

# Chapter 4

## Quantum Master Equations in Electronic Transport

B. Novakovic and I. Knezevic

**Abstract** In this chapter we present several quantum master equations (QMEs) that describe the time evolution of the density matrix at various levels of approximations. We emphasize the similarity between the single-particle QME and the Boltzmann transport equation (BTE), starting from truncating the BBGKY chain of equations and ending with similar Monte-Carlo approaches to solve them stochastically and show what kind of boundary conditions are needed to solve the single-particle QME in the light of the *open nature* of modern electronic devices. The Pauli master equation (PME) and a QME in the perturbation expansion are described and compared both with one another and with the BTE. At the level of the reduced many-particle density matrix, we show several approaches to derive many-particle QMEs starting from the formal Nakajima–Zwanzig equation and ending with the partial-trace-free time-convolutionless equation of motion with memory dressing. Using those results we derive the correct distribution functions of the Landauer-type, for a small, ballistic open system attached to two large reservoirs with ideal black-body absorption characteristics.

**Keywords** Quantum transport · Master equation · Density matrix · Distribution function · Transient

### 1 Introduction

Electronic devices are many-particle objects. Therefore, they must be analyzed within the realm of statistical mechanics, with the goal to describe the time evolution of the full set of degrees of freedom belonging to a particular device.<sup>1</sup> Considering

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<sup>1</sup> This gives an exact solution for the device's dynamical behavior (transient or steady state), but is not always necessary, because suitable approximations may suffice.

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that every particle, an electron, a phonon or another particle of interest, such as an exciton or a plasmon, can be described by several degrees of freedom (classical or quantum), the choice of which depends on the particular problem, and that there might be many particles in a single device, the problem clearly becomes intractable. In reality, one has to apply suitable approximations in order to reduce the problem to the one that is, at least, numerically feasible. This proceeds by choosing the relevant degrees of freedom and reducing the system of equations to describe their evolution, while the rest of the system is included by applying some assumptions about the irrelevant degrees of freedom. By degrees of freedom we mean, for example, the position and momentum of each particle (classically), or quantum numbers that span the Hamiltonian eigenstates (momentum, spin...).

Roughly speaking, each major approximation applied leads to a certain method or class of methods that are standardly used by device physicists and engineers to calculate the device transport properties. One possible classification of methods is done by approximating just how many particles/states in the many-particle problem are considered, so we can speak of a one-body problem (single particle states), two-body problem, and so on... This is commonly done by truncating the BBGKY hierarchy of equations [1, 2], that are able to describe the many-particle problem exactly, with all the mutual interactions between many-particle subsets. Along with the assumption of how the many degrees of freedom per particle are treated exactly we arrive at the kinetic and hydrodynamic models, most commonly in use. Kinetic models are at the level of distribution functions defined on a single-particle phase space, therefore treating one-body problems with interactions exactly, while hydrodynamic models incorporate additional assumptions about the momentum, therefore not treating the momentum exactly [3]. Most often [4–6], we account for interparticle interactions in the single-electron picture through the mean-field approximation (Hartree approximation), by self-consistently solving the Poisson equation along with any single-particle transport equation. Essentially, what we do is to solve the Poisson equation with the nonlinear charge density calculated by using the transport equation. When this system of equations converges, all other quantities of interest (e.g. current) can be calculated separately.

Another criterion we can use to distinguish between different models is whether they are quantum or semiclassical [7], classical being irrelevant in the context of small electronic devices. The simplest quantum model relies on particles populating the eigenstates of the single-particle Hamiltonian, obtained by solving the time-independent Schrödinger equation. This model can account for quantum tunneling, interference effects, sharp potentials and other quantum mechanical features, but is unable to handle the time dynamics of far from equilibrium states in the presence of scattering and coupling to the contacts [3]. More advanced quantum models define mixed states allowing for spatial localization of particles due to their coupling to the surroundings. Among these methods we can mention the single-particle density matrix method where the central equation is the Liouville–von Neumann equation [8], the Wigner function method with the Wigner equation [9] and the non-equilibrium Green's function method with the Dyson equation [10, 11]. Usually, these are all quantum kinetic equations, with the Liouville–von Neumann equation being known as the quantum master equation (QME), since it is an equation of motion for the

