega_1\cos(\omega t) & -\omega_0 \end{pmatrix} \tag{124}$$

with

$$h_1 = \sqrt{2}\,\omega_1\cos(\omega t)\ , \quad h_2 = 0\ , \quad h_3 = \frac{\omega_0}{\sqrt{2}}\ , \tag{125}$$

but A is kept constant. This is the situation commonly dealt with in most magnetic or optical resonance experiments but, of course, the present equations are much more general. We stress that we do not perform a rotating wave approximation (RWA) on $H(t)$ but work out the full time-dependent equations and introduce finally an averaging procedure that, in the special case of ordinary Bloch equations, will turn out to be equivalent to RWA. Some aspects of the related problem are discussed in the book by Agarwal [9] (or also Ref. [13]). Keeping in mind the advantages of common RWA we also go to a frame rotating at frequency ω although, at first glance, this only seems to complicate the situation for our general equations. The rotating frame is introduced [13] by an orthogonal transformation O_t in the (u, v)-plane,

$$O_t = \begin{pmatrix} \cos(\omega t) & \sin(\omega t) & 0 \\ -\sin(\omega t) & \cos(\omega t) & 0 \\ 0 & 0 & 1 \end{pmatrix} , \tag{126}$$

and the original equation $\dot{\underline{v}} = G\,\underline{v} + \underline{k}$ is written as

$$\dot{\tilde{\underline{v}}}(t) = \tilde{G}_t\,\tilde{\underline{v}}(t) + \tilde{\underline{k}}(t) , \tag{127}$$

where

$$\tilde{\underline{v}}(t) = O_t\,\underline{v}(t) , \quad \tilde{\underline{k}}(t) = O_t\,\underline{k} , \tag{128}$$

$$\tilde{G}_t = O_t G O_{-t} - O_t \dot{O}_{-t} = O_t G O_{-t} + \dot{O}_t O_{-t} . \tag{129}$$

The details are in Appendix A.3. To eliminate the double-frequency terms and to finally transform (127) into a system of equations with constant coefficients one defines an appropriate time average of $\tilde{G}_t$ by

$$\mathbb{G} = \frac{\omega}{\pi} \int_0^{\pi/\omega} \tilde{G}_\tau \; d\tau . \tag{130}$$

Whether this particular choice is meaningful or not depends on the details of the alternating field and the resolution available in a time-resolved experiment. In generalization of the procedure for constructing the solution (57) one finds for the solution of

$$\dot{\tilde{\underline{v}}}(t) = \mathbb{G}\,\tilde{\underline{v}}(t) + \tilde{\underline{k}}(t) \tag{131}$$

the representation

$$\tilde{\underline{v}}(t) = e^{\mathbb{G}t}\,\tilde{\underline{v}}(0) + \int_0^t e^{\mathbb{G}(t-s)} \tilde{\underline{k}}(s)\; ds , \tag{132}$$

where the exponential form can be calculated from the fundamental matrix solution [22, 29] Y_t of the homogeneous part of (131),

$$e^{\mathbb{G}t} = Y_t\, Y_0^{-1} , \tag{133}$$

the columns of Y_t being given by

$$Y_t = \left\{ e^{\lambda_k t} \underline{x}^{(k)} \right\}_1^M , \tag{134}$$

as obtained from solving the eigenvalue problem $\mathbb{G}\underline{x}^{(k)} = \lambda_k\,\underline{x}^{(k)}$.

Consider again the very special case as in (112)–(113) but now for $\omega_1 \neq 0$ and replace $\tilde{\underline{v}}(t) \to \underline{\tilde{M}} = (\tilde{M}_x, \tilde{M}_y, \tilde{M}_z)^T$ to recover the old familiar Bloch-equations in an alternating field and rotating frame,

$$\begin{aligned} \dot{\tilde{M}}_x &= -\frac{\tilde{M}_x}{T_2} - \Delta\,\tilde{M}_y , \\ \dot{\tilde{M}}_y &= \Delta\,\tilde{M}_x - \frac{\tilde{M}_y}{T_2} - \omega_1 \tilde{M}_z , \\ \dot{\tilde{M}}_z &= \omega_1 \tilde{M}_y - \frac{1}{T_1}(\tilde{M}_z - M_0) , \end{aligned} \tag{135}$$

where Δ is the frequency detuning

$$\Delta = \omega_0 - \omega \ . \tag{136}$$

In contrast, the full generalized Bloch-equations (131) are given in terms of the matrix

$$\mathbb{G} = \begin{pmatrix} -\Gamma_2 & -\Delta & \frac{2}{\pi}\delta \\ \Delta & -\Gamma_2 & -\frac{2}{\pi}\beta - \omega_1 \\ \frac{2}{\pi}\delta & -\frac{2}{\pi}\beta + \omega_1 & -\gamma_1 \end{pmatrix} \tag{137}$$

with the average decay constant Γ_2 for the (u, v)-components,

$$\Gamma_2 = \frac{1}{2}(\gamma_2 + \gamma_3) \ , \tag{138}$$

and the average constant vector

$$\underline{\tilde{k}} = \sqrt{2} \left(\frac{2}{\pi}\mu \, , \, \frac{2}{\pi}\lambda \, , \, -\nu \right)^T \ . \tag{139}$$

Somewhat surprising, there is again only one transverse relaxation constant Γ_2 although in the original equations in the laboratory frame there were two different ones ($\gamma_2 \neq \gamma_3$). The most noticeable difference between (137) and (135) appears in the coupling $\frac{2}{\pi}\delta$ between the u- and w- components which is absent in the Bloch-equations due to rotational symmetry with respect to the static field. Furthermore, the parameter α disappears, evidently due to the form chosen for (130) the latter also being responsible for an exchange between β and δ if (137) is compared with (104)–(106). Finally, it should be stressed that only in the case of small additional terms in (137) relative to (135) is the transformation to a rotating frame together with (130) meaningful. In a general situation with all parameters of comparable order of magnitude the proposed procedure would certainly fail to give reliable answers. On the other hand, it is certainly interesting to analyze, e.g., the effect of the additional δ-coupling and this will be done in the following section.

3.3 Modified Lineshapes and Free Induction Decay

The generalized relaxation equations in a periodically varying field will give rise to modifications in the well-known lineshapes obtained from ordinary Bloch equations. Note that the conventional definition of lineshape implies existence of a stationary solution $\underline{\tilde{v}}^{(\infty)}$ that can directly be obtained from the formulas (120)–(123), at least for the case considered in the following,

$$\lambda = \mu = 0 \ , \quad \nu \neq 0 \ , \tag{140}$$

upon replacing there $\omega_0 \to \Delta$, $\gamma_2 = \gamma_3 \to \Gamma_2$, $\beta \to 2\delta/\pi$, $\delta \to -2\beta/\pi$ and $\omega_2 = 0$. Explicitely, one finds

$$\tilde{u}_\infty = \frac{\sqrt{2}\nu}{D}\left\{\frac{2}{\pi}\delta\Gamma_2 + \Delta\,(\omega_1 + \frac{2}{\pi}\beta)\right\}\ , \tag{141}$$

$$\tilde{v}_\infty = \frac{\sqrt{2}\nu}{D}\left\{\frac{2}{\pi}\delta\Delta - \Gamma_2(\omega_1 + \frac{2}{\pi}\beta)\right\}\ , \tag{142}$$

$$\tilde{w}_\infty = -\frac{\sqrt{2}\nu}{D}\left\{\Delta^2 + \Gamma_2^2\right\}\ , \tag{143}$$

where the determinant is

$$D = \Gamma_2\left[\left(\frac{2}{\pi}\beta\right)^2 + \left(\frac{2}{\pi}\delta\right)^2 - \omega_1^2\right] + \frac{4}{\pi}\delta\Delta\,\omega_1 - \gamma_1(\Delta^2 + \Gamma_2^2)\ . \tag{144}$$

In terms of D the lineshape function [48] is given by

$$\mathcal{L}(\omega;\beta,\delta) = -\frac{\gamma_1\Gamma_2^2}{D}\ , \tag{145}$$

and we write for the Bloch-lineshape

$$\mathcal{L}_{\rm B}(\omega) = \left[1 + T_2^2(\omega_0 - \omega)^2 + T_1T_2\omega_1^2\right]^{-1}\ , \tag{146}$$

where $\gamma_2 = \gamma_3 = T_2^{-1}, \gamma_1 = T_1^{-1}$ and $\Delta = \omega_0 - \omega$ have been used. Thus,

$$\mathcal{L}^{-1}(\omega;\beta,\delta) = \mathcal{L}_{\rm B}^{-1}(\omega) + \mathcal{L}_{\rm K}^{-1}(\omega;\beta,\delta)\ , \tag{147}$$

such that the modifications arising from the more general terms in the Kossakowski-generator are given directly by

$$\mathcal{L}_{\rm K}^{-1}(\omega;\beta,\delta) = -\frac{4T_1T_2}{\pi^2}\left[\beta^2 + \delta^2 + \pi T_2\delta(\omega_0 - \omega)\omega_1\right]\ , \tag{148}$$

with the consequence that, in general, all characteristics of the resonance peak are affected, i.e., its position, height and width. Note in particular, that there is an asymmetric contribution to power broadening proportional to the frequency off-set Δ whereas ordinary power broadening is independent of Δ and quadratic in ω_1. On resonance there is some reduction of broadening according to

$$\mathcal{L}(\omega = \omega_0;\beta,\delta) = \left[1 + T_1T_2\left\{\omega_1^2 - \frac{4}{\pi^2}(\beta^2 + \delta^2)\right\}\right]^{-1}\ , \tag{149}$$

whereas a similar reduction is present in the full time-dependent on-resonance signal whose exponential time-factors are obtained from case (367) as

$$\lambda_1 = -\Gamma_2\ , \tag{150}$$

$$\lambda_{2,3} = -\frac{1}{2}(\gamma_1 + \Gamma_2) \pm i\Omega\ , \tag{151}$$

where the effective Rabi-frequency is given by

$$\Omega = \left[\omega_1^2 - \frac{4}{\pi^2}(\beta^2 + \delta^2) - \frac{1}{4}(\gamma_1 - \Gamma_2)^2\right]^{1/2} , \tag{152}$$

for a sufficient strong transverse field, of course.

Next, we consider a particular example of free induction decay (FID) in order to extract information on the additional asymmetry parameter δ. The common techniques may be found in References [12, 13, 48, 49]. Normally, an FID experiment is used for an independent measurement of the transverse relaxation time T_2 but, under suitable conditions, other parameters can be measured as well. For our purposes it is enough to consider a special case of (137),

$$\mathbb{G} = \begin{pmatrix} -\gamma & -\Delta & \tilde{\delta} \\ \Delta & -\gamma & -\omega_1 \\ \tilde{\delta} & \omega_1 & -\gamma \end{pmatrix} \tag{153}$$

with all three diagonal relaxation parameters equal to γ and the abbreviation $\tilde{\delta} = 2\delta/\pi$. In a first preparative step a strong and short τ-pulse with detuning Δ is applied such that relaxation plays no role ($\omega_1 \gg \gamma, \tilde{\delta}$). The system, originally being in an equilibrium state described by $\underline{v}^{(\infty)}$, is transformed into a state

$$\underline{v}(\tau) \cong P_\tau \underline{v}^{(\infty)} \tag{154}$$

where the matrix P_τ is given by [13]

$$P_\tau = \frac{1}{\Omega_0^2} \begin{pmatrix} \omega_1^2 + \Delta^2 \cos(\Omega_0 \tau) & -\Omega_0 \Delta \sin(\Omega_0 \tau) & \omega_1 \Delta[1 - \cos(\Omega_0 \tau)] \\ \Omega_0 \Delta \sin(\Omega_0 \tau) & \Omega_0^2 \cos(\Omega_0 \tau) & -\Omega_0 \omega_1 \sin(\Omega_0 \tau) \\ \omega_1 \Delta[1 - \cos(\Omega_0 \tau)] & \Omega_0 \omega_1 \sin(\Omega_0 \tau) & \Delta^2 + \omega_1^2 \cos(\Omega_0 \tau) \end{pmatrix} \tag{155}$$

with the approximate generalized Rabi-frequency

$$\Omega_0 \cong \left(\omega_1^2 + \Delta^2\right)^{1/2} . \tag{156}$$

In a second step the power of the alternating field is drastically reduced to fulfill the conditions $\omega_1^2 \ll (\Delta^2 - \tilde{\delta}^2), \gamma^2, \tilde{\delta}^2$ such that the solutions of (131) can be obtained to a good approximation by setting $\omega_1 = 0$ in (153). We use the abbreviations

$$u_0 = u(\tau) - \tilde{u}_\infty , \quad v_0 = v(\tau) - \tilde{v}_\infty , \quad w_0 = w(\tau) - \tilde{w}_\infty , \tag{157}$$

where $\underline{v}^{(\infty)}$ in (154) is given by (121)–(123) for $\lambda = \mu = 0$, $\gamma_1 = \gamma_2 = \gamma_3 \equiv \gamma$, $\alpha = \beta = 0$, $\omega_1 = \omega_2 = 0$. $\tilde{\underline{v}}^{(\infty)}$ in (157) is calculated from $\tilde{\underline{v}}^{(\infty)} = -\mathbb{G}^{-1}\tilde{\underline{k}}$ with $\tilde{\underline{k}}$ given by (139). In terms of the frequency

$$\Omega \cong \left(\Delta^2 - \tilde{\delta}^2\right)^{1/2} , \tag{158}$$

the solutions in the rotating frame are as follows.

$$\tilde{u}(t) \cong u_0 e^{-\gamma t}\cos(\Omega t) - \frac{1}{\Omega}(v_0\Delta - w_0\tilde{\delta})e^{-\gamma t}\sin(\Omega t) + \tilde{u}_\infty \ , \tag{159}$$

$$\tilde{v}(t) \cong \frac{e^{-\gamma t}}{\Omega^2}\Big\{\Delta(v_0\Delta - w_0\tilde{\delta})\cos(\Omega t) + u_0\Omega\Delta\sin(\Omega t) - \tilde{\delta}(v_0\tilde{\delta} - w_0\Delta)\Big\} + \tilde{v}_\infty \ , \tag{160}$$

$$\tilde{w}(t) \cong \frac{e^{-\gamma t}}{\Omega^2}\Big\{\tilde{\delta}(v_0\Delta - w_0\tilde{\delta})\cos(\Omega t) + u_0\Omega\tilde{\delta}\sin(\Omega t) - \Delta(v_0\tilde{\delta} - w_0\Delta)\Big\} + \tilde{w}_\infty \ . \tag{161}$$

For sufficiently small $\tilde{\delta}$ one may have $u_\infty, v_\infty \ll w_\infty$, such that a strong $(\pi/2)$-pulse ($\Omega_0\tau = \pi/2, \omega_1 \gg \Delta$) yields approximately $u(\tau) \cong 0$, $w(\tau) \cong 0$ and $v(\tau) \cong -w_\infty$. This gives for (161), for instance, the approximate formula

$$\tilde{w}(t) \cong \frac{w_\infty \Delta\,\tilde{\delta}}{\Omega^2} e^{-\gamma t}\{1 - \cos(\Omega t)\} \ . \tag{162}$$

This is interesting since ordinary FID shows no oscillations at all in the $\tilde{w}$-component, and by a suitable choice of the detuning Δ one has a rather direct detection of the anisotropy parameter $\tilde{\delta}$.

4 Three-level Systems

4.1 General Equations

The description of the general dynamics of a three-level system including relaxation is extremely complicated and the equations are no longer analytically solvable as has been the case for two-level systems. The jump in dimension from 3 to 8 makes it impossible to use simple physical pictures as earlier for the Bloch- or coherence-vector. Recall that according to Appendix A.1 the SU(3)-decomposition for ρ is

$$\rho(t) = \frac{1}{3}\mathbb{1}_3 + \sum_{k=1}^{8} v_k(t) F_k \ , \tag{163}$$

such that, at any instant of time, 8 parameters are needed to fix the state. The relaxation matrix A is also (8×8) and, if diagonal, contains 8 independent (positive) parameters or, else, 36 similar parameters but bounded among each other by inequalities according to Subsect. 2.2. Furthermore, the relations between the elements of G and those of A fill large tables and will not be reproduced here. For instance, the (11)-element is given by

$$g_{11} = -\frac{1}{4}\{4(a_{22} + a_{33}) + a_{44} + a_{55} + a_{66} + a_{77} + 2\,\mathrm{Im}(a_{45} + a_{67})\} \ , \tag{164}$$

and a complete list may be found in [50]. Obviously, the diagonal relaxation constants g_{ii} are also linked to off-diagonal elements of A and even if the a_{ik}'s were calculated as Fourier transforms of correlation functions of reservoir observables would it become almost hopeless to get a reasonable overlook over the relaxation mechanism. Therefore, one must seek simplifications and physically acceptable approximations by using as few relaxation parameters as ever possible, together with a somewhat special Hamiltonian. Nice examples of this type are provided by so-called decaying two-level systems [51] where, essentially, the interesting dynamics involves only the upper two levels. The third ground state level plays a relatively unimportant role in that it is coupled to the excited states just via decay constants such that, in the long time limit, it represents the final state of the system. We are going to consider such a situation in the following.

