9

PROJECTION OPERATOR TECHNIQUES

As discussed in Chapter 3 the laws describing the dynamics of open quantum systems can be derived from the unitary dynamics of the total system. In general, the reduction of the degrees of freedom in the effective description of the open system results in non-Markovian behaviour. It is the aim of this part to introduce the reader to some powerful techniques which allow a systematic description of the non-Markovian features of the dynamics of open systems.

A general framework to derive exact equations of motion for an open system is provided by projection operator techniques. These techniques were introduced by Nakajima (1958) and Zwanzig (1960) and independently by the Brussels school (Prigogine, 1962). They are widely used in non-equilibrium statistical mechanics (Haake, 1973; Balescu, 1975; Grabert, 1982; Kubo, Toda and Hashitsume, 1985).

The basic idea underlying the application of projection operator techniques to open quantum systems is to regard the operation of tracing over the environment as a formal projection $\rho \mapsto \mathcal{P}\rho$ in the state space of the total system. The superoperator $\mathcal{P}$ has the property of a projection operator, that is $\mathcal{P}^2 = \mathcal{P}$, and the density matrix $\mathcal{P}\rho$ is said to be the *relevant* part of the density ρ of the total system. Correspondingly, one defines a projection $\rho \mapsto \mathcal{Q}\rho$ onto the *irrelevant* part $\mathcal{Q}\rho$, where $\mathcal{P} + \mathcal{Q}$ is equal to the identity map. The aim is then to derive a closed equation of motion for the relevant part $\mathcal{P}\rho$.

We are going to discuss in this chapter two variants of projection operator techniques, the Nakajima–Zwanzig and the time-convolutionless technique. Both methods lead to an exact equation of motion for the relevant part $\mathcal{P}\rho$. In the case of the Nakajima–Zwanzig method this is an integro-differential equation involving a retarded time integration over the history of the reduced system, while the time-convolutionless equation of motion provides a first-order differential equation which is local in time.

The time-convolutionless projection operator technique leads to a time-local expansion of the equation of motion with respect to the strength of the system–environment coupling. It thus supports an investigation of non-Markovian effects beyond the Born approximation. To each order in the coupling the equation of motion involves a time-dependent but local generator. The rules for the perturbation expansion of the convolutionless generator will be developed. We are mainly concerned in this chapter with the derivation of the most important general results; specific physical applications will be studied in the next chapter.

9.1 The Nakajima–Zwanzig projection operator technique

We consider the general physical situation of an open system S coupled to an environment B. The dynamics of the density matrix $\rho(t)$ of the combined system is specified by some microscopic Hamiltonian of the form

$$H = H_0 + \alpha H_I, \tag{9.1}$$

where H_0 generates the uncoupled time evolution of the system and environment. H_I describes their interaction, and α denotes a dimensionless expansion parameter. When working in the interaction representation, the equation of motion for the density matrix reads

$$\frac{\partial}{\partial t}\rho(t) = -i\alpha[H_I(t), \rho(t)] \equiv \alpha\mathcal{L}(t)\rho(t), \tag{9.2}$$

where we have set $\hbar = 1$ and the interaction picture representation of the interaction Hamiltonian is defined by

$$H_I(t) = \exp(iH_0t)H_I \exp(-iH_0t). \tag{9.3}$$

The Liouville super-operator is denoted by $\mathcal{L}(t)$.

9.1.1 *Projection operators*

In order to derive an exact equation of motion for the reduced density matrix ρ_S of the open system it is convenient to define a super-operator $\mathcal{P}$ according to

$$\rho \mapsto \mathcal{P}\rho = \mathrm{tr}_B\{\rho\} \otimes \rho_B \equiv \rho_S \otimes \rho_B, \tag{9.4}$$

where ρ_B is some fixed state of the environment. This super-operator projects on the relevant part of the density matrix ρ in the sense that $\mathcal{P}\rho$ gives the complete information required to reconstruct the reduced density matrix ρ_S of the open system. Accordingly, a complementary super-operator $\mathcal{Q}$,