density matrix, either a single-particle (quantum kinetic level), or a full/reduced many-particle density matrix. In some situations one can use the single-particle Pauli master equation (PME) [12], which, by its ability to model dissipation of eigenstates, can be situated between the pure Schrödinger equation (eigenstates without dissipation) and the single-particle density matrix method (mixed states with dissipation). The Boltzmann transport equation (BTE) is semiclassical. Its solution is a distribution function in the phase space that, therefore, does not respect the uncertainty relations and represents electrons as point-like particles for the purpose of drift and diffusion, making features like the tunneling, resonances, interference, etc. impossible. On the other hand, electrons are represented by plane waves during collisions, which makes the BTE unable to capture sharp potential changes (of the order of electron's wavelength). The BTE can be formally obtained by truncating the BBGKY chain [13]. Alternatively, it can be obtained from the NEGF method in the strong scattering limit [10].

Today, integrated circuits are made of many small electronic devices connected by leads to large reservoirs that supply them with charged particles (or other kind of matter/information). The natural framework in which modern electronic devices should be studied is the open system formalism, providing the necessary mathematical tools for handling a large number of variables and focusing on the most relevant ones [14, 15]. It requires the use of the reduced many-particle density matrix, that stores the information about the relevant variables after all the others have been traced out (a single-particle density matrix is generally insufficient). Most generally, we can refer to the electronic device in question as *the system*, which contains all the relevant variables, while everything else is *the environment* (e.g. reservoirs spatially separated from the system; other particles, like phonons, that share the same volume as the system). Therefore, the object of research is now a composite system, consisting of two, or more, physically coupled subsystems. The accuracy and the relevancy of our model will depend on what assumptions we apply to the environment.

In Sect. 2 we give an introduction to the exact many-particle density matrix and the corresponding equation for its time evolution, the Liouville–von Neumann equation. Then, we introduce the approximate single particle QME and describe some of its properties in closed and open systems. As examples of single-electron QMEs, two equations are mentioned: the PME, as applied to small electronic devices (open systems) [16, 17], in the Born–Markov limit and Hartree approximation, and the single-electron/many-phonon QME for bulk (closed system) [18–20], in the perturbation expansion and beyond the Born–Markov approximation. Monte Carlo solutions for both equations are described and compared to the conventional ensemble Monte Carlo technique. In Sect. 3 we introduce the reduced many-particle density matrix formalism, by starting from the formal derivation of the Nakajima–Zwanzig equation. In the following various techniques are introduced in order to make the Nakajima–Zwanzig equation more tractable: the Born–Markov approximation, the conventional time-convolutionless equation of motion, the partial-trace-free time-convolutionless equation of motion and the memory-dressing approach. In the final section, we build on the previous section and, by using the coarse-graining procedure and the short-time expansion of the generator of the time evolution, ultimately arrive at the correct steady-state distribution functions of the Landauer type, for the ballistic open quantum system.

## 2 The Single-Particle Quantum Master Equation

The QME is an equation of motion for the density matrix. In the single-particle picture, with off-diagonal elements included, it is a kinetic equation, where diagonal elements provide information about the population of single-particle states, while off-diagonal elements represent coherences between different single-particle states, describing localized particles. The single-particle QME is approximate and can be formally derived by truncating the BBGKY chain of equations, similar to the BTE. It describes the time-irreversible, dissipative time evolution for the single-particle states. In this section, we will discuss the general form of the single-particle QME, as well as two particular equations, starting from the full many-particle density matrix and its equation of motion, the Liouville–von Neumann equation.

### 2.1 The Density Matrix and the Liouville–von Neumann Equation

The density matrix formalism was pioneered by John von Neumann in 1927 [21,22] and is used to describe a mixed ensemble of states of a physical system, where by mixed we have in mind an ensemble that contain at least two, or more, different states of a physical system. Two extremes would be a pure ensemble, where all the states are the same, described by some state ket  $|\alpha\rangle$ , and a completely randomized ensemble, with each one of  $N$  states described by a different state ket  $|\alpha_i\rangle$ , where  $i = 1, \dots, N$ . Here, the state  $|\alpha\rangle$ , or  $|\alpha_i\rangle$ , is, in general, a linear combination of the eigenstates of the Hamiltonian. For a physical system with many particles the most exact density matrix is the one that describes a mixed ensemble of a full set of many-particle states, taking into account all the mutual interactions between the particles in the system. Such a many-particle density matrix at some initial time 0 is defined as

