On the other hand, the entropy flux J is due to those changes of the internal energy $E = \text{tr}\{H\rho\}$ which result from dissipative effects. Thus we may define the entropy flux by means of

$$J = -\frac{1}{T}\frac{d}{dt}\bigg|_{\text{diss}} E \equiv -\frac{1}{T}\text{tr}\{H\mathcal{D}(\rho)\} = -\frac{1}{T}\text{tr}\{H\mathcal{L}(\rho)\}. \qquad (3.107)$$

Using the explicit expression (3.103) for the thermal distribution we find

$$-\frac{1}{T}H = k_{\text{B}}\ln\rho_{\text{th}} + k_{\text{B}}\ln Z, \qquad (3.108)$$

so that the entropy flow can be written as

$$J = k_{\text{B}}\text{tr}\left\{\mathcal{L}(\rho)\ln\rho_{\text{th}}\right\}, \qquad (3.109)$$

where we have made use of the fact that the generator is trace-preserving, i.e. $\text{tr}\{\mathcal{L}(\rho)\} = 0$. Adding eqns (3.106) and (3.109) we see that the thermodynamic entropy production rate σ defined by the balance equation (3.105) coincides with expression (3.100) for the negative rate of change of the relative entropy with respect to the thermal equilibrium state. In this context the inequality $\sigma(\rho) \geq 0$ expresses the second law of thermodynamics. Note also that $\sigma(\rho_{\text{th}}) = 0$, that is the entropy production vanishes in the thermal equilibrium state. Thus we conclude that the entropy production rate $\sigma(\rho)$ is a convex functional on the space of density matrices which vanishes in the thermal equilibrium state.

3.3 Microscopic derivations

From a fundamental viewpoint it is desirable to derive the generator of a quantum dynamical semigroup from the underlying Hamiltonian dynamics of the total system. The aim of this section is to show under which assumptions such derivations can be given on the grounds of various approximation schemes.

3.3.1 Weak-coupling Limit

We begin by considering a quantum mechanical system S weakly coupled to a reservoir B. The Hamiltonian of the total system is assumed to be of the form

$$H = H_S + H_B + H_I, \qquad (3.110)$$

where H_S and H_B denote respectively the free Hamiltonian of the system and of the reservoir and H_I describes the interaction between the system and the reservoir. The derivation of a quantum Markovian master equation is most easily performed in the interaction picture. Our starting point is thus the interaction picture von Neumann equation (see Section 3.1.2)

$$\frac{d}{dt}\rho(t) = -i[H_I(t), \rho(t)] \qquad (3.111)$$

for the total density matrix $\rho(t)$ and its integral form

$$\rho(t) = \rho(0) - i \int_0^t ds [H_I(s), \rho(s)]. \qquad (3.112)$$

Note that we omit here for ease of notation the index I which served to indicate the interaction picture in Section 3.1.2. Inserting the integral form into (3.111) and taking the trace over the reservoir we find

$$\frac{d}{dt}\rho_S(t) = - \int_0^t ds \operatorname{tr}_B [H_I(t), [H_I(s), \rho(s)]]. \qquad (3.113)$$

Here, we have assumed that

$$\operatorname{tr}_B [H_I(t), \rho(0)] = 0. \qquad (3.114)$$

Equation (3.113) still contains the density matrix of the total system $\rho(t)$ on its right-hand side. In order to eliminate $\rho(t)$ from the equation of motion we perform a first approximation, known as the *Born approximation*. This approximation assumes that the coupling between the system and the reservoir is weak, such that the influence of the system on the reservoir is small (weak-coupling approximation). Thus, the density matrix of the reservoir ρ_B is only negligibly affected by the interaction and the state of the total system at time t may be approximately characterized by a tensor product

$$\rho(t) \approx \rho_S(t) \otimes \rho_B. \qquad (3.115)$$

We emphasize that this does not imply that there are no excitations in the reservoir caused by the reduced system. The Markovian approximation to be derived below provides a description on a coarse-grained time scale and the assumption is that environmental excitations decay over times which are not resolved. Inserting the tensor product into the exact equation of motion (3.113) we obtain a closed integro-differential equation for the reduced density matrix $\rho_S(t)$

$$\frac{d}{dt}\rho_S(t) = - \int_0^t ds \operatorname{tr}_B [H_I(t), [H_I(s), \rho_S(s) \otimes \rho_B]]. \qquad (3.116)$$