$$\mathcal{Q}\rho = \rho - \mathcal{P}\rho, \tag{9.5}$$

may be introduced, which projects on the irrelevant part of the density matrix. The super-operators $\mathcal{P}$ and $\mathcal{Q}$ are maps in the state space of the combined system. that is in the space of density matrices of the total Hilbert space $\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B$. They have the obvious properties

$$\mathcal{P} + \mathcal{Q} = I, \tag{9.6}$$

$$\mathcal{P}^2 = \mathcal{P}, \tag{9.7}$$

$$\mathcal{Q}^2 = \mathcal{Q}, \tag{9.8}$$

$$\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0, \tag{9.9}$$

which can be easily checked using the definitions (9.4) and (9.5) and assuming ρ_B to be normalized, $\mathrm{tr}_B\rho_B = 1$.

The density matrix ρ_B used in definition (9.4) is an operator in $\mathcal{H}_B$. It may represent a quite arbitrary, but known environmental state, called the reference state. The choice of ρ_B strongly depends on the specific application one has in mind. In the following we shall suppose this state to be time independent. Typically, it is taken to be the stationary Gibbs state of the environment. In many cases it may also be assumed that the odd moments of the interaction Hamiltonian with respect to the reference state vanish

$$\mathrm{tr}_B \{H_I(t_1)H_I(t_2)\dots H_I(t_{2n+1})\rho_B\} = 0, \tag{9.10}$$

which leads to the relation

$$\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_2)\dots\mathcal{L}(t_{2n+1})\mathcal{P} = 0 \tag{9.11}$$

for $n = 0, 1, 2, \dots$. This technical assumption is not required for the derivation of the equation of motion. It will however be used later on in order to simplify the expressions of the perturbation expansion. It is important to remark that we do not demand any particular form for the initial conditions at this point. In particular we do not assume factorizing initial conditions.

9.1.2 *The Nakajima–Zwanzig equation*

Our aim is now to derive a closed equation for the relevant part $\mathcal{P}\rho(t)$, i.e. for the density matrix $\rho_S(t) = \mathrm{tr}_B\rho(t)$ of the open system. By applying the projection operators $\mathcal{P}$ and $\mathcal{Q}$ to the Liouville–von Neumann equation (9.2) and by invoking the time independence of the reference state the following set of coupled differential equations for the relevant and the irrelevant part of the density matrix is obtained,

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \mathcal{P}\frac{\partial}{\partial t}\rho(t) = \alpha\mathcal{P}\mathcal{L}(t)\rho(t), \tag{9.12}$$

$$\frac{\partial}{\partial t}\mathcal{Q}\rho(t) = \mathcal{Q}\frac{\partial}{\partial t}\rho(t) = \alpha\mathcal{Q}\mathcal{L}(t)\rho(t). \tag{9.13}$$

On inserting the identity $I = \mathcal{P} + \mathcal{Q}$ between the Liouville operator and the density matrix ρ this may also be written as

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \alpha\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) + \alpha\mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho(t), \tag{9.14}$$

$$\frac{\partial}{\partial t}\mathcal{Q}\rho(t) = \alpha\mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho(t) + \alpha\mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho(t). \tag{9.15}$$

To get a closed equation for the relevant part of the density matrix we solve eqn (9.15) and insert the solution into eqn (9.14). The formal solution of eqn (9.15) corresponding to a given $\rho(t_0)$ at some initial time t_0 may be expressed as

$$\mathcal{Q}\rho(t) = \mathcal{G}(t, t_0)\mathcal{Q}\rho(t_0) + \alpha\int_{t_0}^{t} ds\, \mathcal{G}(t, s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho(s), \tag{9.16}$$

where we have introduced the propagator

$$\mathcal{G}(t,s) \equiv \mathrm{T}_{\leftarrow} \exp\left[\alpha \int_s^t ds' \mathcal{Q}\mathcal{L}(s')\right]. \tag{9.17}$$

As usual, the operator $\mathrm{T}_{\leftarrow}$ describes the chronological time ordering: It orders any product of super-operators such that the time arguments increase from right to left. The propagator $\mathcal{G}(t,s)$ thus satisfies the differential equation

$$\frac{\partial}{\partial t}\mathcal{G}(t,s) = \alpha \mathcal{Q}\mathcal{L}(t)\mathcal{G}(t,s) \tag{9.18}$$

with the initial condition

$$\mathcal{G}(s,s) = I. \tag{9.19}$$

Inserting the expression (9.16) for the irrelevant part of the density matrix into the equation of motion (9.14) for the relevant part we obtain the desired exact equation for the time evolution of the relevant part of the density matrix.