4.2 Bloch-equations for Decaying Systems

The coupled differential equations for the 8 components of the coherence-vector can be decoupled into a relevant set for four components and an irrelevant set for the rest [52]. We denote the uppermost level by $|1\rangle$, the middle one by $|2\rangle$ and the lowest one by $|3\rangle$ and suppose that there is irreversible decay from $|1\rangle$ to $|3\rangle$ by a rate constant q_1 and from $|2\rangle$ to $|3\rangle$ by q_2. Note that for $q_1 = q_2 = 0$ the upper two levels represent a stable two-level system described by (104)–(106) if we identify the first three components of the coherence-vector again by u, v and w. To include decay to the third level one certainly needs the v_8-component, but we prefer to introduce the physically more meaningful quantity of the number of excited atoms (or molecules),

$$n(t) = \rho_{11}(t) + \rho_{22}(t) = \sqrt{\tfrac{2}{3}}\ \mathrm{Tr}\{(\sqrt{\tfrac{2}{3}}\,\mathbb{1}_3 + F_8)\,\rho(t)\} \tag{165}$$

normalized to a maximum of 1. Thus, we form a four-component vector

$$\underline{m} = (u, v, w, n)^T \tag{166}$$

obeying the differential equation

$$\dot{\underline{m}} = G\,\underline{m}\ , \tag{167}$$

where the most general form of G under our assumptions is obtained by setting

$$a_{ik} = 0\ , \quad 1 \le i \le 3 < k \le 7\ , \quad 4 \le i \le k = 8\ , \tag{168}$$

for the relaxation matrix and

$$h_i = 0\ , \quad 4 \le i \le 7 \tag{169}$$

for the Hamiltonian. This is a result of detailed analysis of all relations like (164). In addition one gets

$$2\,\mathrm{Im}(a_{45}) = a_{44} + a_{55} = q_1 \ , \tag{170}$$

$$2\,\mathrm{Im}(a_{67}) = a_{66} + a_{77} = q_2 \ , \tag{171}$$

and we abbreviate,

$$q = \frac{1}{2}(q_1 + q_2) \ , \quad \chi = \frac{1}{2}(q_1 - q_2) \ . \tag{172}$$

The final form of the matrix G is then given by $G = Q + R$ with the antisymmetric contributions (level-shifts) in (53) reabsorbed in Q leading to

$$Q = \begin{pmatrix} 0 & -\sqrt{2}\,h_3 + \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{38}) & \sqrt{2}\,h_2 - \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{28}) & 0 \\ \sqrt{2}\,h_3 - \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{38}) & 0 & -\sqrt{2}\,h_1 + \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{18}) & 0 \\ -\sqrt{2}\,h_2 + \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{28}) & \sqrt{2}\,h_1 - \frac{1}{\sqrt{3}}\,\mathrm{Im}(a_{18}) & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{173}$$

$$R = \begin{pmatrix} -(\gamma_3 + q) & \mathrm{Re}(a_{12}) & \mathrm{Re}(a_{13}) & -\sqrt{2}\,\mathrm{Im}(a_{23}) \\ \mathrm{Re}(a_{12}) & -(\gamma_2 + q) & \mathrm{Re}(a_{23}) & -\sqrt{2}\,\mathrm{Im}(a_{13}) \\ \mathrm{Re}(a_{13}) & \mathrm{Re}(a_{23}) & -(\gamma_1 + q) & -\sqrt{2}\,\mathrm{Im}(a_{12}) - \chi \\ 0 & 0 & -\chi & -q \end{pmatrix} \tag{174}$$

It is instructive to still reduce the above forms to the simplest non-trivial generalization of (114) in order to get an idea about the detailed influence of the new decay terms. As mentioned, we use slightly more general equations than those in (114) by allowing for some anisotropy and replacing therefore T_2 by T_3 in the equation for $\dot{M}_x$. This causes the stationary magnetization $\underline{M}^0 = (M_x^0, M_y^0, M_z^0)^T$, a property of the stable two-level system only ($q_1 = q_2 = 0$), to have three components different from zero. Apart from this we use exactly the same conventions as in Subsects. 3.1, replace $n \to N$, set $a_{18} = a_{28} = a_{38} = 0$ and obtain finally,

$$\begin{aligned} \dot{M}_x(t) &= -(T_3^{-1} + q)M_x(t) - \omega_0\, M_y(t) + (M_x^0\, T_3^{-1} + \omega_0\, M_y^0)N(t) \ , \\ \dot{M}_y(t) &= \omega_0\, M_x(t) - (T_2^{-1} + q)M_y(t) + (M_y^0\, T_2^{-1} - \omega_0\, M_x^0)N(t) \ , \qquad (175) \\ \dot{M}_z(t) &= -(T_1^{-1} + q)M_z(t) + (M_z^0\, T_1^{-1} - \chi)N(t) \ , \end{aligned}$$

$$\dot{N}(t) = -\chi\, M_z(t) - q\, N(t) \ . \tag{176}$$

Evidently, this procedure has introduced a further decoupling of the four components into two pairs (175) and (176). It is interesting to note that the level-selectivity of decay ($q_1 \neq q_2$) may cause oscillations in the M_z-component even though there is only a static field present. More precisely, the time-dependence is like

$$M_z(t) \sim e^{-\frac{1}{2}(T_1^{-1} + q_1 + q_2)t} \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} \left([M_z^0\, T_1^{-1}(q_1 - q_2) - (2\,T_1)^{-2}]^{1/2} t \right) \ , \tag{177}$$

showing periodical damped behavior if the radicand is positive. In comparison, the well-known Torrey-oscillations [49] obtained from ordinary Bloch-equations occur only in presence of an alternating field.

To treat the action of an additional alternating external field we choose a Hamiltonian

$$H(t) = H_0 + W_-(t) \ , \quad H_0 = \frac{\omega_0}{\sqrt{2}} F_3 \ , \tag{178}$$

where the common form $W(t) = \sqrt{2}\omega_1 F_1 \cos(\omega t)$ for the frequency field has been reduced by the ordinary RWA to

$$W_-(t) = \frac{\omega_1}{2} \left(P^{(1,2)} e^{-i\omega t} + P^{(2,1)} e^{i\omega t} \right) \ . \tag{179}$$

The transformation to the rotating system is performed through the unitary operator

$$U(t) = \exp \left[i \frac{\omega}{\sqrt{2}} F_3 t \right] \ , \tag{180}$$

and any operator O is thus transformed into

$$\hat{O}(t) = U(t) O U^\star(t) \ . \tag{181}$$

In particular, $\hat{H}(t)$ is independent of t and given by

$$\hat{H} = H_0 + \hat{W}_- \ , \quad \hat{W}_- = \frac{\omega_1}{\sqrt{2}} F_1 \ , \tag{182}$$

and the master equation in the rotating frame is

$$\dot{\hat{\rho}}(t) = \left\{ \hat{\mathrm{L}}_{\mathrm{H}} + \hat{\mathrm{L}}_{\mathrm{D}}(t) \right\} \hat{\rho}(t) \ , \tag{183}$$

$$\hat{\mathrm{L}}_{\mathrm{H}} \hat{\rho}(t) = -\frac{i}{\sqrt{2}} \left[(\omega_1 F_1 + \Delta F_3), \hat{\rho}(t) \right] \ , \quad \Delta = \omega_0 - \omega \ , \tag{184}$$

$$\hat{\mathrm{L}}_{\mathrm{D}}(t) \hat{\rho}(t) = \frac{1}{2} \sum_{i,j=1}^{8} a_{ij} \left\{ [\hat{F}_i(t), \hat{\rho}(t) \hat{F}_j(t)] + [\hat{F}_i(t) \hat{\rho}(t), \hat{F}_j(t)] \right\} \ , \tag{185}$$

assuming again constant relaxation A.

Now, the simplest equations are obtained by trying to reestablish the original structure of the master equation, that is to require that the generator be time-independent in the rotating frame. To sketch the procedure we write for the dissipative contribution in terms of matrix elements,

$$\dot{\hat{\rho}}^{(D)}_{kl}(t) = \sum_{m,n=1}^{3} \left\{ \hat{\mathrm{L}}_{\mathrm{D}}(t) \right\}^{mn}_{kl} \hat{\rho}_{mn}(t) \ , \tag{186}$$

where in this "supermatrix" notation the elements $\{\hat{\mathrm{L}}_{\mathrm{D}}(t)\}^{mn}_{kl}$ are certain linear combinations of the a_{ij}'s. The relations between L_{D} in the laboratory frame and $\hat{\mathrm{L}}_{\mathrm{D}}(t)$ in the rotating frame are given by

$$\left\{\hat{\mathrm{L}}_{\mathrm{D}}(t)\right\}_{kl}^{mn} = \varphi_{kl}(t)\varphi_{nm}(t)\left\{\mathrm{L}_{\mathrm{D}}\right\}_{kl}^{mn} \ , \tag{187}$$

with

$$\varphi_{kl}(t) = U_{kk}(t)\overline{U}_{ll}(t) \ , \tag{188}$$

with time-constant products only for

$$\varphi_{kl}(t)\varphi_{nm}(t) = 1 \ \begin{cases} k = l \ , & n = m \\ k = m \ , & l = n \end{cases} \ . \tag{189}$$

Thus, the set of non-zero $\mathrm{L_D}$-elements which admit a constant generator $\hat{\mathrm{L}}_{\mathrm{D}}$ is selected through

$$\left\{\hat{\mathrm{L}}_{\mathrm{D}}\right\}_{kl}^{mn} = \left\{\mathrm{L}_{\mathrm{D}}\right\}_{kl}^{mn}\left(\delta_{kl}\,\delta_{mn}(1-\delta_{km}) + \delta_{km}\,\delta_{ln}\right) \ . \tag{190}$$

This, in turn, sets most of the a_{ij}-elements equal to zero [52] and forces the system to be rotationally symmetric around the 3-axis with the consequence that

$$a_{11} = a_{22} \ , \quad M_x^0 = M_y^0 = 0 \ , \tag{191}$$

or else, that there are only two diagonal relaxation times $T_2 = T_3$ and T_1. The corresponding generalized Bloch-equations in the rotating frame read, finally,

$$\begin{aligned} \dot{\hat{M}}_x(t) &= -(T_2^{-1} + q)\hat{M}_x(t) - \Delta\,\hat{M}_y(t) \ , \\ \dot{\hat{M}}_y(t) &= \Delta\,\hat{M}_x(t) - (T_2^{-1} + q)\hat{M}_y(t) - \omega_1\hat{M}_z(t) \ , \\ \dot{\hat{M}}_z(t) &= \omega_1\hat{M}_y(t) - (T_1^{-1} + q)\hat{M}_z(t) + (M_z^0\,T_1^{-1} - \chi)\hat{N}(t) \ , \\ \dot{\hat{N}}(t) &= -\chi\,\hat{M}_z(t) - q\,\hat{N}(t) \ . \end{aligned} \tag{192}$$

Some other details and a discussion of physical implications regarding chemically reacting systems or excited triplet states in organic molecular crystals are in [52] and the references cited therein.

5 Comparison with Common Versions of Master Equations

5.1 General Considerations

Most published master equations are somehow modeled by copying the structure of ordinary Bloch-equations and, very rarely, one can draw definite conclusions on the magnitude of all parameters which have been introduced phenomenologically since the experimental information is too incomplete. As has been shown in Subsects. 3.1 and 3.2 such equations follow from a very restricted form of a Kossakowski-generator and are potential candidates for satisfying the requirements of complete positivity if the parameters are subject

to the inequalities given in Subsect. 2.2. One can state that the most precise determination of parameters is provided by magnetic resonance experiments and, in fact, no experimental violation of the inequality $T_1 \geq \frac{1}{2}T_2$ is known to the author. Regarding optical Bloch equations one can say that in the wide literature of quantum optics and related fields, particularly on coherence spectroscopy [10,11,13,53], mostly conventional versions are used, sometimes with slight generalizations that cause no problems except for those to be briefly discussed in Subsect. 5.2. On the other hand, derivations of master equations by projection operator techniques and use of any kind of perturbation theory may fail [4,6,7] or may happen to satisfy complete positivity. The latter point has to be checked in all those equations explicitly since there is no a priori-structure of the generator whose form depends on the ad hoc-approximations used in the derivation.

In the following, two types of master equations will be discussed that may be taken as prototypes for many related similar equations of broad applicability in various branches of physics.

5.2 Equations for Spontaneous Emission

As representative for equations describing spontaneous emission we shall take a rather complicated version for N identical two-level atoms located at fixed positions $\underline{r}_i$ $(1 \leq i \leq N)$ and radiating at frequency ω. The model is worked out in [9] and references cited therein, and we only give here the necessary definitions in order to analyze complete positivity. For every atom i the operator basis is chosen in terms of the spin-$\frac{1}{2}$-matrices S_i^α, $\alpha = x, y, z$, $1 \leq i \leq N$, as

$$\left\{ S_i^\pm = S_i^x \pm i S_i^y \; ; \quad S_i^z \right\} \; , \tag{193}$$

and the Hamiltonian is given by

$$H = \omega \sum_{i=1}^{N} S_i^z + \sum_{\substack{i,k=1 \\ (i \neq k)}}^{N} \Omega_{ik} S_i^+ S_i^- \; , \tag{194}$$

where the details of Ω_{ik}'s need not concern us further. The master equation reads

$$\dot{\rho} = -i[H, \rho] + \frac{1}{2} \sum_{i,k=1}^{N} a_{ik}(x_{ik}, \Theta_{ik}) \left\{ 2\, S_k^- \rho\, S_i^+ - S_i^+ S_k^- \rho - \rho\, S_i^+ S_k^- \right\} \; , \tag{195}$$

but the parameters a_{ik} are functions of the geometrical arrangement and one has to prove positive-semidefiniteness for all values of x_{ik} and Θ_{ik} where

$$x_{ik} = \frac{\omega}{c} r_{ik} \; , \quad r_{ik} = \|\underline{r}_{ik}\| = \|\underline{r}_i - \underline{r}_k\| \; , \tag{196}$$

$$\cos(\Theta_{ik}) = (\underline{d} \cdot \underline{r}_{ik})/d\, r_{ik} \; , \tag{197}$$

$\underline{d}$ being the dipole-moment and c the velocity of light. The explicit functional dependence is then

$$a_{ik}(x_{ik}, \Theta_{ik}) = 2\gamma \left\{ j_0(x_{ik}) + P_2(\cos\Theta_{ik}) j_2(x_{ik}) \right\} \ , \tag{198}$$

in terms of the spherical Bessel-functions

$$j_0(z) = \frac{1}{z} \sin(z) \ , \tag{199}$$

$$j_2(z) = \left(\frac{3}{z^3} - \frac{1}{z} \right) \sin(z) - \frac{3}{z^2} \cos(z) \ , \quad z \in [0, \infty) \ , \tag{200}$$

the Legendre-polynomial

$$P_2(\varphi) = \frac{1}{2}(3\,\varphi^2 - 1) \ , \quad \varphi \in [-1, +1] \ , \tag{201}$$

and the positive (Einstein-A) coefficient

$$\gamma = 2\, d^2 \omega^3 / 3\, c^3 \ . \tag{202}$$

We note first that $a_{ii} > 0$, $\forall i$, since $j_0(0) = 1$ and $j_2(0) = 0$. Next, for $z \neq 0$ (198) must be analyzed carefully since there exist the bounds

$$-\frac{1}{4} \ < \ j_0(z) \ \leq \ 1 \ , \tag{203}$$

$$-\frac{1}{6} \ < \ j_2(z) \ < \ \frac{1}{3} \ , \tag{204}$$

$$-\frac{1}{2} \ \leq \ P_2(\phi) \ \leq \ 1 \ . \tag{205}$$

From the behavior of the functions [54] one concludes that in order to prove (10) it is sufficient to show that

$$j_0(z) + j_2(z) \leq 1 \ , \quad 0 \leq z \leq 2 \ . \tag{206}$$

This must be done numerically by taking care of the instability problems arising with Bessel-functions [55]. The result is that (206) is satisfied indeed and this, in turn, means that for $N = 2$ eq. (195) satisfies complete positivity. For $N > 2$ one should prove that all minors of dimension larger than 2 are also positive-semidefinite (see Subsect. 2.2) and this, again, is a formidable numerical task. We renounce on completing this proof, therefore, by giving a plausibility argument. Since in the derivation of (195) it has been assumed that every atom is well kept apart from any other to avoid mutual interaction the variable z will never be very small. On the other hand, the Bessel-functions decrease rapidly to zero for larger arguments. Thus, the off-diagonal elements of the relaxation matrix A will generally be extremely small as compared to the diagonal ones and one might even have the situation of diagonal dominance. Evidently, this a posteriori verification is tedious. As pointed out by Alicki there is a much more direct and elegant proof by rederiving (195) in the weak coupling limit and applying Bochner's positivity theorem to the Fourier-transforms of the reservoir-correlation functions (see also Sect. 7).