In order to simplify the above equation further we perform the *Markov approximation*, in which the integrand $\rho_S(s)$ is first replaced by $\rho_S(t)$. In this way we obtain an equation of motion for the reduced system's density matrix in which

the time development of the state of the system at time t only depends on the present state $\rho_S(t)$,

$$\frac{d}{dt}\rho_S(t) = -\int_0^t ds \mathrm{tr}_B\left[H_I(t),[H_I(s),\rho_S(t)\otimes\rho_B]\right].\qquad(3.117)$$

This equation is called the Redfield equation (Redfield, 1957; Blum, 1981).

The Redfield equation is local in time, but it is not yet a Markovian master equation since the time evolution of the reduced density matrix still depends upon an explicit choice for the initial preparation at time $t = 0$. This implies that the dynamics of the reduced system is not yet described by a dynamical semigroup. In order to achieve this we substitute s by $t - s$ in the integral in eqn (3.117) and let the upper limit of the integral go to infinity. This is permissible provided the integrand disappears sufficiently fast for $s \gg \tau_B$. The Markov approximation is therefore justified if the time scale τ_R over which the state of the system varies appreciably is large compared to the time scale τ_B over which the reservoir correlation functions decay. Thus, we finally obtain the Markovian quantum master equation

$$\frac{d}{dt}\rho_S(t) = -\int_0^\infty ds \mathrm{tr}_B\left[H_I(t),[H_I(t-s),\rho_S(t)\otimes\rho_B]\right].\qquad(3.118)$$

It is important to realize that in a description of the reduced system dynamics on the basis of a Markovian quantum master equation the dynamical behaviour over times of the order of magnitude of the correlation time τ_B is not resolved. As mentioned before, the evolution is described in this sense on a coarse-grained time axis.

The approximations performed above are usually termed the *Born–Markov approximation*. In general they do not guarantee, however, that the resulting equation (3.118) defines the generator of a dynamical semigroup (Davies, 1974: Dümcke and Spohn, 1979). One therefore performs a further secular approximation which involves an averaging over the rapidly oscillating terms in the master equation and is known as the rotating wave approximation. To explain the procedure let us write the Schrödinger picture interaction Hamiltonian H_I in the form

$$H_I = \sum_\alpha A_\alpha \otimes B_\alpha,\qquad(3.119)$$

where $A_\alpha^\dagger = A_\alpha$ and $B_\alpha^\dagger = B_\alpha$. This is the most general form of the interaction. The secular approximation is easily carried out if one decomposes the interaction Hamiltonian H_I into eigenoperators of the system Hamiltonian H_S. Supposing the spectrum of H_S to be discrete this may be achieved as follows. Let us denote

the eigenvalues of H_S by ε and the projection onto the eigenspace belonging to the eigenvalue ε by $\Pi(\varepsilon)$. Then we can define the operators

$$A_\alpha(\omega) \equiv \sum_{\varepsilon' - \varepsilon = \omega} \Pi(\varepsilon) A_\alpha \Pi(\varepsilon'). \tag{3.120}$$

The sum in this expression is extended over all energy eigenvalues ε' and ε of H_S with a fixed energy difference of ω. An immediate consequence of this definition is that the following relations are satisfied,

$$[H_S, A_\alpha(\omega)] = -\omega A_\alpha(\omega), \tag{3.121}$$

$$[H_S, A_\alpha^\dagger(\omega)] = +\omega A_\alpha^\dagger(\omega). \tag{3.122}$$