$$\begin{aligned}\frac{\partial}{\partial t}\mathcal{P}\rho(t) = {} & \alpha \mathcal{P}\mathcal{L}(t)\mathcal{G}(t,t_0)\mathcal{Q}\rho(t_0) + \alpha \mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) \\ & + \alpha^2 \int_{t_0}^t ds \mathcal{P}\mathcal{L}(t)\mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho(s).\end{aligned} \tag{9.20}$$

This equation is known as the Nakajima–Zwanzig equation. It is an exact equation for the relevant degrees of freedom of the reduced system. The right-hand side involves an inhomogeneous term $\mathcal{P}\mathcal{L}(t)\mathcal{G}(t,t_0)\mathcal{Q}\rho(t_0)$ depending on the initial condition at time t_0, and an integral over the past history of the system in the time interval $[t_0,t]$. It thus describes completely non-Markovian memory effects of the reduced dynamics. If condition (9.11) is satisfied for $n = 0$, the second term in the Nakajima–Zwanzig equation vanishes and we may cast it into the compact form

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \int_{t_0}^t ds\, \mathcal{K}(t,s)\mathcal{P}\rho(s) + \alpha \mathcal{P}\mathcal{L}(t)\mathcal{G}(t,t_0)\mathcal{Q}\rho(t_0). \tag{9.21}$$

The convolution or memory kernel

$$\mathcal{K}(t,s) = \alpha^2 \mathcal{P}\mathcal{L}(t)\mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P} \tag{9.22}$$

represents a super-operator in the relevant subspace.

The integro-differential equation (9.21) is exact and holds for all initial conditions and for almost arbitrary systems and interactions. Unfortunately, the

Nakajima–Zwanzig equation is usually as difficult to solve as the Liouville equation describing the dynamics of the total system. This means that perturbation expansions are needed in order to discuss the relevant dynamics in a way accessible to analytical or numerical computations. Obviously, the equation may be expanded in the coupling constant α, i.e. in powers of the interaction Hamiltonian H_{I}. Alternatively, it may be expanded around t in powers of the memory time, i.e. in the width of the kernel $\mathcal{K}(t,s)$, where, of course, for $\mathcal{K}(t,s) \approx \delta(t-s)$ in the absence of memory effects we obtain the Markovian description. Sometimes it might also be convenient to perform the perturbation expansion for the Laplace transform of $\rho_{\mathrm{S}}(t)$ in the Schrödinger picture.

For a factorizing initial condition $\rho(t_0) = \rho_S(t_0) \otimes \rho_B$ we have $\mathcal{P}\rho(t_0) = \rho(t_0)$ and, therefore, $\mathcal{Q}\rho(t_0) = 0$. Hence the inhomogeneous term of the Nakajima–Zwanzig equation (9.21) vanishes and the exact equation for the relevant part of the density matrix reduces to

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \int_{t_0}^{t} ds \mathcal{K}(t,s)\mathcal{P}\rho(s). \tag{9.23}$$

To second order in the coupling strength α we obtain

$$\mathcal{K}(t,s) = \alpha^2 \mathcal{P}\mathcal{L}(t)\mathcal{Q}\mathcal{L}(s)\mathcal{P} + \mathcal{O}(\alpha^3), \tag{9.24}$$

which leads to an equation of motion of second order for $\mathcal{P}\rho(t)$

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \alpha^2 \int_{t_0}^{t} ds \mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho(s), \tag{9.25}$$

where we again made use of $\mathcal{P}\mathcal{L}(t)\mathcal{P} = 0$. If we now introduce the explicit expressions for the projection operator $\mathcal{P}$ and for the generator $\mathcal{L}(t)$ we get the Born approximation of the master equation

$$\frac{\partial}{\partial t}\rho_S(t) = -\alpha^2 \int_{t_0}^{t} ds \, \mathrm{tr}_B[H_I(t), [H_I(s), \rho_S(s) \otimes \rho_B]], \tag{9.26}$$

which we already met in eqn (3.116).