5.3 Equations of Lamb-type

Most of the master equations encountered in the literature can be traced back to a form given by Lamb in his famous paper on the theory of optical masers (lasers) [56, 57]. In common notation it reads

$$\dot{\rho}(t) = -i[H, \rho(t)] - \frac{1}{2}\{\Gamma, \rho(t)\} + \Lambda \ , \tag{207}$$

and can be considered in N dimensions with Γ and Λ real-symmetric, positive-semidefinite $(N \times N)$-matrices and $\{\Gamma, \rho\} = \Gamma\rho + \rho\Gamma$. Γ incorporates exclusively decay terms and Λ accounts for excitation (pumping). However, there are special physical conditions required in order to make this equation meaningful, as has been discussed very clearly in [56] but, despite that, misunderstandings have arisen in later applications. This is due to the fact that, obviously, a solution $\rho(t)$ of (207) is no density matrix satisfying the von Neumann-conditions [5] since the trace is a function of time, in general, its derivative being given by

$$\frac{d}{dt}\mathrm{Tr}\{\rho(t)\} = -\mathrm{Tr}\{\Gamma\rho(t)\} + \mathrm{Tr}\{\Lambda\} \ , \tag{208}$$

and this shows that the trace may decrease or increase during time-evolution making impossible any reasonable probability interpretation. The only way out of this inconsistency is to assume that $\rho(t)$ is only a physically relevant part of a complete density matrix $\rho^{(+)}(t)$ with $\mathrm{Tr}\{\rho^{(+)}(t)\} = 1$, $t \geq 0$. For instance, if we take (207) for a two-level system, $\rho^{(+)}(t)$ is at least (3×3) such that in a special representation it has the form

$$\rho^{(+)}(t) = \begin{pmatrix} \rho_{11}(t) & \rho_{12}(t) & 0 \\ \rho_{21}(t) & \rho_{22}(t) & 0 \\ 0 & 0 & \rho_{33}^{(+)}(t) \end{pmatrix} \ , \tag{209}$$

and the additional trivial equation omitted in (207) reads

$$\dot{\rho}_{33}^{(+)}(t) = -\mathrm{Tr}\{\dot{\rho}(t)\} \ . \tag{210}$$

Thus, (207) refers to the upper two excited states of a three-level system with ground state occupancy $\rho_{33}^{(+)}(t)$, and the physical situation must guarantee that, at all times, $\rho_{33}^{(+)}(t) \cong 1$ and, of course, $\{\rho_{11}(t), \rho_{22}(t)\} \ll 1$. It is only for this case that the feeding term Λ can be constant in good approximation since, in fact, $\Lambda_{ii} = c_i\, \rho_{33}^{(+)}(t)$ with c_i a constant. This means that there must be an inexhaustivly large reservoir of ground state particles from which only a very small fraction is being excited. Finally, there can not be any Hamiltonian coupling of the ground state to the excited states.

In most applications Γ and Λ are taken diagonal,

$$\Gamma = \begin{pmatrix} \gamma_1 & 0 \\ 0 & \gamma_2 \end{pmatrix} , \qquad \Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} , \tag{211}$$

and it is straightforward to find the exact solutions to (207) that have been used recently in an application to singlet-triplet quantum beats in organic molecules [51, 58–60]. Of course, they have also been used in one or the other version in so many other applications in all fields of spectroscopy [8,10,11,49,53,61–65]. In the particular case of molecular quantum beats it is interesting to note that, e.g., the otherwise intrinsically given decay constant γ_2 of the triplet level may be controlled experimentally through irradiation such that the fluorescence signal displays all qualitatively different solutions of (207) (as discussed in general in Subsect. 2.5) as a function of γ_2. The change from one type of behavior to another one appears to be quite analogous to a nonequilibrium phase-transition due to the existence of a bifurcation point in the frequency versus γ_2. Thus, there is a critical value γ_c given by

$$\gamma_c = |4\,\epsilon - \gamma_1| \ , \tag{212}$$

where ϵ is the off-diagonal singlet-triplet matrix element of the Hamiltonian and the solutions for the fluorescence intensity $I(t)$ can be distinguished as follows,

$$I(t) = \begin{cases} A_f\, e^{-k_f t} + A_s\, e^{-k_s t} + A\, e^{-kt}\,, & \gamma_2 > \gamma_c \ , \\ A_0\, e^{-kt}[1 - \frac{1}{2}(\gamma_1 - \gamma_c)\, t + \epsilon^2\, t^2] \ , & \gamma_2 = \gamma_c \ , \\ A_b\, e^{-kt}[1 + \sin(2\omega t + \delta)] \ , & \gamma_2 < \gamma_c \ , \end{cases} \tag{213}$$

with

$$\left.\begin{matrix} k_s \\ k_f \end{matrix}\right\} = k \pm 2\,\Omega \ , \qquad k = \frac{1}{2}(\gamma_1 + \gamma_2) \ , \tag{214}$$

$$\left.\begin{matrix} \Omega \\ \omega \end{matrix}\right\} = \left[\frac{1}{2}|s|(1 \pm \mathrm{sgn}(s))\right]^{1/2} , \qquad s = \frac{1}{16}(\gamma_1 - \gamma_2)^2 - \epsilon^2 \ . \tag{215}$$

Further details are available in [51,58–60] whereas use of (207) in the general context of unstable particles is described by R. Alicki in this volume.

6 Open Quantum Systems with Non-constant Relaxation in Time-dependent External Fields

6.1 Modifications of the Original Semigroup Generator

The derivation of quantum dynamical semigroup generators of Kossakowski-type implies strict time-independence of the Hamiltonian but the additional

effects due to a time-varying external field do not destroy complete positivity as long as the relaxation-inducing reservoir properties are not affected. It has been outlined in the preceding sections how these cases can be handled in conjunction with some kind of rotating frame with the result of obtaining, finally, time-independent coefficients. All this can be reliable only for relatively weak fields. Next, one may ask the question as to the modification of relaxation in the sense of linear response theory. The only rigorous treatment in this direction known to the author is due to Davies and Spohn [66] who obtained results in the weak-coupling limit for an open system initially in thermal equilibrium with an infinite free reservoir and subject to an external driving potential varying on the scale of dissipation, all under the condition that the dynamics of the open system in absence of the field is given by a uniquely relaxing semigroup in the sense of (74). From another point of view, not related to linear response theory, Kielau and Alberti [67] have discussed conditions under which a completely positive time-evolution can be traced back to some time-dependent stochastic generators for arbitrary initial states of the open system, at least for sufficiently small starting-time intervals.

To explore the situation for stronger fields we let us guide by some physical ideas which lead to an extension of generators to a time-dependent form which allows to obtain results in agreement with experiments [68, 69]. However, no rigorous mathematical derivations from unitary dynamics are available so far for this case and in this sense the following considerations have to be considered tentative. Assume then that, for a field of strength λ and frequency ω, the time-dependence of the original generator L in (2) is not only due to the Hamiltonian $H^{(\lambda)}(t)$ but also to relaxation functions $a_{ik}^{(\lambda)}(t)$ in place of the original constants a_{ik}. The latter are thought to be composed of a relatively large time-independent contribution $h_{ik}^{(\lambda)}$ depending on the time-averaged field intensity and a superimposed small contribution $g_{ik}^{(\lambda)}(t)$ varying at the frequency of the field, possibly with some phase shift,

$$a_{ik}^{(\lambda)}(t) = h_{ik}^{(\lambda)} + g_{ik}^{(\lambda)}(t) \ . \tag{216}$$

The so obtained generator,

$$\begin{aligned} \mathrm{L}^{(\lambda)}(t)\rho(t) = &-i\left[H^{(\lambda)}(t), \rho(t)\right] \\ &+\frac{1}{2}\sum_{i,k=1}^{M} a_{ik}^{(\lambda)}(t)\left([F_i, \rho(t)F_k^\star] + [F_i\,\rho(t), F_k^\star]\right) \ , \end{aligned} \tag{217}$$

does no longer infinitesimally generate a one-parameter semigroup but the global time-evolution depends upon starting and final time,

$$\rho(t) = \Lambda_{t,s}\,\rho(s) \ , \tag{218}$$

with

$$\Lambda_{t,s} = \mathbf{T}\left\{\exp\int_s^t \mathrm{L}^{(\lambda)}(\tau)d\tau\right\} \ , \tag{219}$$

where $\mathbf{T}$ is the time-ordering, and there is still the composite law

$$\Lambda_{t,s} = \Lambda_{t,r}\,\Lambda_{r,s} \ , \quad s \le r \le t \ . \tag{220}$$

Now, the field-strength and time dependence $A^{(\lambda)}(t) = \{a_{ik}^{(\lambda)}(t)\}_1^M$ can not be arbitrary but, to maintain the spectral von Neumann-condition on ρ, one must have

$$A^{(\lambda)}(t) \ge 0 \ , \quad t \ge 0 \ , \quad \forall\lambda \ , \tag{221}$$

where the admitted range of λ-values is restricted to a suitable finite interval, of course. By this condition, formula (219) shows that $\Lambda_{t,s}$ is a positive functional of positive terms [43,46] and, as a consequence, the master equation

$$\dot\rho(t) = \mathrm{L}^{(\lambda)}(t)\,\rho(t) \tag{222}$$

is still meaningful and has as solution a density operator satisfying the von Neumann-conditions. Explicit solutions to (222) will be tedious to work out and one will certainly try to look for applications where the techniques of the former sections for the construction of approximate time-independent coefficients can be used.

As a general result to be expected after such procedures the relevant relaxation time in Bloch-like equations will appear as suitable constants in time but still functions of the field-strength. This point is very interesting since it opens access to experimentally studied phenomena like nonlinear power-dependent relaxation and saturation effects as observed in magnetic and optical resonance investigations [70–72]. Such an example will be worked out in the following section.

6.2 A Model with Field-Strength-dependent Relaxation

Very early already, in a pioneering paper by Redfield [70] on nuclear magnetic resonance saturation in solids, the violation of ordinary Bloch-equations with two relaxation times T_1 and T_2 has been analyzed for increasing field-strength λ leading to the final conclusion that, at intermediate λ-values, there must be three different relaxation times T_1, T_2, T_3. Possibly, only T_3 depends on λ with limiting behavior

$$\lim_{\lambda\to 0} T_3(\lambda) = T_2 \ , \tag{223}$$

guaranteeing the validity of the conventional Bloch-equations at low power. On the other hand,

$$\lim_{\lambda\to 0} T_3(\lambda) = T_1 \tag{224}$$

must evidently be true to account for the experimental results at high power. Surprisingly, analogous findings in the optical range could be confirmed

only very recently trough quite sophisticated experiments by De Voe and Brewer [71] on free induction decay in a low temperature solid containing ion-impurities. Note that in our theory described so far no $T_3 \neq T_2$ exists in the rotating frame since a possibly existing difference in absence of the field will be averaged out (see (138)) in presence of the field. It is our aim to show that $T_3 \neq T_2$ can be recovered by allowing for a generator in the form (217) and that the limits (223) and (224) are compatible with complete positivity which is not trivial in view of the existing inequalities.

Again, we consider a two-level system with Hamiltonian

$$H^{(\lambda)}(t) = \frac{1}{2}\begin{pmatrix} \omega_0 & 2\lambda\cos(\omega t) \\ 2\lambda\cos(\omega t) & -\omega_0 \end{pmatrix} , \tag{225}$$

and introduce only the absolutely necessary functions,

$$a_{11}^{(\lambda)}(t) = \alpha^{(\lambda)} - g^{(\lambda)}(t) , \tag{226}$$

$$a_{22}^{(\lambda)}(t) = \alpha^{(\lambda)} + g^{(\lambda)}(t) , \tag{227}$$

$$a_{33}^{(\lambda)}(t) = \alpha_{33}^{(\lambda)} , \quad \mathrm{Im}\left(a_{12}^{(\lambda)}(t)\right) = \alpha_{12}^{(\lambda)} , \tag{228}$$

with a special form for $g^{(\lambda)}(t)$,

$$g^{(\lambda)}(t) = p(\lambda)\sin(\omega t) , \quad p(\lambda) \geq 0 , \tag{229}$$

that could be chosen in a more general way with arbitrary phase shift. We omit the detailed calculations [69] that are performed exactly along the lines described in Subsect. 3.2 and obtain for the averaged matrix $\mathbb{G}$ the final form (see also (137)),

$$\mathbb{G} = \begin{pmatrix} -T_3^{-1}(\lambda) & -\Delta & 0 \\ \Delta & -T_2^{-1}(\lambda) & -\lambda \\ 0 & \lambda & -T_1^{-1}(\lambda) \end{pmatrix} , \tag{230}$$

with three different power-dependent relaxation times

$$T_1^{-1}(\lambda) = 2\alpha^{(\lambda)} \tag{231}$$

$$T_2^{-1}(\lambda) = \alpha^{(\lambda)} + \alpha_{33}^{(\lambda)} - \frac{2}{3\pi}p(\lambda) , \tag{232}$$

$$T_3^{-1}(\lambda) = \alpha^{(\lambda)} + \alpha_{33}^{(\lambda)} + \frac{2}{3\pi}p(\lambda) . \tag{233}$$

Positivity requires

$$\alpha^{(\lambda)} > 0 , \quad \alpha_{33}^{(\lambda)} > 0 , \quad p(\lambda) < \alpha^{(\lambda)} , \tag{234}$$

and the restriction of the variation of $p(\lambda)$ to the interval

$$0 \leq p(\lambda) \leq \frac{3\pi}{2}\left(\alpha_{33}^{(\infty)} - \alpha^{(\infty)}\right) \tag{235}$$

accounts for the correct limiting behavior (223) and (224) provided that the lower and upper limit in (235) are exactly reached for $\lambda \to 0$ and $\lambda \to \infty$, respectively. Thus, $p(\lambda)$ can be taken to be a smoothly interpolating function between the two limits. Then, the generalized form (217) of the generator together with (221) contains enough freedom to account for experimental results such as reported in [70, 71].

7 Determination of Relaxation Parameters from First Principles

7.1 Relationship between Kossakowski- and Davies-generators

The rigorous treatment of the weak coupling limit due to Davies [17] leads to a semigroup generator D containing relaxation constants which can be represented in terms of certain Fourier transforms of correlation functions between reservoir operators. It might seem, therefore, that a term by term comparison between D and the Kossakowski-generator L provides a basis for a first principles calculation of the constants occurring in the latter if a suitable model for the reservoir dynamics has been worked out. However, the Davies generator is a special version of L, although this is not immediately obvious from its general form. To show this we line out the mutual relationship in two dimensions. Since the basic derivations for the form of D can be found in several references [2, 3, 17, 18, 73] and in R. Alicki's treatment in this volume only the absolutely necessary formulas will be given.