The operators $A_\alpha(\omega)$ and $A_\alpha^\dagger(\omega)$ are therefore said to be eigenoperators of H_S belonging to the frequencies $\pm\omega$, respectively. It follows from relations (3.121) and (3.122) that the corresponding interaction picture operators take the form

$$e^{iH_S t} A_\alpha(\omega) e^{-iH_S t} = e^{-i\omega t} A_\alpha(\omega), \tag{3.123}$$

$$e^{iH_S t} A_\alpha^\dagger(\omega) e^{-iH_S t} = e^{+i\omega t} A_\alpha^\dagger(\omega). \tag{3.124}$$

Finally, we note that

$$[H_S, A_\alpha^\dagger(\omega) A_\beta(\omega)] = 0, \tag{3.125}$$

and

$$A_\alpha^\dagger(\omega) = A_\alpha(-\omega). \tag{3.126}$$

Summing (3.120) over all energy differences and employing the completeness relation we get

$$\sum_\omega A_\alpha(\omega) = \sum_\omega A_\alpha^\dagger(\omega) = A_\alpha. \tag{3.127}$$

This enables us to cast the interaction Hamiltonian into the following form

$$H_I = \sum_{\alpha,\omega} A_\alpha(\omega) \otimes B_\alpha = \sum_{\alpha,\omega} A_\alpha^\dagger(\omega) \otimes B_\alpha^\dagger. \tag{3.128}$$

This is the desired decomposition of the interaction into eigenoperators of the system Hamiltonian. Note that the frequency spectrum $\{\omega\}$ is, in general, degenerate: For a fixed ω the index α labels the different operators $A_\alpha(\omega)$ belonging to the same frequency. A specific example will be encountered in Section 3.4, where α labels the Cartesian components of the dipole operator.

The reason for introducing the eigenoperator decomposition (3.128) is that the interaction picture interaction Hamiltonian can now be written in the particularly simple form

$$H_I(t) = \sum_{\alpha,\omega} e^{-i\omega t} A_\alpha(\omega) \otimes B_\alpha(t) = \sum_{\alpha,\omega} e^{+i\omega t} A_\alpha^\dagger(\omega) \otimes B_\alpha^\dagger(t), \qquad (3.129)$$

where

$$B_\alpha(t) = e^{iH_B t} B_\alpha e^{-iH_B t} \qquad (3.130)$$

are interaction picture operators of the environment. We also note that condition (3.114) becomes

$$\langle B_\alpha(t) \rangle \equiv \mathrm{tr}\{B_\alpha(t)\rho_B\} = 0, \qquad (3.131)$$

which states that the reservoir averages of the $B_\alpha(t)$ vanish.

Inserting now the form (3.129) into the master equation (3.118) we obtain after some algebra

$$\frac{d}{dt}\rho_S(t) = \int_0^\infty ds \, \mathrm{tr}_B \left\{ H_I(t-s)\rho_S(t)\rho_B H_I(t) - H_I(t)H_I(t-s)\rho_S(t)\rho_B \right\} + \mathrm{h.c.}$$

$$= \sum_{\omega,\omega'} \sum_{\alpha,\beta} e^{i(\omega'-\omega)t} \Gamma_{\alpha\beta}(\omega) \left(A_\beta(\omega)\rho_S(t)A_\alpha^\dagger(\omega') - A_\alpha^\dagger(\omega')A_\beta(\omega)\rho_S(t) \right)$$

$$+\mathrm{h.c.} \qquad (3.132)$$

Here h.c. means the Hermitian conjugated expression and we have introduced the one-sided Fourier transforms

$$\Gamma_{\alpha\beta}(\omega) \equiv \int_0^\infty ds \, e^{i\omega s} \langle B_\alpha^\dagger(t) B_\beta(t-s) \rangle \qquad (3.133)$$

of the *reservoir correlation functions*

$$\langle B_\alpha^\dagger(t) B_\beta(t-s) \rangle \equiv \mathrm{tr}_B \left\{ B_\alpha^\dagger(t) B_\beta(t-s)\rho_B \right\}. \qquad (3.134)$$

Let us suppose that ρ_B is a stationary state of the reservoir, that is $[H_B, \rho_B] = 0$. The reservoir correlation functions are then homogeneous in time which yields

$$\langle B_\alpha^\dagger(t) B_\beta(t-s) \rangle = \langle B_\alpha^\dagger(s) B_\beta(0) \rangle, \qquad (3.135)$$

showing that the quantities $\Gamma_{\alpha\beta}(\omega)$ do not depend on time. We remark that there are interesting cases in which the reservoir correlation functions do depend on the time argument t. This happens, for example, if the reservoir represents a squeezed vacuum state (see Section 3.4.3).