This approach to the non-Markovian dynamics of open quantum systems has some practical disadvantages. The perturbative approximation of the memory kernel simplifies the derivation of the equations of motion, but unfortunately not their structure. The approximate equation of motion is again an integro-differential equation, whose numerical solution may be quite involved.

9.2 The time-convolutionless projection operator method

In practice the time convolution in the memory kernel of the Nakajima–Zwanzig equation is difficult to treat. In this section we show how to remove the time

convolution in the master equation. This is achieved through a method which is known as the time-convolutionless projection operator technique. This technique has been developed by Shibata *et al.* (Shibata, Takahashi and Hashitsume, 1977; Chaturvedi and Shibata, 1979; Shibata and Arimitsu, 1980) and we are going to apply it here to the microscopic theory of an open quantum system which is coupled to an environment. The method yields a systematic expansion of the dynamics of the system of interest in terms of the coupling strength. In particular, we will develop expressions for the quantum master equation up to fourth order in the coupling for factorizing and for non-factorizing initial conditions.

9.2.1 *The time-local master equation*

The idea of the time-convolutionless projection operator technique is to eliminate the dependence of the future time evolution on the history of the system from the Nakajima–Zwanzig master equation and thus to derive an exact master equation for the open system which is local in time. In order to achieve this objective we proceed in the following way: The density matrix $\rho(s)$ on the right-hand side of eqn (9.16) is replaced by the expression

$$\rho(s) = G(t,s)(\mathcal{P}+\mathcal{Q})\rho(t), \tag{9.27}$$

where $G(t,s)$ is the backward propagator of the composite system, i.e. the inverse of the unitary time evolution of the total system. Formally, we may write

$$G(t,s) = \mathrm{T}_{\rightarrow} \exp\left[-\alpha \int_s^t ds'\, \mathcal{L}(s')\right], \tag{9.28}$$

where $\mathrm{T}_{\rightarrow}$ indicates the antichronological time-ordering.

With the help of the relation (9.27) the equation (9.16) for the irrelevant part of the density matrix may now be written as

$$\mathcal{Q}\rho(t) = \mathcal{G}(t,t_0)\mathcal{Q}\rho(t_0) + \alpha \int_{t_0}^t ds\, \mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}G(t,s)(\mathcal{P}+\mathcal{Q})\rho(t). \tag{9.29}$$

Introducing the super-operator

$$\Sigma(t) = \alpha \int_{t_0}^t ds\, \mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}G(t,s), \tag{9.30}$$

we can express the irrelevant part of the density matrix through

$$[1-\Sigma(t)]\,\mathcal{Q}\rho(t) = \mathcal{G}(t,t_0)\mathcal{Q}\rho(t_0) + \Sigma(t)\mathcal{P}\rho(t). \tag{9.31}$$

Note that the super-operator $\Sigma(t)$ contains both propagators $\mathcal{G}$ and G, so that it does not specify a well-defined chronological order. $\Sigma(t)$ has the obvious properties $\Sigma(t_0) = 0$ and $\Sigma(t)|_{\alpha=0} = 0$. Hence, $1-\Sigma(t)$ may be inverted for not too large couplings and in any case for small $t - t_0$. Thus, we get

$$\mathcal{Q}\rho(t) = [1 - \Sigma(t)]^{-1}\,\Sigma(t)\mathcal{P}\rho(t) + [1 - \Sigma(t)]^{-1}\,\mathcal{G}(t, t_0)\mathcal{Q}\rho(t_0). \tag{9.32}$$

This equation states that the irrelevant part $\mathcal{Q}\rho(t)$ of the density matrix can in principle be determined from the knowledge of the relevant part $\mathcal{P}\rho(t)$ at time t and from the initial condition $\mathcal{Q}\rho(t_0)$. The dependence on the history of the relevant part which occurs in the Nakajima–Zwanzig equation has thus been removed by the introduction of the exact backward propagator $G(t, s)$. It must be noted, however, that for strong couplings and/or large time intervals $t - t_0$ it may happen that eqn (9.31) cannot be solved uniquely for $\mathcal{Q}\rho(t)$ such that the inverse of $1 - \Sigma(t)$ does not exist. We are going to exemplify this situation in Section 10.1.2.