For a closed quantum system Q with unitary dynamics one defines a subdivision into an open system S with Hamiltonian H_{S} on $\mathcal{H}_{\mathrm{S}}$ and a complementary reservoir R with H_{R} on $\mathcal{H}_{\mathrm{R}}$ such that for Q the Hamiltonian H on $\mathcal{H} = \mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{R}}$ is given by

$$H = H_{\mathrm{S}} \otimes \mathbb{1}_{\mathrm{R}} + \mathbb{1}_{\mathrm{S}} \otimes H_{\mathrm{R}} + H_{\mathrm{SR}} \ , \tag{236}$$

H_{SR} on $\mathcal{H}$ being a suitably "weak" interaction [18]. The free evolutions are then

$$U_t^{\mathrm{S}} = \exp\left(-iH_{\mathrm{S}}t\right) \ , \quad U_t^{\mathrm{R}} = \exp\left(-iH_{\mathrm{R}}t\right) \ , \quad U_t = U_t^{\mathrm{S}} \otimes U_t^{\mathrm{R}} \ . \tag{237}$$

A first form $\tilde{K} = K + i[H_{\mathrm{S}}, \bullet]$ for the Davies-generator is found to be

$$\tilde{K}\,\rho(t) = -\int_0^\infty d\tau (\mathrm{Tr}_{\mathrm{R}}\{[U_{-\tau} H_{\mathrm{SR}} U_\tau, [H_{\mathrm{SR}}, (\rho(t) \otimes \Omega_{\mathrm{R}})]]\}) \ , \tag{238}$$

where $\rho(t)$ is the density operator of the open system, Ω_{R} the reference state of the quasi-free reservoir and Tr_{R} a trace with respect to $\mathcal{H}_{\mathrm{R}}$ only. The positive form $\tilde{D}$ is then established by averaging over the free evolution U_x^{S},

$$\tilde{D} = \lim_{T\to\infty} \frac{1}{2\,T} \int_{-T}^{+T} dx\, V_x^{\rm S}\, \tilde{K}\, V_{-x}^{\rm S} \ , \tag{239}$$

where $V_x^{\rm S}$ is defined by $V_x^{\rm S}\, Y = U_x^{\rm S}\, Y\, U_{-x}^{\rm S}$ for any Y on $\mathcal{H}_{\rm S}$ with $\dim\mathcal{H}_{\rm S} < \infty$. For $N = \dim\mathcal{H}_{\rm S} = 2$ we choose

$$H_{\rm S} = \frac{\omega}{2}\sigma_3 \ , \quad H_{\rm SR} = \sum_{i=1}^{3} \sigma_i \otimes B_i \ , \tag{240}$$

where the σ_i's are the Pauli matrices and the B_i's self-adjoint operators on $\mathcal{H}_{\rm R}$. Because of (239) one introduces spectral projectors with respect to the difference spectrum

$$\omega_0 = 0\,(\text{twofold}) \ , \quad \omega_{\pm 1} = \pm\omega \tag{241}$$

of $H_{\rm S}$ through

$$\begin{aligned} A_k(\omega_0) &= P_1\sigma_k P_1 + P_2\,\sigma_k P_2 \ , \\ A_k(\omega_{+1}) &= P_2\,\sigma_k P_1 \ , \\ A_k(\omega_{-1}) &= A_k^\star(\omega_{+1}) = P_1\sigma_k P_2 \ , \quad k = 1,2,3 \ , \end{aligned} \tag{242}$$

where P_1 and P_2 are the ordinary projectors

$$P_1 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \ , \quad P_2 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \ . \tag{243}$$

With the above definitions the generator can be written as a sum

$$\tilde{D} = \tilde{D}_{\rm H} + \tilde{D}_{\rm R} \ , \tag{244}$$

where $\tilde{D}_{\rm H}$ and $\tilde{D}_{\rm R}$ have a different structure, i.e., $\tilde{D}_{\rm H}$ yields a correction to the Hamiltonian part $-i[H_{\rm S}, \rho(t)]$ of the dynamics whereas $\tilde{D}_{\rm R}$ contains the purely non-Hamiltonian contributions,

$$\tilde{D}_{\rm H}\,\rho(t) = -i \sum_{i,k=1}^{3} \sum_{l=-1}^{+1} s_{ik}(\omega_l)\,[A_k^\star(\omega_l)A_i(\omega_l), \rho(t)] \ , \tag{245}$$

$$\tilde{D}_{\rm R}\,\rho(t) = \frac{1}{2} \sum_{i,k=1}^{3} \sum_{l=-1}^{+1} c_{ik}(\omega_l)\,\{[A_i(\omega_l)\rho(t), A_k^\star(\omega_l)] + [A_i(\omega_l), \rho(t)A_k^\star(\omega_l)]\} \ . \tag{246}$$

The coefficients c_{ik} and s_{ik} are Fourier- and Hilbert-transforms of correlation functions $h_{ik}(t)$,

$$h_{ik}(t) = {\rm Tr}_{\rm R}(B_k(t)B_i\Omega_{\rm R}) \ , \quad B_k(t) = U_{-t}^{\rm R} B_k U_t^{\rm R} \ , \tag{247}$$

$$c_{ik}(\omega) = \int_{-\infty}^{\infty} dt\, h_{ik}(t) e^{-i\omega t} \ , \tag{248}$$

$$s_{ik}(\omega) = i \int_{0}^{\infty} dt\, h_{ik}(t) e^{-i\omega t} - \frac{i}{2} c_{ik}(\omega) \ . \tag{249}$$

Formula (246) seems to be as general as Kossakowski's result but a more detailed evaluation [74] reveals important differences. In fact, for the A-projectors in terms of

$$\sigma_\pm = \frac{1}{2}(\sigma_1 \pm i\sigma_2) \text{ and } \sigma_3 \ , \tag{250}$$

one finds

$$\begin{aligned} A_1(\omega_0) &= 0 \ , & A_2(\omega_0) &= 0 \ , & A_3(\omega_0) &= \sigma_3 \ , \\ A_1(\omega_1) &= \sigma_- \ , & A_2(\omega_1) &= i\sigma_- \ , & A_3(\omega_1) &= 0 \ , \\ A_1(\omega_{-1}) &= \sigma_+ \ , & A_2(\omega_{-1}) &= -i\sigma_+ \ , & A_3(\omega_{-1}) &= 0 \ . \end{aligned} \tag{251}$$

Obviously, the average (239) has as a consequence a sort of a "spectral selection rule" in that all (1,3)- and (2,3)-contributions in (246) vanish and only (1,2)-terms survive. The comparison with (2), (3) and (116) is best made by writing

$$D\rho(t) = -i[\hat{H}_{\rm S}, \rho(t)] + \tilde{D}_{\rm R}\rho(t) \ , \tag{252}$$

with $\hat{H}_{\rm S}$ the modified Hamiltonian including "level shifts",

$$\hat{H}_{\rm S} = H_{\rm S} + \frac{1}{2}\{s_{11}(\omega_{-1}) - s_{11}(\omega_1) + s_{22}(\omega_1) - s_{22}(\omega_{-1})\}\sigma_3 \ , \tag{253}$$

and $\tilde{D}_{\rm R}$ rewritten in analogy to the earlier forms as

$$\tilde{D}_{\rm R}\,\rho(t) = \frac{1}{4}\sum_{i,k=1}^{3} a_{ik}\left\{[\sigma_i, \rho(t)\sigma_k] + [\sigma_i\,\rho(t), \sigma_k]\right\} \ , \tag{254}$$

where the factor $1/4$ accounts for the different normalization of the Pauli-matrices as compared to (4). With the abbreviations

$$f_\pm = c_{11}(\omega_1) + c_{22}(\omega_1) \pm \{c_{11}(\omega_{-1}) + c_{22}(\omega_{-1})\} \ , \tag{255}$$

$$g_\pm = c_{12}(\omega_1) - c_{21}(\omega_1) \pm \{c_{12}(\omega_{-1}) - c_{21}(\omega_{-1})\} \ , \tag{256}$$

the complete list of the a_{ik}'s in terms of correlation functions is given by

$$a_{11} = a_{22} = f_+ - ig_- \ , \tag{257}$$

$$a_{12} = -a_{21} = g_+ + if_- \ , \tag{258}$$

$$a_{13} = a_{23} = 0 \ , \quad a_{33} = 2\,c_{33}(\omega_0) \ . \tag{259}$$

The symmetry of $c_{ik}(\omega)$ implies $\{a_{ii},\ ia_{12}\} \in \mathbb{R}$, $i = 1, 2, 3$, and from (96) and (113) we rediscover the old Bloch equations with

$$T_1 = (2\,a_{11})^{-1} \ , \quad T_2 = (a_{11} + a_{33})^{-1} \ , \quad M_0 = \frac{ia_{12}}{\sqrt{2}a_{11}} \ , \tag{260}$$

This is the most general result obtainable from D. Thus, the physical implications of averaging the original generator $\tilde{K}$ over the free evolution according to (239) are now clearly worked out. The preceding analysis has shown that the generator D describes the dynamics of a system with rotational symmetry around the static field axis.

In the following we will have a look at the consequences if, in place of (245) and (246), a Kossakowski-like generator is constructed, starting from (238) and diregarding (239). In general, this may lead to a violation of positivity since Davies' proofs do not apply. However, depending on the details of a concrete application and the corresponding correlation functions, the relaxation matrix may nevertheless result positive. Similar attempts can be found in the literature, but it must be stressed that positivity has to be verified a posteriory.

We rewrite (238) as

$$\tilde{K}\rho(t) = \int_0^\infty d\tau\ \mathcal{J}(\tau)\rho(t) \tag{261}$$

and find, as a first intermediate result for the integrand,

$$\begin{aligned}\mathcal{J}(\tau)\rho(t) = \mathrm{Tr}_\mathrm{R} \sum_{i,k=1}^{3} \big(\{\sigma_i\rho(t)\sigma_k\} \otimes \{B_i\Omega_\mathrm{R}\mathcal{F}_k(\tau) + \mathcal{F}_i(\tau)\Omega_\mathrm{R}B_k\} \\ -\{\sigma_k\sigma_i\rho(t)\}\otimes\{\mathcal{F}_k(\tau)B_i\Omega_\mathrm{R}\}-\{\rho(t)\sigma_k\sigma_i\}\otimes\{\Omega_\mathrm{R}B_k\mathcal{F}_i(\tau)\}\big)\ ,\end{aligned} \tag{262}$$

where the time-dependence of $\sigma_i(\tau) = U^\mathrm{S}_{-\tau}\sigma_i U^\mathrm{S}_\tau$ has been transferred to the reservoir operators in the Heisenberg-representation according to

$$\begin{aligned}\mathcal{F}_1(\tau) &= B_1(\tau)\cos(\omega\tau) + B_2(\tau)\sin(\omega\tau)\ , \\ \mathcal{F}_2(\tau) &= -B_1(\tau)\sin(\omega\tau) + B_2(\tau)\cos(\omega\tau)\ , \\ \mathcal{F}_3(\tau) &= B_3(\tau)\ .\end{aligned} \tag{263}$$

After introducing the auxiliary correlation functions

$$\xi_{ik}(\tau) = \mathrm{Tr}_\mathrm{R}\left\{\mathcal{F}_k(\tau)B_i\Omega_\mathrm{R}\right\}\ , \tag{264}$$

$$\eta_{ik}(\tau) = \mathrm{Tr}_\mathrm{R}\left\{B_k\mathcal{F}_i(\tau)\Omega_\mathrm{R}\right\}\ , \tag{265}$$

a second form of the integrand is obtained as

$$\begin{aligned}\mathcal{J}(\tau)\rho(t) = \frac{1}{2}\sum_{i,k=1}^{3}\left(\xi_{ik}(\tau)+\eta_{ik}(\tau)\right)\left\{[\sigma_i,\rho(t)\sigma_k] + [\sigma_i\rho(t),\sigma_k]\right\} \\ -\frac{1}{2}\sum_{i,k=1}^{3}\left(\xi_{ik}(\tau)-\eta_{ik}(\tau)\right)[\sigma_k\sigma_i,\rho(t)]\ .\end{aligned} \tag{266}$$

This is, again, the old familiar structure including a Hamiltonian correction term, and the final comparison with the Kossakowski-generator yields the desired relation

$$a_{ik} = 2 \int_0^\infty d\tau \, \{\xi_{ik}(\tau) + \eta_{ik}(\tau)\} \ . \tag{267}$$

In terms of the originally defined elementary correlation functions $h_{ik}(t)$ in (247) and their one-sided Fourier transforms defined by

$$c_{ik}^{\pm}(\omega) = \int_0^\infty dt \, h_{ik}(\pm t) \cos(\omega t) \ , \tag{268}$$

$$s_{ik}^{\pm}(\omega) = \pm \int_0^\infty dt \, h_{ik}(\pm t) \sin(\omega t) \ , \tag{269}$$

obeying the symmetry relations

$$\overline{c_{ik}^{+}(\omega)} = c_{ik}^{-}(\omega) \ , \quad \overline{s_{ik}^{+}(\omega)} = -s_{ik}^{-}(\omega) \ , \tag{270}$$

one finally obtains

$$\begin{aligned}
a_{11} &= 4\, c_{11}^{+}(\omega) - 2\, s_{12}^{-}(\omega) + 2\, s_{21}^{+}(\omega) \ , \\
a_{12} &= -2\, s_{11}^{+}(\omega) + 2\, s_{22}^{+}(\omega) + 2\, c_{21}^{+}(\omega) + 2\, c_{21}^{-}(\omega) \ , \\
a_{13} &= 2\, c_{31}^{+}(0) + 2\, c_{31}^{-}(\omega) - 2\, s_{32}^{-}(\omega) \ , \\
a_{22} &= 4\, c_{22}^{+}(\omega) - 2\, s_{12}^{+}(\omega) + 2\, s_{21}^{-}(\omega) \ , \\
a_{23} &= 2\, c_{32}^{+}(0) + 2\, c_{32}^{-}(\omega) + 2\, s_{31}^{-}(\omega) \ , \\
a_{33} &= 4\, c_{33}^{+}(0) \ .
\end{aligned} \tag{271}$$

We stress again that the above reconstruction "from first principles" of the relaxation matrix A has to be taken with care since $\tilde{K}$ in (261) does not necessarily preserve positivity (for simple counterexamples see [6]). Apart from the required decay behavior of the correlation functions $h_{ik}(t)$ at large times [17, 75, 76] one has to prove a posteriori that their particular properties in a chosen model lead to $A \geq 0$.

It remains to be shown how a physical mechanism can lead to generalized Bloch equations as implied by (270). This will be done in the next section for a suitable model of diluted spins in a ferromagnet where relaxation is caused by a coupling to spin-waves.

7.2 A Model for Spin-relaxation by Spin-waves

Looking back at the full relaxation equations in Subsect. 3.1 we focus attention just on one prominent non-trivial term in the static field case and calculate $\beta = \mathrm{Re}(a_{13})$ for a suitably general model situation. According to the representation of a_{13} in (271) one has

$$\beta = \beta_1 + \beta_2 + \beta_3 \ , \tag{272}$$

$$\beta_1 + 2\,\mathrm{Re}\left\{\int_0^\infty dt\; h_{31}(t)\right\} \ , \tag{273}$$

$$\beta_2 + 2\,\mathrm{Re}\left\{\int_0^\infty dt\; \overline{h_{13}(t)}\cos(\omega t)\right\} \ , \tag{274}$$

$$\beta_3 + 2\,\mathrm{Re}\left\{\int_0^\infty dt\; \overline{h_{23}(t)}\sin(\omega t)\right\} \ . \tag{275}$$

As a model we take for simplicity only one impurity spin $\underline{\sigma}$ at position $\underline{x}$ embedded in a lattice G_V of a Heisenberg ferromagnet of volume V ($V \to \infty$ later on). The latter consists of identical spins $\underline{S}$ at lattice sites $\{\underline{x}^m\}$ and write for brevity $\underline{S}^m \equiv \underline{S}(\underline{x}^m)$. Assume a weak anisotropic dipole-dipole-type interaction of the form

$$H_{\mathrm{SR}} = \sum_{m\in G_V}\sum_{i,k=1}^{3} A_{ik}(\underline{x} - \underline{x}^m)\,\sigma_i(\underline{x}) \otimes S_k(\underline{x}^m) \ , \tag{276}$$

with real scalar functions A_{ik} of rapid decrease. In order to use the results of the preceding section related to reservoir operators B_i one has, by comparison with (240), to put

$$B_i = \sum_{m;k} A_{ik}^m\, S_k^m \tag{277}$$

with $A_{ik}^m \equiv A_{ik}(\underline{x} - \underline{x}^m)$. The quasi-free reservoir model itself is specified in terms of conventional spin-wave theory. Thus, it will be sufficient to give necessary definitions for later use, all details being available elsewhere [77–79]. For identical lattice spins of length S_0 with magnetic moment μ_0 each of them being coupled to a set $\mathcal{N}$ of nearest neighbors by an isotropic ferromagnetic exchange interaction $J > 0$ and placed in an external magnetic field H_0 in 3-direction, the Hamiltonian reads

$$H_{\mathrm{R}} = -J \sum_{\substack{l\in G_V \\ \delta\in\mathcal{N}}} \left(\underline{S}^l \cdot \underline{S}^{l+\delta}\right) - \mu_0 H_0 \sum_{l\in G_V} S_3^l \ . \tag{278}$$