As mentioned before, the basic condition underlying the Markov approximation is that the reservoir correlation functions (3.135) decay sufficiently fast over a time τ_B which is small compared to the relaxation time τ_R. Typical examples for the behaviour of these correlation functions will be discussed in Sections 3.6.2.1 and 12.1.1.3. It is important to note that a decay of the correlations can only be strictly valid for an environment which is infinitely large and involves a continuum of frequencies. In the typical situation the reservoir is provided by a collection of harmonic oscillator modes b_n with frequencies ω_n and the B_α are given by linear combinations of the modes b_n. If the frequency spectrum $\{\omega_n\}$ of the reservoir modes is discrete, it is easy to see that, in general, correlation functions of the type (3.135) are quasi-periodic functions of s. A rapid decay of the reservoir correlations therefore requires a continuum of frequencies: For an infinitely small frequency spacing Poincaré recurrence times become infinite and irreversible dynamics can emerge.

We denote by τ_S the typical time scale of the intrinsic evolution of the system S. This time scale τ_S is defined by a typical value for $|\omega' - \omega|^{-1}$, $\omega' \neq \omega$, that is by a typical value for the inverse of the frequency differences involved. If τ_S is large compared to the relaxation time τ_R of the open system the non-secular terms in (3.132), i.e. the terms for which $\omega' \neq \omega$, may be neglected, since they oscillate very rapidly during the time τ_R over which ρ_S varies appreciably. This condition is typically satisfied for quantum optical systems where it is known as the rotating wave approximation. Thus we have

$$\frac{d}{dt}\rho_S(t) = \sum_\omega \sum_{\alpha,\beta} \Gamma_{\alpha\beta}(\omega) \left(A_\beta(\omega)\rho_S(t)A_\alpha^\dagger(\omega) - A_\alpha^\dagger(\omega)A_\beta(\omega)\rho_S(t)\right) + \text{h.c.}$$

$$(3.136)$$

It is convenient to decompose the Fourier transforms of the reservoir correlation functions as follows

$$\Gamma_{\alpha\beta}(\omega) = \frac{1}{2}\gamma_{\alpha\beta}(\omega) + iS_{\alpha\beta}(\omega),$$

$$(3.137)$$

where for fixed ω the coefficients

$$S_{\alpha\beta}(\omega) = \frac{1}{2i}\left(\Gamma_{\alpha\beta}(\omega) - \Gamma_{\beta\alpha}^*(\omega)\right)$$

$$(3.138)$$

form a Hermitian matrix and the matrix defined by

$$\gamma_{\alpha\beta}(\omega) = \Gamma_{\alpha\beta}(\omega) + \Gamma_{\beta\alpha}^*(\omega) = \int_{-\infty}^{+\infty} ds\, e^{i\omega s}\langle B_\alpha^\dagger(s)B_\beta(0)\rangle$$

$$(3.139)$$

is positive (see below). With these definitions we finally arrive at the interaction picture master equation

$$\frac{d}{dt}\rho_S(t) = -i\left[H_{LS}, \rho_S(t)\right] + \mathcal{D}(\rho_S(t)).\tag{3.140}$$