To complete the derivation of the time-convolutionless master equation, we insert eqn (9.32) into the equation of motion for the relevant part (9.14) and obtain the following exact time-convolutionless (TCL) form of the master equation,

$$\frac{\partial}{\partial t}\mathcal{P}\rho(t) = \mathcal{K}(t)\mathcal{P}\rho(t) + \mathcal{I}(t)\mathcal{Q}\rho(t_0), \tag{9.33}$$

with the time-local generator, called the TCL generator,

$$\mathcal{K}(t) = \alpha\mathcal{P}\mathcal{L}(t)\,[1 - \Sigma(t)]^{-1}\,\mathcal{P}, \tag{9.34}$$

and the inhomogeneity

$$\mathcal{I}(t) = \alpha\mathcal{P}\mathcal{L}(t)\,[1 - \Sigma(t)]^{-1}\,\mathcal{G}(t, t_0)\mathcal{Q}. \tag{9.35}$$

The equation of motion (9.33) is exact and local in time. Although the super-operators $\mathcal{K}(t)$ and $\mathcal{I}(t)$ are, in general, extremely complicated objects, eqn (9.33) can be used as a starting point of a systematic approximation method by expanding $\mathcal{K}(t)$ and $\mathcal{I}(t)$ in powers of the coupling strength α. This will be shown in the following subsections.

9.2.2 *Perturbation expansion of the TCL generator*

Of course, the super-operator $\mathcal{K}(t)$ only exists when it is possible to invert the operator $[1 - \Sigma(t)]$. Let us assume then that $\Sigma(t)$ may be expanded into a geometric series

$$[1 - \Sigma(t)]^{-1} = \sum_{n=0}^{\infty} [\Sigma(t)]^n\,. \tag{9.36}$$

On substituting this into the expression (9.34) one gets

$$\mathcal{K}(t) = \alpha \sum_{n=0}^{\infty} \mathcal{P}\mathcal{L}(t)\,[\Sigma(t)]^n\,\mathcal{P} = \sum_{n=1}^{\infty} \alpha^n \mathcal{K}_n(t). \tag{9.37}$$

To determine the contribution $\mathcal{K}_n(t)$ of n-th order in α to the TCL generator $\mathcal{K}(t)$ we also expand $\Sigma(t)$ in powers of α,

$$\Sigma(t) = \sum_{n=1}^{\infty} \alpha^n \Sigma_n(t), \tag{9.38}$$

insert this into eqn (9.37), and sort equal powers of α. For example, to fourth order in α this gives:

$$\mathcal{K}_1(t) = \mathcal{P}\mathcal{L}(t)\mathcal{P}, \tag{9.39}$$
$$\mathcal{K}_2(t) = \mathcal{P}\mathcal{L}(t)\Sigma_1(t)\mathcal{P}, \tag{9.40}$$
$$\mathcal{K}_3(t) = \mathcal{P}\mathcal{L}(t)\left\{[\Sigma_1(t)]^2 + \Sigma_2(t)\right\}\mathcal{P}, \tag{9.41}$$
$$\mathcal{K}_4(t) = \mathcal{P}\mathcal{L}(t)\left\{[\Sigma_1(t)]^3 + \Sigma_1(t)\Sigma_2(t) + \Sigma_2(t)\Sigma_1(t) + \Sigma_3(t)\right\}\mathcal{P}. \tag{9.42}$$

Finally, the contributions $\Sigma_n(t)$ are found with the help of eqns (9.30) and (9.38) by expanding also the propagators $\mathcal{G}(t,s)$ and $G(t,s)$ defined in eqns (9.17) and (9.28) in powers of α.