The elementary excitations at low temperature (below room-temperature, say) are spin waves whose second-quantized description is given in terms of magnon creation ($a_{\underline{q}}^\star$) and annihilation ($a_{\underline{q}}$) operators with wave-vector $\underline{q}$ and Boson commutation relations

$$[a_{\underline{q}}, a_{\underline{p}}^\star] = \delta_{\underline{q},\underline{p}} \ , \quad [a_{\underline{q}}, a_{\underline{p}}] = [a_{\underline{q}}^\star, a_{\underline{p}}^\star] = 0 \ . \tag{279}$$

After a linearized Holstein-Primakoff and subsequent Fourier transformation the connections to the spin operators are

$$S_1^m = (S_0/2N)^{1/2} \sum_{\underline{q}\in\mathcal{B}} e^{i(\underline{q}\cdot\underline{x}^m)}(a_{\underline{q}}^\star + a_{-\underline{q}}) \ ,$$
$$S_2^m = i(S_0/2N)^{1/2} \sum_{\underline{q}\in\mathcal{B}} e^{i(\underline{q}\cdot\underline{x}^m)}(a_{\underline{q}}^\star - a_{-\underline{q}}) \ ,$$
$$S_3^m = S_0\mathbb{1} - N^{-1} \sum_{\underline{q}\in\mathcal{B}} e^{i(\underline{q}\cdot\underline{x}^m)} a_{\underline{q}}^\star a_{-\underline{q}} \ , \tag{280}$$

where $\mathcal{B}$ denotes the set of points in the first Brillouin-zone and N is the total number of lattice spins. The transformed Hamiltonian operator $\hat{H}_{\mathrm{R}}$ is

$$\hat{H}_{\mathrm{R}} = -(zJS_0 + \mu_0 H_0)NS_0\mathbb{1} + \sum_{\underline{q}\in\mathcal{B}} \omega_{\underline{q}} n_{\underline{q}} \ , \tag{281}$$

where z is the number of nearest neighbors, $n_{\underline{q}} = a_{\underline{q}}^\star a_{\underline{q}}$ the occupation number operator and $\omega_{\underline{q}}$ the magnon frequency

$$\omega_{\underline{q}} = \mu_0 H_0 + 2zJS_0(1 - \gamma_{\underline{q}}) \ , \tag{282}$$
$$\gamma_{\underline{q}} = \frac{1}{z} \sum_{\delta\in\mathcal{N}} e^{-i(\underline{q}\cdot\underline{x}^\delta)} \ . \tag{283}$$

To keep in line with the definitions of correlation functions as commonly used in magnetic neutron scattering theory we introduce the modified van Hove-functions

$$\gamma_{mn}^{kl}(t) = \tilde{\gamma}_{mn}^{kl}(t) - \tilde{\gamma}_{mn}^{kl}(\infty) \ , \tag{284}$$
$$\tilde{\gamma}_{mn}^{kl}(t) = \mathrm{Tr}_{\mathrm{R}} \left\{ S_k^m \, U_{-t}^{\mathrm{R}} \, S_l^n \, U_t^{\mathrm{R}} \Omega_{\mathrm{R}} \right\} \ , \tag{285}$$

where the trace is now in Fock space over all possible quasi-particle states [41]. Note that the subtraction in (284) is required by the Davies-theory [17, 18]. For a ferromagnet in thermal equilibrium at temperature T the state is given by

$$\Omega_{\mathrm{R}} = Z^{-1} \exp\left\{-\tilde{\beta}\hat{H}_{\mathrm{R}}\right\} \ , \quad Z = \mathrm{Tr}_{\mathrm{R}} \left(\exp\left\{-\tilde{\beta}\hat{H}_{\mathrm{R}}\right\}\right) \ , \tag{286}$$

where $\tilde{\beta} = (k_{\mathrm{B}}T)^{-1}$, and the magnons obey the Bose-Einstein occupancy

$$\langle n_{\underline{q}} \rangle_T = \mathrm{Tr}_{\mathrm{R}}\{a_{\underline{q}}^\star a_{\underline{q}} \Omega_{\mathrm{R}}\} = \left(e^{\tilde{\beta}\omega_{\underline{q}}} - 1\right)^{-1} \ . \tag{287}$$

In the infinite volume limit the Fourier-sums in the correlation functions (285) become integrals over the Brillouin zone of volume Γ such that the final representations are found to be

$$\gamma_{mn}^{11}(t) = \frac{S_0}{2\Gamma}\int_\Gamma d^3q \left\{\langle n_{\underline{q}}\rangle_T E + \langle n_{\underline{q}}+1\rangle_T \overline{E}\right\} \ , \tag{288}$$

$$\gamma_{mn}^{12}(t) = i\frac{S_0}{2\Gamma}\int_\Gamma d^3q \left\{-\langle n_{\underline{q}}\rangle_T E + \langle n_{\underline{q}}+1\rangle_T \overline{E}\right\} \ , \tag{289}$$

$$E = \exp\left\{i(\underline{q}\cdot(\underline{x}^m - \underline{x}^n)) - i\omega_{\underline{q}}t\right\} \ ,$$

$$\gamma_{mn}^{22}(t) = \gamma_{mn}^{11}(t) \ , \quad \gamma_{mn}^{21}(t) = -\gamma_{mn}^{12}(t) \ , \tag{290}$$

$$\gamma_{mn}^{13}(t) = \gamma_{mn}^{23}(t) = \gamma_{mn}^{33}(t) = 0 \ , \quad \forall\, m,n \ . \tag{291}$$

It is important to emphasize that all correlation functions behave [76] as $t^{-3/2}$ for $t \to \infty$ and satisfy, consequently, the necessary decay requirements [17,18]. From now on we will assume a Brillouin-zone with inversion symmetry with the consequence that $\omega_{\underline{q}} = \omega_{-\underline{q}}$ and a further intermediate result after using (277) and (247) is obtained,

$$\overline{h_{13}(t)} = \sum_{m,n}\left\{(A_{11}^m\, A_{31}^n + A_{12}^m\, A_{32}^n)\,\gamma_{mn}^{11}(t) + (A_{12}^m\, A_{31}^n - A_{11}^m\, A_{32}^n)\,\gamma_{mn}^{12}(t)\right\} \ . \tag{292}$$

Again, β_2 is split up into

$$\beta_2 = \beta_2^{11} + \beta_2^{12} \ , \tag{293}$$

and only the calculations of the first term will be shown, that is

$$\beta_2^{11} = 2\sum_{m,n}(A_{11}^m\, A_{31}^n + A_{12}^m\, A_{32}^n)\,\mathrm{Re}\left\{\int_0^\infty dt\,\gamma_{mn}^{11}(t)\cos(\omega t)\right\} \ . \tag{294}$$

With the abbreviations

$$\underline{X}^{mn} = \underline{x}^m - \underline{x}^n \ , \tag{295}$$

$$\delta_\pm(\omega) = \pm i \lim_{\epsilon \searrow 0}\left(\frac{1}{\omega \pm i\epsilon}\right) = \pi\delta(\omega) \pm i\mathcal{P}\left(\frac{1}{\omega}\right) \ , \tag{296}$$

where $\delta(\omega)$ is the Dirac-distribution normalized to 1 and $\mathcal{P}$ denotes taking the principal part upon integration, the integral in (294) can be written as

$$\frac{1}{2}\int_\Gamma d^3q \left\{\langle n_{\underline{q}}\rangle_T\, e^{i(\underline{q}\cdot\underline{X}^{mn})}[\delta_+(\omega-\omega_{\underline{q}}) + \delta_-(\omega+\omega_{\underline{q}})] + \langle n_{\underline{q}}+1\rangle_T\, e^{-i(\underline{q}\cdot\underline{X}^{mn})}[\delta_+(\omega+\omega_{\underline{q}}) + \delta_-(\omega-\omega_{\underline{q}})]\right\} \ . \tag{297}$$

For a simple cubic lattice of constant a and sufficiently low temperature one may approximate the spin-wave spectrum by

$$\omega_{\underline{q}} \cong \omega_0 + \omega_1 q^2 \ , \quad q = \|\underline{q}\| \ , \tag{298}$$

and, consequently,

$$\delta(\omega - \omega_{\underline{q}}) = \frac{1}{2\omega_1 Q_0}[\delta(Q_0 - q) + \delta(Q_0 + q)] \ , \tag{299}$$

with the abbreviations

$$\omega_0 = \mu_0 H_0 \quad \omega_1 = 2\, JS_0\, a^2 \ , \quad Q_0 = \left(\frac{\omega - \omega_0}{\omega_1}\right)^{1/2} \ , \tag{300}$$

where $\omega > \omega_0$ is assumed in the following. Accordingly, the integrations are carried out over a sphere of radius $r_0 = (3\Gamma/4\pi)^{1/3}$ yielding, for $0 < Q_0 < r_0$ the final result,

$$\beta_2^{11} \cong \frac{\pi^2 S_0 Q_0}{\omega_1 \Gamma} \left\{ \sum_{m,n \in \mathcal{N}} (A_{11}^m\, A_{31}^n + A_{12}^m\, A_{32}^n)\, j_0(Q_0 X^{mn}) \right\} \coth\left(\frac{\omega}{2k_{\mathrm{B}}T}\right) \ , \tag{301}$$

where $j_0(z) = \sin(z)/z$ and $X^{mn} = \|\underline{X}^{mn}\|$. Recall that, according to the earlier definitions, ω is the energy splitting of the impurity spin due to the external field H_0 whereas the total splitting in the effective local field at the impurity site can be calculated after evaluating the level shifts corresponding to the second term in (265). Regarding temperature variation one concludes from series expansions of $\coth(\omega/2k_{\mathrm{B}}T)$ that, roughly, $\beta_2^{12} \cong$ const. for $\omega > 3k_{\mathrm{B}}T$ (low temperature) but $\beta_2^{12} \sim T$ for $\omega < k_{\mathrm{B}}T$ (high temperature).

8 Entropy and Irreversibility

8.1 Entropy Production

The impact of the second law of thermodynamics has influenced the general thinking about irreversible processes so strongly that its content seems to be present in almost all considerations of nonequilibrium problems either in hidden or in explicit form. Unfortunately, this created serious prejudices mainly regarding the time-dependence of entropy. Here, quantum dynamical semigroups together with a suitably general concept of entropy will provide more general points of view particularly for situations far from thermodynamic equilibrium. Among the many proposed definitions of entropy in quantum theory [40, 80] clear preference has been given to the von-Neumann-entropy because of its many properties of physical relevance [41, 81] and also because of its information-theoretic interpretation [41,42,82] which is particularly useful for nonequilibrium. One is tempted to assume then that the far-reaching consequences which have been attributed to the phenomenological concept of entropy production could possibly be checked in one or the other case by rigorously calculating the time-change of entropy as induced by semigroup time-evolution of the states. However, the analysis of the spectral properties of the evolution matrix G for relaxing semigroups should make it clear that

there are so many irreversible processes for which a meaningful definition of what could be called "entropy production" is by no means trivial and will certainly not fit into the point of view taken by the Onsager theory. Some aspects regarding these questions shall be discussed in the following.

Under certain conditions it is indeed possible to give a rigorous derivation of statements concerning entropy production as have been introduced in the phenomenological theory [39, 40] and proven by Spohn [38] in the framework of completely positive quantum dynamical semigroups. The primary problem consists of constructing a function with appropriate convexity properties since, obviously, the absolute von Neumann-entropy defined by

$$S[\rho] = -\mathrm{Tr}\left\{\rho(t)\ln\rho(t)\right\} \tag{302}$$

may increase or decrease in the course of time-evolution of the open system and, consequently, its difference at any two different times may be positive or negative. Fortunately, there is the more fruitful concept of relative entropy [41–44]

$$\mathcal{R}[\rho_1/\rho_2] = \mathrm{Tr}\left\{\rho_1(\ln\rho_1 - \ln\rho_2)\right\} \ , \tag{303}$$

with the property

$$\mathcal{R}[\rho_1/\rho_2] \geq 0 \ , \quad \forall\rho_1,\rho_2 \tag{304}$$

One can even prove the useful relation [45]

$$\mathcal{R}[\Lambda_t\rho_1/\rho_2] \leq \mathcal{R}[\rho_1/\rho_2] \tag{305}$$

for $\Lambda_t = \exp(Lt)$ with ρ_2 a stationary final state satisfying $\Lambda_t\,\rho_2 = \rho_2$. The physical significance of $\mathcal{R}$ is thus related to the production of entropy, and a careful analysis [38] leads to the following definition. If Λ_t is a genuinely relaxing semigroup with stationary state $\rho^{(\infty)}$ then entropy production Ψ during time-evolution from any initial state $\rho(0)$ to the unique final state $\rho(\infty)$ via $\rho(t) = \Lambda_t\,\rho(0)$ is given by

$$\Psi = -\frac{d}{dt}\mathcal{R}[\rho(t)/\rho^{(\infty)}]\Big|_{t=0} \tag{306}$$

In short, Ψ is the entropy production relative to $\rho^{(\infty)}$ and, as equivalent to (306), one may write $\Psi = \mathrm{Tr}\left\{L\rho(0)[\ln\rho^{(\infty)} - \ln\rho(0)]\right\} \geq 0$. Note that, even for our finite-dimensional case, definition (306) is only formal and some possible difficulties are discussed in [38] whereas extension to time-dependent generators may be found in [44, 46]. To show the technical convenience of the coherence vector formulation for calculations of Ψ we consider a special type of weakly irreversible processes close to the central state characterized by

$$\rho(t) = \zeta + \omega(t) \ , \quad \rho^{(\infty)} = \zeta \ , \tag{307}$$

where

$$\zeta = \frac{1}{N}\mathbb{1}_N \ , \quad \omega(t) = \sum_{k=1}^{M} v_k(t) F_k \ . \tag{308}$$

This implies $\lim_{t\to\infty} v_k(t) = 0, \forall k$. Because of $[\zeta, \omega(t)] = 0$ one gets

$$\ln \rho(t) = \ln \zeta + \ln(\mathbb{1}_N + N\omega(t)) \ . \tag{309}$$

Suppose further that $\omega(t)$ is sufficiently small in norm,

$$\|\omega(t)\| \ll \frac{1}{N} \ , \quad t \geq 0 \ , \tag{310}$$

such that one can approximate

$$\ln \rho(t) - \ln \zeta \cong N\omega(t) - \frac{1}{2}N^2\omega^2(t) \ . \tag{311}$$

For the relative entropy we find in lowest order

$$\mathcal{R}[\rho(t)/\zeta] \cong \frac{N}{2}\mathrm{Tr}\left\{\omega^2(t)\right\} \ , \tag{312}$$

and for the entropy production

$$\Psi \cong -\frac{N}{2}\frac{d}{dt}\eta^2(t)\bigg|_{t=0} \ , \tag{313}$$

where η is defined in (64). Thus, we are back in the coherence vector picture discussed at the end of Subsect. 2.4 and, surprisingly, at least for the simple case under consideration, can relate the production of entropy directly to the time-change of the vector length. Under the approximations already made strict positivity of Ψ is guaranteed by the sufficient additional assumption that $\sigma[G]$ be simple and real. Then, $\eta^2(t)$ is a monotonically decreasing function for increasing t and, consequently, $\Psi > 0$. Since $\rho^{(\infty)} = \zeta$ implies $\underline{k} = 0$ one has $A = A^T$ and $R = R^T$. The solution of $\dot{\underline{v}}(t) = G\,\underline{v}(t)$ for the initial condition

$$\underline{v}(0) = \underline{\xi} \ , \quad \underline{\xi} = (\xi_1, \xi_2, \ldots, \xi_M)^T \ , \tag{314}$$

is $\underline{v} = \exp(Gt)\,\underline{\xi}$ such that for $t \to 0$,

$$\underline{v}(t) = \underline{\xi} + t\,G\,\underline{\xi} \tag{315}$$

and, to first order,

$$\eta^2(t) \cong \|\underline{\xi}\|^2 + t\,(\underline{\xi} \cdot (G + G^T)\,\underline{\xi}) \ . \tag{316}$$

This yields, with $G = Q + R$, $Q^T = -Q$,

$$\frac{d}{dt}\eta^2(t)\bigg|_{t=0} = 2(\underline{\xi} \cdot \mathcal{R}\underline{\xi}) \ . \tag{317}$$

Finally, using (53) we may write Ψ in analogy to an Onsager form [40] as

$$\Psi \cong \sum_{s,m=1}^{M} \mathcal{L}_{sm}\, \xi_s\, \xi_m \ , \tag{318}$$

where the symmetric "Onsager-coefficients" are expressed by the elements of the original relaxation matrix in the Kossakowski-generator and the antisymmetric structure constants of the Lie-algebra of SU(N),

$$\mathcal{L}_{sm} = \frac{N}{4} \sum_{\substack{i,k,l=1 \\ (i\leq k)}}^{M} (2-\delta_{ik})\, a_{ik}\, \{f_{ils} f_{klm} + f_{kls} f_{ilm}\} \ . \tag{319}$$

Formula (318) shows that the vector coordinates of the initial state play the role of the generalized forces of the phenomenological theory which drive the system back to its equilibrium state. In view of the analysis of Sect. 7 one must emphasize that (319) provides a first principles calculation of the phenomenological Onsager coefficients within the context of quantum theory.