The Hermitian operator

$$H_{LS} = \sum_{\omega}\sum_{\alpha,\beta} S_{\alpha\beta}(\omega) A_\alpha^\dagger(\omega) A_\beta(\omega)\tag{3.141}$$

provides a Hamiltonian contribution to the dynamics. This term is often called the *Lamb shift* Hamiltonian since it leads to a Lamb-type renormalization of the unperturbed energy levels induced by the system–reservoir coupling. Note that the Lamb shift Hamiltonian commutes with the unperturbed system Hamiltonian,

$$[H_S, H_{LS}] = 0,\tag{3.142}$$

by virtue of eqn (3.125). Finally, the dissipator of the master equation takes the form

$$\mathcal{D}(\rho_S) = \sum_{\omega}\sum_{\alpha,\beta} \gamma_{\alpha\beta}(\omega)\left(A_\beta(\omega)\rho_S A_\alpha^\dagger(\omega) - \frac{1}{2}\left\{A_\alpha^\dagger(\omega)A_\beta(\omega), \rho_S\right\}\right).\tag{3.143}$$

We note that the master equation (3.140) is of the first standard form (3.63). It can be brought into Lindblad form (3.66) by diagonalization of the matrices $\gamma_{\alpha\beta}(\omega)$ defined in eqn (3.139). In order to prove that these matrices are positive one uses Bochner's theorem according to which the Fourier transform of a function $f(s)$ is positive provided $f(s)$ has the property of being of positive type. The latter property means that for arbitrary $t_1, t_2, \ldots, t_n$ and all n the $(n \times n)$ matrix $a_{kl} = f(t_k - t_l)$ must be positive. Since all homogeneous correlation functions $f(s) = \langle B^\dagger(s)B(0)\rangle$ are of positive type the positivity of the matrices $\gamma_{\alpha\beta}(\omega)$ follows immediately. Finally, we remark that the Schrödinger picture master equation is obtained from (3.140) simply by adding the free system Hamiltonian H_S to H_{LS}, as is easily verified with the help of the properties (3.121), (3.122) and (3.125) of the eigenoperators.

Let us summarize the different approximations used in the above derivation. The first approximation is a consequence of the weak-coupling assumption which allows us to expand the exact equation of motion for the density matrix to second order. Together with the condition $\rho(t) \approx \rho_S(t) \otimes \rho_B$ this leads to the Born approximation to the master equation. The second approximation is the Markov approximation in which the quantum master equation is made local in time by replacing the density matrix $\rho_S(s)$ at the retarded time s with that at the present time $\rho_S(t)$. Furthermore, the integration limit is pushed to infinity to get the Born–Markov approximation of the master equation. The relevant physical condition for the Born–Markov approximation is that the bath correlation time τ_B is small compared to the relaxation time of the system, that is $\tau_B \ll \tau_R$. Finally, in the rotating wave approximation rapidly oscillating terms

proportional to $\exp[i(\omega' - \omega)t]$ for $\omega' \neq \omega$ are neglected, ensuring that the quantum master equation is in Lindblad form. The corresponding condition is that the inverse frequency differences involved in the problem are small compared to the relaxation time of the system, that is $\tau_S \sim |\omega' - \omega|^{-1} \ll \tau_R$.

3.3.2 Relaxation to equilibrium

In the previous section we have assumed that the environment is in a stationary state ρ_B which is invariant with respect to the dynamics of the reservoir. Now we want to consider a situation in which the environment is a heat bath at the inverse temperature β. In the absence of external time-dependent fields one expects the Gibbs state

$$\rho_{\text{th}} = \frac{\exp(-\beta H_S)}{\text{tr}_S \exp(-\beta H_S)} \tag{3.144}$$

to be a stationary solution of the quantum master equation (3.140). It can be shown then that for any initial state the system returns to equilibrium,

$$\rho_S(t) \longrightarrow \rho_{\text{th}}, \quad \text{for} \quad t \longrightarrow +\infty, \tag{3.145}$$

provided the quantum dynamical semigroup has the property of being ergodic. This means that the relations

$$[X, A_\alpha^\dagger(\omega)] = [X, A_\alpha(\omega)] = 0 \quad \text{for all} \quad \alpha, \omega \tag{3.146}$$

imply that X is proportional to the identity.