Let us determine more explicitly the first four terms of the expansion. To simplify the expressions we use condition (9.11) and take $t_0 = 0$. Equation (9.39) immediately gives

$$\mathcal{K}_1(t) = \mathcal{P}\mathcal{L}(t)\mathcal{P} = 0. \tag{9.43}$$

The first-order term $\Sigma_1(t)$ is given by

$$\Sigma_1(t) = \int_0^t dt_1\, \mathcal{Q}\mathcal{L}(t_1)\mathcal{P}, \tag{9.44}$$

which yields

$$\mathcal{K}_2(t) = \int_0^t dt_1 \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)\mathcal{P}. \tag{9.45}$$

The second-order term $\Sigma_2(t)$ is found to be

$$\Sigma_2(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \left[\mathcal{Q}\mathcal{L}(t_1)\mathcal{Q}\mathcal{L}(t_2)\mathcal{P} - \mathcal{Q}\mathcal{L}(t_2)\mathcal{P}\mathcal{L}(t_1)\right]. \tag{9.46}$$

Since $\mathcal{P}\mathcal{Q} = 0$ we conclude from eqn (9.44) that $[\Sigma_1(t)]^2 = 0$ and, therefore,

$$\mathcal{K}_3(t) = \mathcal{P}\mathcal{L}(t)\Sigma_2(t)\mathcal{P} = \int_0^t dt_1 \int_0^{t_1} dt_2 \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)\mathcal{L}(t_2)\mathcal{P} = 0, \tag{9.47}$$

where we made use of condition (9.11) for $n = 0$ and $n = 1$. To find $\mathcal{K}_4(t)$ we first note that $[\Sigma_1(t)]^3 = \Sigma_1(t)\Sigma_2(t) = 0$ because of $\mathcal{PQ} = 0$. Thus we have from eqn (9.42)

$$\mathcal{K}_4(t) = \mathcal{P}\mathcal{L}(t)\left[\Sigma_2(t)\Sigma_1(t) + \Sigma_3(t)\right]\mathcal{P}. \tag{9.48}$$

Invoking eqns (9.44) and (9.46) the first term is found to be

$$\mathcal{P}\mathcal{L}(t)\Sigma_2(t)\Sigma_1(t)\mathcal{P} = -\int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \tag{9.49}$$
$$\times\mathcal{P}\mathcal{L}(t)\left[\mathcal{L}(t_2)\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_3)\mathcal{P} + \mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_2)\mathcal{L}(t_1)\mathcal{P} + \mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_2)\mathcal{P}\right].$$

Note that to get this expression the triple time integral has been brought into time-ordered form, $t \geq t_1 \geq t_2 \geq t_3 \geq 0$. Similarly, one finds

$$\mathcal{P}\mathcal{L}(t)\Sigma_3(t)\mathcal{P} \tag{9.50}$$
$$= \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \mathcal{P}\mathcal{L}(t)\left[\mathcal{L}(t_1)\mathcal{Q}\mathcal{L}(t_2)\mathcal{L}(t_3)\mathcal{P} + \mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_2)\mathcal{L}(t_1)\mathcal{P}\right].$$

Summarizing, the fourth-order contribution to the TCL generator takes the form,

$$\mathcal{K}_4(t) = \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \Big(\mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)\mathcal{L}(t_2)\mathcal{L}(t_3)\mathcal{P} - \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_1)\mathcal{P}\mathcal{L}(t_2)\mathcal{L}(t_3)\mathcal{P}$$
$$-\mathcal{P}\mathcal{L}(t)\mathcal{L}(t_2)\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_3)\mathcal{P} - \mathcal{P}\mathcal{L}(t)\mathcal{L}(t_3)\mathcal{P}\mathcal{L}(t_1)\mathcal{L}(t_2)\mathcal{P}\Big). \tag{9.51}$$

The second-order generator $\mathcal{K}_2(t)$ of the TCL master equation leads to the following equation for the reduced density matrix $\rho_S(t)$,

$$\frac{\partial}{\partial t}\rho_S(t) = -\alpha^2 \int_0^t ds\, \mathrm{tr}_B[H_I(t), [H_I(s), \rho_S(t) \otimes \rho_B]], \tag{9.52}$$

which should be contrasted to the corresponding second-order approximation (9.26) of the Nakajima–Zwanzig equation: Both equations are of second order and it is therefore to be expected that they approximate the exact dynamics with the same accuracy. This point will be illustrated in Section 10.1.2 with the help of a simple example. In practice, the TCL form is to be preferred because it involves a time-local generator instead of a convolution kernel.