Another illustrative application of the coherence-vector representation to two-level systems [44] yields general exact analytical formulas for the relative entropy as well as for entropy production. Note first that due to unitary invariance of the trace the equality

$$\mathrm{Tr}(\rho_1 \ln \rho_2) = \sum_{i,k=1}^{N} |(\underline{x}^{(i)} \cdot \underline{y}^{(k)})|^2\, \lambda_i \ln \mu_k \tag{320}$$

holds for two density operators ρ_1 and ρ_2 with associated normalized eigensolutions

$$\rho_1 \underline{x}^{(i)} = \lambda_i \underline{x}^{(i)} \ , \quad \rho_2 \underline{y}^{(i)} = \mu_i \underline{y}^{(i)} \ , \quad 1 \leq i \leq N \ , \tag{321}$$

Restricting to $N = 2$ and writing, for convenience in terms of the unnormalized Pauli-matrices $\underline{\sigma} = \{\sigma_1, \sigma_2, \sigma_3\}$ and t as lower index from now on,

$$\rho_t = \frac{1}{2}\mathbb{1}_2 + (\underline{v}_t \cdot \underline{\sigma}) \ , \quad \eta_t = \|\underline{v}_t\| \leq \frac{1}{2} \ , \tag{322}$$

one finds, upon replacing $\rho_1 \to \rho_t$ and $\rho_2 \to \rho_\infty$ for the relative entropy

$$\begin{aligned} \mathcal{R}[\rho_t/\rho_\infty] = {} & \frac{1}{2} \ln \left(\frac{1-4\eta_t^2}{1-4\eta_\infty^2} \right) + 2\eta_t\, \mathrm{artanh}(2\eta_t) \\ & - \frac{2}{\eta_\infty} (\underline{v}_t \cdot \underline{v}_\infty)\, \mathrm{artanh}(2\eta_\infty) \ . \end{aligned} \tag{323}$$

It is interesting to note that, in contrast to (312), not only the length but also the scalar product between the coherence vectors $\underline{v}_t$ and $\underline{v}_\infty$ determines $\mathcal{R}$. Since in this representation the von-Neumann entropy reads

$$S[\rho] = \ln 2 - \frac{1}{2}\ln(1-4\eta^2) - 2\eta\,\mathrm{artanh}(2\eta)\ , \tag{324}$$

the deviation of $R[\rho_t/\rho_\infty]$ from the difference

$$\Delta S[\rho_t/\rho_\infty] = S[\rho_t] - S[\rho_\infty] \tag{325}$$

is given by the formula

$$\mathcal{R}[\rho_t/\rho_\infty] = \Delta S[\rho_t/\rho_\infty] + \frac{2}{\eta_\infty}((\underline{v}_\infty - \underline{v}_t)\cdot\underline{v}_\infty)\,\mathrm{artanh}(2\eta_\infty)\ . \tag{326}$$

Finally, from (306) and (323) one obtains for entropy production [83]

$$\begin{aligned}\Psi[\rho_0/\rho_\infty] = {} & \frac{2}{\eta_\infty}(\underline{v}_\infty\cdot G(\underline{v}_0-\underline{v}_\infty))\,\mathrm{artanh}(2\eta_\infty)\\ & -\frac{2}{\eta_0}(\underline{v}_0\cdot G(\underline{v}_0-\underline{v}_\infty))\,\mathrm{artanh}(2\eta_0)\ .\end{aligned} \tag{327}$$

According to the splitting of the semigroup generator $\mathrm{L} = \mathrm{L_H} + \mathrm{L_D}$ and, consequently, for the associated evolution matrix $G = Q + R$ with $Q^T = -Q$ and $R^T = R$ one can extract "Hamiltonian" and "non-Hamiltonian" contributions to $\Psi = \Psi_\mathrm{H} + \Psi_\mathrm{D}$. Recall that for the two vectors $\underline{x}$ and $\underline{y}$ we have $(\underline{x}\cdot G\underline{x}) = (\underline{x}\cdot R\underline{x})$ but due to (45)

$$(\underline{x}\cdot G\underline{y}) = (\underline{x}\cdot R\underline{y}) - (\underline{h}\cdot(\underline{x}\wedge\underline{y}))\ , \tag{328}$$

if the Hamiltonian is written as $H = \frac{1}{2}(\underline{h}\cdot\underline{\sigma})$. Then, with the abbreviations

$$X = -\frac{2}{\eta_0}\,\mathrm{artanh}(2\eta_0)\ , \tag{329}$$

$$Y = \frac{2}{\eta_\infty}\,\mathrm{artanh}(2\eta_\infty)\ , \tag{330}$$

we get, finally,

$$\Psi_\mathrm{H}[\rho_0/\rho_\infty] = (\underline{h}\cdot(\underline{v}_0\wedge\underline{v}_\infty))\{X+Y\}\ , \tag{331}$$

$$\Psi_\mathrm{D}[\rho_0/\rho_\infty] = (\underline{v}_0\cdot R(\underline{v}_0-\underline{v}_\infty))X + (\underline{v}_\infty\cdot R(\underline{v}_0-\underline{v}_\infty))Y\ . \tag{332}$$

The obvious geometrical interpretation for Ψ_H shows that this contribution depends only upon the component of the Hamilton-vector $\underline{h}$ normal to the plane spanned by the initial and final coherence-vectors.

Further considerations of entropy production, also in relation to detailed balance, can be found in the literature [3,35,46,84,85] whereas our discussion in the next section will concern some shortcomings of the basic definitions used so far.

8.2 Measure of Irreversibility

The considerations of the preceding section might suggest a classification of nonequilibrium processes according to their "degree" or "measure" of irreversibility, the latter being suitably defined by the corresponding entropy production. Unfortunately, there are too many physically interesting cases where such ideas fail and it seems necessary to develop other concepts. One possible proposal will be outlined in the following.

First of all, we should mention that the presented version of entropy production is well-defined and physically meaningful for all situations close to thermodynamic equilibrium at any finite non-zero temperature since $\rho_t = \Lambda_t \rho_0$ will be faithful (ρ_t^{-1} exists for $0 \leq t \leq \infty$) where Λ_t is uniquely relaxing, of course. On the other hand, the general structure of the Kossakowski-generator admits much more general processes, in particular also those involving pure initial or final states as, e.g., in (71) which we rewrite in slightly different notation as

$$\rho_t = \frac{1}{2}\mathbb{1}_2 + \left(e^{-\gamma t} - \frac{1}{2}\right)\sigma_3 \ . \tag{333}$$

Although this is a prototype of an irreversible process $\rho_0 \to \rho_\infty$ with a lifetime γ^{-1} its details do not fit into commonly accepted properties such as entropy increase or some finite entropy production. In fact, we have

$$\rho_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \ , \quad \rho_\infty = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \ , \quad S[\rho_0] = S[\rho_\infty] = 0 \ ,$$

and, surprisingly, $\Psi[\rho_0/\rho_\infty] = \infty$. From formula (327) it is immediately clear that $\Psi = \infty$ occurs for all processes starting from a pure initial state. Thus, there is a strange discrimination between states, and this also in view of the fact that for $N < \infty$ there are the bounds

$$0 \leq S[\rho] \leq \ln N \ . \tag{334}$$

For the relative entropy (323) the problems arise with pure final states for $N = 2$, and for $N > 2$ it can be seen from (320) at once that things are only getting worse.

In terms of the coherence-vector representation an irreversible process starts from a point $\underline{v}_0$, traces some trajectory through state space $\mathbb{R}^{(M)}$ and ends finally at $\underline{v}_\infty$ such that the whole history of time-evolution must somehow be taken into account for a characterization of the process. Note that the von-Neumann entropy may increase or decrease or also oscillate as a function of time, as can be seen from the general analysis in Subsect. 2.5. If one intends to define something like a measure (or degree) of irreversibility which does not suffer from the above mentioned shortcomings of $\mathcal{R}$ and Ψ and is valid for any generator L of a completely positive semigroup two interrelated problems must be solved. First, in place of $\mathcal{R}$ there is need for a "measure of

distance" $\mathcal{M}[\rho/\omega]$ between any two density operators ρ and ω, well-defined and finite for all pairs, and second, in place of Ψ one must look for a suitable quantity $\mathcal{P}$ obtained by integrating the details of time-evolution along the trajectory through state space. Evidently, the former concept of entropy production must be abandoned but one could try to find $\mathcal{M}$ and $\mathcal{P}$ in such a way that they turn out to be closely analogous to $\mathcal{R}$ and Ψ whenever the latter make sense. A possible attempt will be outlined in the following [86].

Let us consider an operator-valued function $f(\rho,\omega)$ of two arbitrary density operators ρ and ω satisfying

$$i) \qquad f(\rho,\omega) = f(\omega,\rho) \geq 0 \ , \quad f = 0 \text{ iff } \rho = \omega \ , \tag{335}$$

$$ii) \qquad f(U\rho U^\star, U\omega U^\star) = U f(\rho,\omega) U^\star \ , \quad UU^\star = \mathbb{1}_N \ , \tag{336}$$

$$iii) \qquad f(\tilde{\rho},\omega) = f(\rho,\omega) \text{ iff } \tilde{\rho} = \rho \ , \tag{337}$$

$$iv) \qquad \pi\{f(\rho,\omega)\} \subset [0,1] \ , \tag{338}$$

where $\pi\{f\}$ denotes the spectrum of f. Recall now that according to the information-theoretic interpretation of the von-Neumann entropy the quantity $S[\rho]$ measures the information contained in ρ or more precisely, since $S[\rho] = -\sum_{k=1}^{M} \lambda_k \ln \lambda_k$ where λ_k are the eigenvalues of ρ one can say that S measures the information stored in $\pi\{\rho\}$. Therefore, we use S to extract from $\pi\{f\}$ the information on the "relative distance" between ρ and ω and define

$$\mathcal{M}[\rho/\omega] \hat{=} -2 \operatorname{Tr}\{f(\rho,\omega)\ln f(\rho,\omega)\} \ , \tag{339}$$

where the factor in front of the trace is a matter of convenience but the value of 2 is gauged for $N = 2$, as will become clear immediately later on. Note further that for an irreversible process $\rho \to \omega$ one has maximum information given by $\mathcal{M} = 0$ in the infinite time-limit when we know with certainty that $\rho = \omega$ but less information ($\mathcal{M} > 0$) at any finite time. In terms of the earlier notation $\mathcal{M}[\rho_t/\rho_\infty]$ contains the time-dependent information about the approach to stationarity. We emphasize again that, unlike $\mathcal{R}$, the value of $\mathcal{M}[\rho/\omega]$ is finite for all pairs $\{\rho,\omega\}$ provided that for the function $g(\lambda) = -\lambda \ln \lambda$ the value at $\lambda = 0$ is understood to be $g(0) = \lim_{\lambda\to 0} g(\lambda)$.

Tentatively, for an explicit calculation, we will use a concrete realization f_0 of f given by

$$f_0(\rho,\omega) = \frac{1}{2}(\rho-\omega)^2 \ . \tag{340}$$

Note, however, that this plausible choice does not satisfy (337). To show that (338) is satisfied we need

$$\rho\, \underline{x}^{(i)} = \lambda_i\, \underline{x}^{(i)} \ , \quad \omega\, \underline{y}^{(i)} = \mu_i\, \underline{y}^{(i)} \ , \quad 1 \leq i \leq N \ , \tag{341}$$

$$\operatorname{Tr}(\rho\omega) = \sum_{i,k=1}^{N} |(\underline{x}^{(i)} \cdot \underline{y}^{(k)})|^2 \lambda_i\, \mu_k \ , \tag{342}$$

and note that, from the Schwarz-inequality $|(\underline{x}^{(i)} \cdot \underline{y}^{(k)})|^2 \leq 1$, we have the bounds

$$0 \leq \mathrm{Tr}(\rho\,\omega) \leq 1 \,. \tag{343}$$

Since $f_0 \geq 0$ the trace is an upper bound for its largest eigenvalue and satisfies

$$0 \leq \mathrm{Tr} f_0(\rho, \omega) \leq 1 \,, \tag{344}$$

which proves (338). Next, let us briefly point out an important property of $\mathcal{M}_0[\rho_0/\rho_\infty] = -2\,\mathrm{Tr}\{f_0(\rho_0, \rho_\infty)\ln(\rho_0, \rho_\infty)\}$ in the case of our simple model of spontaneous emission (333). There, time-evolution is very unorthodox in the sense that for $0 \leq t \leq \gamma^{-1}\ln 2$, $S[\rho_t]$ is monotonically increasing from zero to its maximum of $\ln 2$ but subsequently decreases monotonically again to zero for $\gamma^{-1}\ln 2 < t \leq \infty$. For this process we find $\mathcal{M}_0 = 2\ln 2$ and this result keeps holding even in arbitrary dimension N for any two commuting but different pure state density operators. Thus, we have found a certain relative measure between different pure states. However, this consideration takes only initial and final states into account whereas for a general process with non-monotonic behavior of S the relevant quantity is $\mathcal{M}_0[\rho_t/\rho_\infty]$ which is a well-behaved positive function of time and integrable over the entire positive axis with respect to dt. This follows essentially from the spectral analysis of the evolution matrix G in Subsect. 2.5 and the corresponding solutions for ρ_t whose matrix elements are polynomials in t multiplied by an exponentially decaying function. Finally, the complete integral $\int_0^\infty M_0[\rho_t/\rho_\infty]dt$ keeps track of the systems history of time-evolution along the trajectory through state space. All considerations suggest that the provided information is analogous to entropy production if the integral is divided by the square of a characteristic lifetime τ of the system, a convenient choice being

$$\frac{1}{\tau} = \int_0^\infty \mathrm{Tr}(\dot{\rho}_t)^2 dt = \int_0^\infty \mathrm{Tr}\{\mathrm{L}\,\Lambda_t\,\rho_0\}^2 dt \,, \tag{345}$$

where integrability follows by the same arguments as above. It must be emphasized that τ should not be confused with what is generally called "lifetime of a state (or level)" since it somehow comprises all relaxation constants which appear in the generator L. Based on the foregoing considerations we are in position to give a concluding definition:

For an irreversible process $\rho_0 \to \rho_\infty$ of an N-level system described by a uniquely relaxing, completely positive quantum dynamical semigroup $\Lambda_t = \exp(\mathrm{L}t)$ with Kossakowski-generator L the measure (or degree) of irreversibility $\mathcal{P}$ is defined by

$$\mathcal{P} \hat{=} \frac{1}{\tau^2}\int_0^\infty \mathcal{M}[\Lambda_t\,\rho_0/\rho_\infty]dt \,. \tag{346}$$

To have some practical illustrations we analyze once more our model of spontaneous emission (333) and get

$$\tau = \gamma^{-1} \ , \quad \mathcal{P} = \gamma(1 + \ln 2) \ , \tag{347}$$

where τ comes out as expected and $\mathcal{P}/\gamma$ is, of course, larger than the relative measure between initial and final state because of integration, i.e., $\mathcal{P}/\gamma > \mathcal{M}_0[\rho_o/\rho_\infty] = 2\ln 2$. The trajectory is a straight line from a point on the surface of the Bloch-sphere and passing through the center to a diametrically opposite point on the surface again. The factor of $(1 + \ln 2)$ is a memory of this type of time-evolution whereas $\Psi[\rho_0/\rho_\infty] = \infty$, as already mentioned.