In order to show that (3.144) is indeed a stationary solution of the master equation (3.140) we make use of the KMS condition according to which the bath correlation functions are related through

$$\langle B_\alpha^\dagger(t) B_\beta(0) \rangle = \langle B_\beta(0) B_\alpha^\dagger(t + i\beta) \rangle. \tag{3.147}$$

The KMS condition can easily be verified if the reservoir is a heat bath with canonical equilibrium distribution

$$\rho_B = \frac{\exp(-\beta H_B)}{\text{tr}_B \exp(-\beta H_B)}. \tag{3.148}$$

It can also be shown to hold for thermal equilibrium systems in the thermodynamic limit. Equation (3.147) leads to the following relations between the Fourier transforms (3.139) of the bath correlation functions,

$$\gamma_{\alpha\beta}(-\omega) = \exp(-\beta\omega)\gamma_{\beta\alpha}(\omega). \tag{3.149}$$

We further have by virtue of eqns (3.121) and (3.122),

$$\rho_{\text{th}} A_\alpha(\omega) = e^{\beta\omega} A_\alpha(\omega)\rho_{\text{th}}, \tag{3.150}$$

$$\rho_{\text{th}} A_\alpha^\dagger(\omega) = e^{-\beta\omega} A_\alpha^\dagger(\omega)\rho_{\text{th}}. \tag{3.151}$$

The proof of the stationarity of ρ_{th} is now easily carried out with the help of the relations (3.142), (3.149), (3.150) and (3.151).

We mention a further important property of the quantum master equation (3.140). Namely, if the spectrum of the system Hamiltonian $H_S = \sum_n \varepsilon_n |n\rangle\langle n|$ is non-degenerate it gives rise to a closed equation of motion for the populations

$$P(n,t) = \langle n|\rho_S(t)|n\rangle \tag{3.152}$$

of the eigenstates $|n\rangle$. Thus, the equation for the diagonals of the density matrix in the eigenbasis of H_S decouples from the off-diagonal elements. As is easily checked using the quantum master equation the populations are governed by the equation

$$\frac{d}{dt}P(n,t) = \sum_m [W(n|m)P(m,t) - W(m|n)P(n,t)]. \tag{3.153}$$

This equation is of the form of the classical discrete master equation (1.89) with time-independent transition rates given by

$$W(n|m) = \sum_{\alpha,\beta} \gamma_{\alpha\beta}(\varepsilon_m - \varepsilon_n)\langle m|A_\alpha|n\rangle\langle n|A_\beta|m\rangle. \tag{3.154}$$

Equation (3.153) is also known as the Pauli master equation. The rates (3.154) are real and non-negative as a consequence of the positivity of the matrices $\gamma_{\alpha\beta}(\omega)$. They are just those obtained with the help of Fermi's golden rule.

The relations (3.149) give

$$W(m|n)\exp(-\beta\varepsilon_n) = W(n|m)\exp(-\beta\varepsilon_m) \tag{3.155}$$

which is known as the condition of detailed balance and which leads to the conclusion that the equilibrium populations $P_s(n)$ follow the Boltzmann distribution

$$P_s(n) = \text{const} \times \exp(-\beta\varepsilon_n) \tag{3.156}$$

over the energy eigenvalues ε_n.

3.3.3 Singular-coupling limit

In the weak-coupling limit the perturbation caused by the interaction between the system and the environment is assumed to be small. As a result the degrees of freedom of the environment are the fast variable and can be effectively eliminated. With an appropriate scaling of the time parameter it is possible to derive under certain conditions a linear quantum master equation also for the case of strong coupling. In this so-called singular-coupling limit one considers a total Hamiltonian of the form

$$H = H_S + \varepsilon^{-2}H_B + \varepsilon^{-1}H_I, \tag{3.157}$$

where the interaction Hamiltonian is again written as

$$H_I = \sum_\alpha A_\alpha \otimes B_\alpha \tag{3.158}$$

with $A_\alpha^\dagger = A_\alpha$ and $B_\alpha^\dagger = B_\alpha$. The aim is to derive an equation of motion for the reduced density matrix in the limit $\epsilon \to 0$. To motivate the form of the