As a further example let us turn attention to some special solutions of the traditional Bloch-equations used to describe free induction decay by

$$\rho_t = \frac{1}{2}\begin{pmatrix} 1 - w(1 - e^{-\gamma_1 t}) & 2ue^{-(\gamma_2 - i\Delta)t} \\ 2ue^{-(\gamma_2 + i\Delta)t} & 1 + w(1 - e^{-\gamma_1 t}) \end{pmatrix} \ , \tag{348}$$

$$0 \le u \le \frac{1}{2} \ , \quad 0 \le w \le 1 \ , \tag{349}$$

with frequency off-set Δ (136) and $\gamma_1 \le 2\gamma_2$ (113), (115). The somewhat lengthy calculations are omitted since all necessary integrals can be found in standard tables [54, 87]. The general result is

$$\tau = 4\left[\gamma_1 w^2 + \frac{4u^2}{\gamma_2}(\gamma_2^2 + \Delta^2)\right]^{-1} \ , \tag{350}$$

$$\begin{aligned} \mathcal{P}\,\tau^2 = {} & \frac{1}{8\gamma_1\gamma_2^2}(\gamma_2^2 + 4u^2\gamma_1^2) - \frac{1}{8\gamma_1\gamma_2}(\gamma_2 + 4u^2\gamma_1)\ln\left(\frac{1 + 4u^2}{8}\right) \\ & + \frac{2u^2}{\gamma_1 b}F(1, b; b + 1; -4u^2) + \frac{8u^4}{\gamma_2(b+1)}F(1, b + 1; b + 2; -4u^2) \ , \end{aligned} \tag{351}$$

where F is the Gaussian hypergeometric function

$$F(a, b; c; z) = 1 + \sum_{n=1}^{\infty} \frac{[a]_n[b]_n}{[c]_n n!} z^n \ ,$$

$$[a]_n = a(a + 1)(a + 2)\ldots(a + n - 1) \ , \tag{352}$$

and $b = \gamma_2/(\gamma_2 - \gamma_1)$. For the special values, e.g.,

$$u = \frac{1}{2} \ , \quad w = 1 \ , \quad \gamma_2 = 2\gamma_1 \ , \tag{353}$$

one can use the recursion relations for F to obtain

$$F(1, 2; 3; -z) = \frac{2}{z^2}[z - \ln(1 + z)] \ , \tag{354}$$

$$F(1, 3; 4; -z) = \frac{3}{2z^2}[z^2 - 2z + \ln(1 + z)^2] \ , \tag{355}$$

and (351) reduces to

$$\mathcal{P} = \frac{\gamma_2}{64}\,(7 + \ln 2)\left[\frac{3}{2} + \left(\frac{\Delta}{\gamma_2}\right)^2\right]^2 . \tag{356}$$

From (146) the absorbed power for this type of decay process (weak external field $\omega_1 \approx 0$) is inversely proportional to $[1 + (\Delta/\gamma_2)^2]$ and, thus, $\mathcal{P}$ is a minimum if the system is driven to resonance and increases towards the wings of the lineshape.

One may regret that $\mathcal{M}[\rho/\omega]$, despite of its obvious advantages over $\mathcal{R}[\rho/\omega]$, does not necessarily share the nice property [42]

$$\mathcal{R}[\rho_1 \otimes \rho_2/\omega \otimes \rho_2] = \mathcal{R}[\rho_1/\omega] \tag{357}$$

for the composition of systems, and this point suggests the necessity of further improvements. On the other hand, there is hope to extend the results to $\dim\mathcal{H} = \infty$ by choosing for L the Lindblad-generator [26] in its general form and admitting only processes with $S[\rho_t] < \infty$, $t \geq 0$. The existence of τ and $\mathcal{P}$ then seems to be guaranteed if the evolution matrix G contains at most finite-dimensional Jordan-blocks. However, this will need further detailed investigations and rigorous proofs, of course.

In conclusion, the introduced new concept of a measure of irreversibility is of remarkable general validity and extends, in particular, to all those processes for which the common notion of entropy production is meaningless.

9 Conclusion

After all, it should have become clear that the concept of quantum Markovian master equations is of extremely wide applicability in so many branches of physics but has to be handled with care since the introduction of relaxation parameters on purely phenomenological grounds may lead to inconsistencies. The latter are definitely avoided if the structure imposed on the differential equations for the density operator matrix elements is such that, at all times, the solutions satisfy the von Neumann-conditions of hermiticity, trace-preservation and positivity, as required by the general laws of quantum theory and guaranteed finally by the concept of complete positivity. The details worked out so far in the preceeding sections should be sufficient to provide the necessary guidelines to those who want to use the results of this theory without going further into the mathematical problems. Even if one were to introduce relaxation parameters by heuristic reasoning, as certainly unavoidable many times in the interpretation of experiments, there are definite rules regarding the maximum number of independent quantities that can be chosen for fixed N, and there are useful inequalities imposing mutual restrictions among them. This, in turn, may help to decide whether N has been chosen appropriately or, more than that, whether a description by a Markovian master equation is in place at all. Of course, even for few-level systems the explicite

calculations may become tedious and lengthy and contain many finer details that can not be resolved in an experiment. The introduction of the absolutely minimal parameter set required may then become a question of art. It is for this reason that we have not presented results for four-level systems as certainly of interest in problems of nonlinear optics such as coherent anti-stokes Raman scattering (CARS) or second harmonic generation. For those cases A is already (15×15) but future investigations in this direction will certainly be welcome. One may regret the lack of further complete models comprising the dynamics of the reservoir for concrete physical situations since only then can one compute ab ovo the a_{ik}'s in the Kossakowski-generator by means of correlation functions once the interaction Hamiltonian between open system and reservoir is known.

Finally, regarding the theoretical foundations most open questions are linked to the problems discussed in Sect. 6 and concern a mathematically sound treatment of externally applied strong alternating fields with simultaneous modification of relaxation due to field-strength and frequency. Obviously, many assumptions used in the Davies-theory of the weak-coupling limit as well as convenient model situations like infinite free reservoirs in KMS-states must be abandoned. Unless unexpected new ideas come up it is hard to see how by the conventional techniques of reducing the unitary dynamics of the combined systems to the irreversible one of the open system only can one obtain generators of type (217) with mathematical rigor. Perhaps, this will only be achieved in extremely special models, and one can certainly say that much interesting work should be done in this direction.

Appendix

A.1 Generators and Structure Constants for SU(N), $N = 2, 3, 4$

All generating matrices and structure constants are based on the normalization

$$\mathrm{Tr}(F_i F_k) = \delta_{ik}$$

and the relations (23) and (24).

I. SU(2):

$$F_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} , \quad F_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} , \quad F_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

$$f_{ikl} = \sqrt{2} , \quad d_{ikl} = 0 , \quad i, k, l = 1, 2, 3 .$$

II. SU(3):

$$F_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \qquad F_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} ,$$

$$F_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} , \qquad F_4 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} ,$$

$$F_5 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix} , \qquad F_6 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} ,$$

$$F_7 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix} , \qquad F_8 = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} .$$

$f_{ikl} = \sqrt{2}$		$1/\sqrt{2}$	$-1/\sqrt{2}$	$\sqrt{6}/2$
	1 2 3	1 4 7	1 5 6	4 5 8
		2 4 6	3 6 7	6 7 8
i k l		2 5 7		
		3 4 5		

$d_{ikl} = 2/\sqrt{6}$		$1/\sqrt{2}$	$-1/\sqrt{2}$	$-1/\sqrt{6}$	$-2\sqrt{6}$
	1 1 8	1 4 6	2 4 7	4 4 8	8 8 8
	2 2 8	1 5 7	3 6 6	5 5 8	
i k l	3 3 8	2 5 6	3 7 7	6 6 8	
		3 4 4		7 7 8	
		3 5 5			

III. SU(4):

$$F_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} , \qquad F_2 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} ,$$

$$F_3 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \qquad F_4 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$F_5 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -i & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \qquad F_6 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$F_7 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \qquad F_8 = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix},$$

$$F_9 = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \qquad F_{10} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix},$$

$$F_{11} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \qquad F_{12} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & 0 & 0 \\ 0 & i & 0 & 0 \end{pmatrix},$$

$$[5pt] F_{13} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \qquad F_{14} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \end{pmatrix},$$

$$F_{15} = \frac{1}{2\sqrt{3}} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -3 \end{pmatrix}.$$

The structure constants for index combinations with $1 \leq i,k,l \leq 8$ are the same as those for SU(3). Only the additional values are given below.

$f_{ikl} = 1/\sqrt{2}$		$-1/\sqrt{2}$	$1/\sqrt{6}$	$-2/\sqrt{6}$	$2/\sqrt{3}$
	1,9,12	1,10,11	8,9,10	8,13,14	9,10,15
	2,9,11	3,11,12	8,11,12		11,12,15
	2,10,12	4,10,13			13,14,15
	3,9,10	6,12,13			
i,k,l	4,9,14				
	5,9,13				
	5,10,14				
	6,11,14				
	7,11,13				
	7,12,14				

$d_{ikl} = 1/\sqrt{2}$		$-1/\sqrt{2}$	$1/\sqrt{6}$	$1/\sqrt{3}$	$-1/\sqrt{3}$	$-2/\sqrt{6}$	$-2\sqrt{3}$
	1,9,11	2,9,12	8,9,9	1,1,15	9,9,15	8,13,13	15,15,15
	1,10,12	3,11,11	8,10,10	2,2,15	10,10,15	8,14,14	
	2,10,11	3,12,12	8,11,11	3,3,15	11,11,15		
	3,9,9	5,9,14	8,12,12	4,4,15	12,12,15		
	3,10,10	7,11,14		5,5,15	13,13,15		
i,k,l	4,9,13			6,6,15	14,14,15		
	4,10,14			7,7,15			
	5,10,13			8,8,15			
	6,11,13						
	6,12,14						
	7,12,13						

A.2 Eigenvalues of the General Two-level Evolution Matrix

The three coupled linear inhomogeneous first-order differential equations (104)-(106) or, else, $\dot{\underline{v}} = G\underline{v} + \underline{k}$, with

$$G = \begin{pmatrix} -\gamma_3 & \alpha - \omega_0 & \beta - \omega_2 \\ \alpha + \omega_0 & -\gamma_2 & \delta - \omega_1 \\ \beta + \omega_2 & \delta + \omega_1 & -\gamma_1 \end{pmatrix} , \tag{358}$$

are solved by the standard procedure outlined in Subsect. 2.5 where the construction of eigenvectors is found. The corresponding eigenvalues λ_i are calculated from

$$\lambda^3 + a\lambda^2 + b\lambda + c = 0 , \tag{359}$$

where

$$a = \gamma_1 + \gamma_2 + \gamma_3 , \tag{360}$$

$$b = \gamma_1\gamma_2 + \gamma_1\gamma_3 + \gamma_2\gamma_3 + \omega_0^2 + \omega_1^2 + \omega_2^2 - (\alpha^2 + \beta^2 + \delta^2) , \tag{361}$$

$$c = \gamma_1\gamma_2\gamma_3 + \gamma_1(\omega_0^2 - \alpha^2) + \gamma_2(\omega_2^2 - \beta^2) + \gamma_3(\omega_1^2 - \delta^2) + 2\alpha\,\omega_1\,\omega_2 - 2\beta\,\omega_0\,\omega_1 + 2\delta\,\omega_0\,\omega_2 - 2\alpha\,\beta\,\delta . \tag{362}$$

The discriminant d of (359) is

$$d = \left(\frac{q}{2}\right)^2 + \left(\frac{p}{3}\right)^3 , \tag{363}$$

in terms of

$$p = b - \frac{a^2}{3} , \quad q = \frac{2}{27}a^3 - \frac{ab}{3} + c . \tag{364}$$

With the abbreviations

$$x = \left(-\frac{q}{2} + \sqrt{d}\right)^{1/3} , \quad y = \left(-\frac{q}{2} - \sqrt{d}\right)^{1/3} , \tag{365}$$

$$z = \left(\frac{|p|}{3}\right)^{1/2} , \quad \varphi = \frac{1}{3}\arccos(-q/2z^3) , \tag{366}$$

the roots are as follows:

$$d \geq 0 \ : \begin{cases} \lambda_1 = x + y - \frac{a}{3}, \\ \lambda_2 = -\frac{1}{2}(x+y) + i\frac{\sqrt{3}}{2}(x-y) - \frac{a}{3} , \\ \lambda_3 = -\frac{1}{2}(x+y) - i\frac{\sqrt{3}}{2}(x-y) - \frac{a}{3} , \end{cases} \tag{367}$$

$$d < 0 \ : \begin{cases} \lambda_1 = 2z\cos(\varphi) - \frac{a}{3} , \\ \lambda_2 = -2z\cos(\varphi - \frac{\pi}{3}) - \frac{a}{3} , \\ \lambda_3 = -2z\cos(\varphi + \frac{\pi}{3}) - \frac{a}{3} . \end{cases} \tag{368}$$

A.3 Elements of the Time-dependent Two-level Evolution Matrix

We use O_t given in (126), the abbreviations

$$c = \cos(\omega t) \ , \quad s = \sin(\omega t) \ , \tag{369}$$

and the frequency detuning

$$\Delta = \omega_0 - \omega \tag{370}$$

to obtain $\tilde{G}_t$ of (129). The list of components is as follows:

$$(\tilde{G}_t)_{11} = -(\gamma_2 \, s^2 + \gamma_3 \, c^2) + 2\alpha \, s \, c \ , \tag{371}$$

$$(\tilde{G}_t)_{12} = -\Delta - \alpha(s^2 - c^2) - (\gamma_2 - \gamma_3) s \, c \ , \tag{372}$$

$$(\tilde{G}_t)_{13} = (\beta - \omega_2)c - (2\omega_1 c - \delta)s \ , \tag{373}$$

$$(\tilde{G}_t)_{21} = \Delta - \alpha(s^2 - c^2) - (\gamma_2 - \gamma_3) s \, c \ , \tag{374}$$

$$(\tilde{G}_t)_{22} = -(\gamma_2 \, c^2 + \gamma_3 \, s^2) - 2\alpha s \, c \ , \tag{375}$$

$$(\tilde{G}_t)_{23} = (\omega_2 - \beta)s - (2\omega_1 c - \delta)c \ , \tag{376}$$

$$(\tilde{G}_t)_{31} = (\beta + \omega_2)c + (2\omega_1 c + \delta)s \ , \tag{377}$$

$$(\tilde{G}_t)_{32} = -(\beta + \omega_2)s + (2\omega_1 c + \delta)c \ , \tag{378}$$

$$(\tilde{G}_t)_{33} = -\gamma_1 \ . \tag{379}$$

The constant vector $\underline{k}$ transforms into

$$\tilde{\underline{k}}(t) = \sqrt{2} \, (\mu \, s - \lambda \, c, \, \mu \, c + \lambda \, s, -\nu)^T \ . \tag{380}$$

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Recent Developments

Robert Alicki and Karl Lendi

The following survey collects various treatments from different fields, in one or the other form related to the methods presented in this book. Nowadays, applications range from elementary particle and nuclear physics to atomic, molecular, solid state and chemical physics with increasing use for the direct interpretation of experiments. In view of the abounding and wide-spread literature the following restricted collection of papers necessarily reflects our personal point of view. Nevertheless, the extra list of references complemented by references cited therein is expected to give a rather fair overview on developments over the last twenty years. Referring to sections or formulas in Alicki's or Lendi's contribution will be marked by (A,...) and (L,...), respectively.

1 Complete Positivity, Entanglement and Decoherence

Complete positivity (CP) has experienced its absolute breakthrough in the wide and very active fields of quantum information, particularly in quantum computing. It has been recognized that the CP requirement must unavoidably be imposed on operations affecting only one component of entangled systems, since otherwise artificial and unphysical correlations or ill-defined states may emerge. The same is true for continuous time-evolution of such systems under the mere influence of the surroundings, whithout any external manipulations. That positive, but not completely positive maps applied to one two-level component of a bipartite four-level system, e.g., do not preserve positivity of the entangled entire system, has been shown [1–4]. In view of the abounding recent literature in these fields it is impossible and outside the scope of this chapter to give a comprehensive overview. Many important aspects can be found in books and the references cited therein (see, e.g., [3, 5–15]). As entanglement became an important resource in quantum information the preparation and analysis of highly entangled states is a subject of many theoretical and expertimental efforts. For example, the CP-property in context of entangled physical systems in elementary particle physics and neutron interferometry are discussed

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by F. Benatti, R. Floreanini and R. Romano [16,17]. In teleportation, realized by the propagation of polarized photons, disturbing environmental influencies may affect the relialibility of results and can most probably and succesfully be acounted for by quantum dynamical semigroup (QDS) evolution [18].

Environmental noise, or decoherence, is the main obstacle for the implementation of the bold ideas of quantum information processing, in particular for efficient quantum computation [19]. The topic of decoherence became fashionable in the last decade also due to the progress in experimental techniques which allow the observation of irreversible processes in single micro and mesoscopic open quantum systems (see [9] for a review and many relevant references). Very often this noise is described by Markovian models, in particular by suitable QDS. The models of collective noise considered earlier by R. Alicki [20] in terms of QDS were independently developed in the context of the so-called decoherence-free subspaces and subsystems, as reviewed by D. Lidar and K. B. Whaley [21]. Another example provides a class of Poisson type QDS with solutions of the form (A, Eq. (31)) used to describe decoherence of the center of motion for large molecules [22] and then generalized and derived from the Hamiltonian model [23]. Regarding loss of purity by decoherence effects a monotonic decrease could be proven to arise from a special class of QDS which are bistochastic [24]. In finite-dimensional Hilbert spaces this class covers all possible cases, whereas in infinite dimensions it can be proven to be sufficient only.

Usually, it is assumed that during time-evolution an initial entanglement will be destroyed by decoherence effects induced by the unavoidable coupling to some environment. Apart from some possible minor revivals of entanglement under special periodic actions the loss seems to be rather general [9, 25, 26]. Somewhat surprising, the opposite effect has also been shown to be possible, namely the dynamical emergence of entanglement out of uncorrelated (separable) states. For instance, two mutually noninteracting two-level systems, immersed in a common bath, may even acquire considerable correlation during QDS time-evolution [27–30].

2 Unbounded Generators and Stochastic Equations

The fundamental mathematical problem in the theory of QDS regarding the general structure of an unbounded generator remains unsolved. However, as noticed for the first time in [31] the formal expressions (A, Eq. (39)) with unbounded H and V_j are meaningful under certain conditions. We can solve the corresponding equation of motion in terms of a *minimal solution*. The minimal solution need neither be unique nor trace preserving ("probability can escape to infinity"). The useful sufficient conditions for the existence of a minimal solution and its trace preservation were given in [32]. The detailed characterization of a class of covariant QDS with unbounded generators is presented in [33].

The weak coupling or low density limit method described in (A, Subsubsect. 1.2.2) produce well-defined QDS for open systems with discrete spectrum Hamiltonians only. There are, however, important systems with continuous energy spectrum like, for example, a free Brownian particle or infinite lattice systems (e.g. a Heisenberg ferromagnet). An interesting construction of the generator for a particle in a heat bath consisting of a quantum fluid is presented in [34]. The first attempt to construct a QDS for a rather general infinite quantum system which satisfies quantum detailed balance in the sense of (A, Subsubsect. 1.3.4) was given in [35]. A number of examples of QDS for infinite quantum systems can be found in [36] and [37].

Similarly to classical theory, where Markov semigroups can be derived from the stochastic differential equations, often called Langevin equations, QDS can be also obtained from stochastic Schrödinger equations. Two different constructions were developed. The first one, proposed in [38] and summarized in [39] is called quantum stochastic calculus. It uses noncommutative stochastic differential equations (NSDE) with quantum noise defined as operator-valued fields acting on the bosonic or fermionic Fock spaces. The solutions of NSDE yield certain unitary dilations of QDS.

Another type of unitary dilations proposed in [40] lead to the Itô type (classical or commutative) stochastic differential equations for the wave function of the open system. Such equations can be more convenient for the analysis of a quantum Markovian system than the original master equations for a density matrix. Indeed, a certain modification of this approach has independently been developed under the name *stochastic wave function method* and became a useful tool in numerical computations [41].

3 Nonlinear QDS

Equations with nonlinear structure are frequently used in physics as, for instance, equations of Hartree or quantum-Boltzmann type. Nonlinear dynamical semigroups discussed in (A, Subsubsects. 1.4.3–1.4.5) which provide approximative single-particle description of many-body open systems have been used mainly in the context of mean-field models [42, 43] and recently also for fermionic systems where unbounded Lindblad generators were combined with the interaction in Hartree-Fock approximation [44]. A discrete-in-time analog of nonlinear QDS has been developed under the notion of *statistical dynamics* by R. Streater [45]. Mathematical relations between nonlinear QDS and the notion of nonlinear completely positive maps on algebras and the possible form of generators have been studied by Majewski [46].

4 Geometry of States and Symmetries of Generators

The systematic representation of density matrices by real coherence-vectors, as proposed and used in our text, has found relatively broad appreciation

by many authors in later treatments. One particularly interesting aspect is the possibility to explore the geometry of state space. Although its convexity properties are clear [47] the details for N-level systems are rather unknown and may be very surprising. In fact, the naive idea that the Bloch sphere for two-level systems would just carry over to spheres in higher dimensions is incorrect. Note that the upper bound on the vector length (L, Eq. (67)) is necessary but by far not sufficient for $N \geq 3$. For instance, already for a three-level system with eight-dimensional state space a selected two-dimensional subspace contains allowed vectors only within a triangle. A detailed analysis with illustrative examples may be found in [10, 48–50]. Another instructive application in quantum computing regards the characterization of reachable sets for open systems driven by unitary control [51].

As shown in the main text there are two approaches to QDS based on different ideas for a derivation of quantum Markovian master equations. On the one hand, for a given total Hamiltonian inducing unitary dynamics of the entire, closed system comprising the open system and the reservoir, the Davies theory yields exact representations for the relaxation constants in terms of initially defined quantities and, consequently, reveals their physical meaning. On the other hand, the algebraic derivation of genuinely reduced dynamics defines generators involving non-negative matrices, but the physically detailed meaning of the matrixelements may not a priori be clear. In a series of papers Artem'ev has shown how additional information can be used in this connection, particularly for open spin systems [52] or in problems of optical resonance [53] by taking into account known symmetry properties. In order to treat the effect on a quantum particle by a local interaction with a spatially homogeneous and isotropic environment a family of master equations has been proposed by Gallis [54]. The corresponding infinitesimal generators with the constraints that dissipation is linear (so-called Ohmic), isotropic and translationally invariant, are of Lindblad type. As a consequence, fluctuation-dissipation relations and the relaxation of the average kinetic energy to effective thermal equilibrium values are obtained.

5 QDS and Thermodynamics

As already shown by Spohn, Lebowitz and Alicki [55, 56] QDS and their non-homogeneous-in-time adiabatic generalizations can be used to derive the laws of thermodynamics and describe quantum engines. Extending the classical Onsager theory to the quantum domain by strictly using QDS dynamics has been shown to be feasible and to allow even a systematic calculation of higher order coefficients [57, 58]. In this context, formulas for entropy production are based on the notion of relative entropy. In order to avoid shortcommings of the latter if pure states are involved, a generalized version has been proposed which preserves the required properties of ordinary relative entropy under QDS time-evolution [59].

In an application of QDS to a quantum version of the Carnot machine [60] a collection of noninteracting three-level systems is coupled to two reservoirs at different temperatures. The power output is via stimulated emission of radiation from the upper two levels in a semiclassical approximation. The time scale of the external field must be slow compared to that associated with the bath fluctuations. In contrast to simpler treatments where the relaxation constants are field-independent, this more general treatment yields field-dependent values as necessary consequence of satisfying thermodynamic constraints. Furthermore, the power is found to have maxima as a function of important control parameters, such as field amplitude, frequency and coupling strengths. Note that field-dependent relaxation times have already earlier been worked out for generalized Bloch equations in agreement with optical experiments in stronger fields (L, Subsect. 6.2).

Another detailed thermodynamic analysis of quantum light amplification [61] is based on an extended dissipative Jaynes-Cummings model within the framework of a quantum heat engine. In contrast to similar earlier work matter and radiation field are treated as fully quantized bipartite systems for which heat flux and power output can be calculated and the validity of the second law of thermodynamics verified.

Finally, a model for a quantum refrigerator with the working substance of noninteracting spin-(1/2) systems has been shown to provide coefficients of performance, cooling rate and necessary power input from the QDS treatment [62].

6 Applications in Atomic and Molecular Physics

In this section we present few applications of the QDS formalism to particular problems in atomic and molecular physics.

The QDS framework has been used for a rather general treatment of proton-spin relaxation in water [63]. Basically, one deals with a four-level system coupled to a reservoir in thermal equilibrium for which the specifications of the infinitesimal generator, either in Kossakowski or in Davies form, are worked out in detail. The usual, relevant correlation functions are additionally supplemented by a stochastic process corresponding to formation or breaking of hydrogen bridges. The so obtained generalized Bloch-like equations allow reduction to ordinary Bloch equations under suitable, physically reasonable simplifications. The results provide an identification of relevant relaxation times with a particular interpretation of rotational correlation times and an analysis of numerical values over a wide temperature range.

In an investigation of femtosecond laser pulse induced molecular desorption from a metal surface a Lindblad generator has been used to account both for electronic and vibrational bath-induced transitions. Detailed results show very satisfactory agreement with experiments [64]. In problems of molecular scattering from surfaces the common linear coupling assumption has been

replaced by a more realistic nonlinear choice in order to achieve a decreasing coupling strength for increasing distance from the sources [65].

For an active atom which interacts collisionally with a reservoir of perturber atoms a combined quantum mechanical-classical treatment is required and yields completely positive Bloch-Boltzmann equations [66].

In connection to complete positivity, it should be remembered that the traditional Bloch-Wangsness-Redfield theory [67] has been very successful, even though it suffers from possibly violating positivity. However, after choosing some classical stochastic processes for the correlation functions, the failure can often be avoided but, of course, the proof for positivity must explicitly be given for the final results. One way to still take advantage of useful Redfield components is to keep only those terms which fit, e.g., the structure of a Davies generator. An example is found in a paper by Sadygov and Neuhauser on the dynamics of primary charge separation reactions in bacterial photosynthesis [68]. In this application it is found that the simple Markovian results agree well with those from much more elaborate treatments such as, e.g., rigorous path integral calculations.

7 Beyond a Markovian Approximation

Undoubtly, many physical phenomena ask for an extended so-called non-Markovian description. In particular, the QDS-assumption of disentangled initial states may not be appropriate and, additionally, long-time memory effects may came into play giving rise to considerable technical complications. Unfortunately, there is then no counterpart to the beautiful closed mathematical framework of QDS, and progress with rigorous results is extremely slow. A few related aspects will be addressed below.

The results of the non-Markovian lowest order approximation of quantum computing show that common assumptions made in the theory of fault-tolerant quantum computation may not be realistic [19,69]. It is found, in particular, that a long range quantum memory in conjunction with self-dynamics of the quantum computer implies a highly nonlocal structure of noise with remarkable implications for the error correction concept. Finally, a minimal decoherence model is proposed in which the only source of decoherence is the unavoidable vacuum. The fidelity of quantum information processing is optimized under the trade-off between the speed of the gate and the strength of decoherence. One may hope that this analysis will be helpful for future implementations of the quantum computer involving a large number of qubits and relatively long computation time.

An interesting further development beyond the traditional Markovian case, commonly based on second order perturbation theory, has been worked out by Kossakowski [70]. A rigorous treatment of a spherical oscillator interacting with a radiation field takes particular care of embedded eigenvalues for which regular perturbation theory can not be applied, as due to the appearance of

resonances. It is possible to extract from a non-Markovian equation an exact reduced semigroup dynamics involving multi-time correlation functions which include corrections of all orders in the coupling constant. Irreversibility of the dynamics emerges as a consequence of resonances.

In general, it is difficult or even impossible to reconcile a QDS structure with applied external fields. This is due to the different conflicting time scales in the limiting weak or singular coupling procedures [19, 71]. External fields may have an appreciable influence also on the reservoir dynamics, and a genuinely reduced description does not exist. On the other hand, experience with many physical situations has shown that, under particular conditions, a QDS structure or, at least, a Kraus quantum dynamical map conserving CP may be appropriate. In the latter case, the infinitesimal generators still are given in Kossakowski or Lindblad form but with time-dependent coefficients. A careful study of related problems can also be found in [72] where particularly the use of Floquet theory has been worked out. In a study of the limitations of Markovian master equations with time-dependent generators [73] Bloch equations with time-dependent parameters have been obtained under special conditions. For a much more general case, a time-local equation for the Jaynes-Cummings model with atomic damping is derived, valid only on a finite time interval, as due to divergencies in the generator.

In some analogy to an exactly solvable model for oscillators by Ullersma [74] a second solvable model has been analyzed by van Kampen [75]. The open system consists of a single particle residing on different sites of a linear chain and coupled to an assembly of harmonic oscillators. From the general, non-Markovian solution it is possible to extract a Markovian equation with generators of Kossakowski or Lindblad form, but only after a certain initial transit time and a so-called coarse graining procedure. Another advantage is the detailed discussion of conditions on relevant parameters in order to make the Markovian version reliable.

At this stage, it is important to pronounce some warnings. There seems to be a believe that non-Markovian dynamics, after a very short initial period, goes over into Markovian behaviour and one has to shift only some initial conditions, at least for moderate couplings to the reservoir. This then encourages to use some approximate equations not obeying CP, even violating simple positivity for a short interval but at least relaxing to a final stationary state. Another trick is to use such equations only for a very restricted set of initial conditions in order to avoid non-positivity. Even though there may be very special cases where such methods yield half-way acceptable results they are useless in general. From a rigorous point of view the following must be said. Many non-Markovian equations, indeed, tend to have a long-time behaviour that can be well appoximated by Markovian equations. However, it is not true that this always happens after a very short initial period. A clear counterexample is the generalized Jaynes-Cummings model where the Markovian-like decay of a two-level atom occurs after an appreciable period of collapse and revival dynamics and, in particular, after residing for a very long intermediate

period in a quasi-stationary state of maximum entropy [76,77]. It has also been shown that initial slip tricks may yield wrong relaxation times [78]. And last but not least, it is not even guaranteed that there is a Markovian long-time behaviour with exponential decay, as strikingly shown in the pioneering early Emch model [79].

An attempt to transfer the completely positive Markovian structure into a non-Markovian integro-differential equation is due to Daffer et al. [80]. The memory integral kernel in a homogeneous Nakajima-Zwanzig type equation is chosen as a product of a scalar function with a semigroup generator. This structure could be extracted from a reservoir model based on a random telegraph stochastic process. For such a parametrized ansatz an a posteriori proof for CP is still necessary and has been worked out by the authors in order to define the range of allowed parameter values. Another case of a scalar kernel function has been chosen by Shabani and Lidar to obtain an analytically solvable master equation which interpolates between an exact and a Markovian case [81]. Similar procedures may prove quite promising for future applications. A different approach is by directly constructing a non-phenomenological Kraus map in terms of a perturbative series with respect to the reservoir interaction. By retaining all reservoir correlation functions which factorize into products of pair-correlations a resummation of the expansion up to infinite order is possible. The density operator can then be expressed in terms of an auxiliary system operator that satisfies an analytically tractable integral equation. One can show that, for special interactions, common phenomena like, e.g., Rabi oscillations or spontaneous emission of Wigner-Weisskopf type are covered [82]. In a more advanced, similar treatment the perturbation expansion keeps a generalized nearest-neighbour class of Wick contractions involving all cyclic permutations of interaction potentials. As important property, the Markovian limit exists and reproduces the complete Davies theory [83].

For more general kernels no criteria for their properties with respect to completely positive evolution, not even for positivity of solutions, are exactly known but a few attempts in this direction may be mentioned. If a concrete parametrized kernel is given, based either on some physically reasonable or mathematically sound arguments, the existence and positivity of solutions can at least approximately be analyzed. For various cases of relatively simple functions this has been done, even for the Nakajima-Zwanzig equation including the inhomogeneity due to entangled initial states. At the same time, a very accurate and efficient computer code has been developed in order to test details numerically, particularly analytical guesses [84–86]. An improvement of estimates of upper bounds for solutions, use of Liapunov functions and other techniques for the study of asymptotics and application to a spin-boson model may be found in [87]. Investigations along these lines are still in progress.

Regarding CP, one must stress again that it is guaranteed by the general Kraus representation under the requirement of disentangled (uncorrelated) initial states. Of course, the same is true for QDS which, under appropriate conditions, emerge as a special case of quantum dynamical Kraus maps

(A, Subsubsect. 1.2.4). On the other hand, the complete Nakajima-Zwanzig integro-differential equation contains a nasty inhomogeneity term due to entanglement of initial states and is trivially incompatible with CP. Nevertheless, one may try to explore Kraus-like maps, although with little success. Either, very special conditions must be satisfied [88] or the maps become nonlinear, not completely positive and, only for simple cases, may lead to Bloch-like equations [89].

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