$$\rho_{12\dots N}(0) = \sum_{i=0}^M W_{12\dots N}^{(i)} \left| \Psi_{12\dots N}^{(i)}(0) \right\rangle \left\langle \Psi_{12\dots N}^{(i)}(0) \right|, \quad (4.1)$$

where  $M$  is the maximum number of many-particle states in the ensemble and  $W_{12\dots N}^{(i)}$ 's are real positive numbers, representing the probability of occupation of the many-particle states  $|\Psi_{12\dots N}^{(i)}(0)\rangle$ , which are symmetrized or anti-symmetrized linear combinations of products of a complete set of single-particle states [23]. The density matrix in (4.1) is normalized with the condition  $\text{Tr}(\rho_{12\dots N}(0)) = 1$ . From (4.1) follows that  $\rho$  is also hermitian,  $\rho_{12\dots N}^\dagger(0) = \rho_{12\dots N}(0)$ .

The time-evolution of the states  $|\Psi_{12\dots N}^{(i)}(0)\rangle$  is given by the many-particle time-dependent Schrödinger equation

$$i\hbar \frac{d}{dt} \left| \Psi_{12\dots N}^{(i)}(t) \right\rangle = H_{12\dots N} \left| \Psi_{12\dots N}^{(i)}(t) \right\rangle. \quad (4.2)$$

These states are not necessarily orthogonal. Since states  $|\Psi_{12\dots N}^{(i)}(0)\rangle$  in (4.1) evolve according to (4.2), we have that the many-particle density matrix at some later time  $t$  will be given by

$$\rho_{12\dots N}(t) = \sum_{i=0}^M W_{12\dots N}^{(i)} \left| \Psi_{12\dots N}^{(i)}(t) \right\rangle \left\langle \Psi_{12\dots N}^{(i)}(t) \right|. \quad (4.3)$$

By differentiating (4.3) with respect to time and making use of (4.2) we arrive at the most general form of the Liouville–von Neumann equation, describing the time evolution of the full many-particle density matrix for a closed system

$$i\hbar \frac{d}{dt} \rho_{12\dots N}(t) = [H_{12\dots N}, \rho_{12\dots N}(t)] \equiv \mathcal{L}_{12\dots N} \rho_{12\dots N}, \quad (4.4)$$

where  $\mathcal{L}_{12\dots N}$  is defined as a commutator superoperator generated by the many-particle Hamiltonian  $H_{12\dots N}$ . Because this equation was generated by the Schrödinger equation, it preserves the previously stated properties of the density matrix, namely the normalization and hermiticity. If we use a shorthand notation  $|\Psi_{12\dots N}^{(i)}(t)\rangle \equiv |\alpha_i\rangle$ , the expectation value of an observable  $A$  in a mixed ensemble described by the initial condition (4.1) and by (4.4), is given by

$$\begin{aligned} \langle A \rangle &= \sum_{i=1}^M w_i \langle \alpha_i | A | \alpha_i \rangle = \sum_{i=1}^M w_i \langle \alpha_i | \alpha_i \rangle \langle \alpha_i | A | \alpha_i \rangle \\ &= \sum_{i=1}^M \langle \alpha_i | \rho_{12\dots N} A | \alpha_i \rangle = \text{Tr}(\rho_{12\dots N} A), \end{aligned} \quad (4.5)$$

where we use the fact the many-particle states,  $|\alpha_i\rangle$  are properly normalized.

## 2.2 The BBGKY Chain and the Single-Particle QME

Instead of one exact many-particle Liouville–von Neumann equation (4.4), we can construct  $N$  coupled equations for the reduced density matrices,  $\rho_1, \rho_{12}, \dots, \rho_{12\dots N}$ , that form the BBGKY chain of equations [2]. Similar to the way the BTE, as a single particle equation for the distribution function over a single-particle phase space  $(\mathbf{r}, \mathbf{p})$ , is derived by applying approximations to the BBGKY chain of equations [13], we can derive the single-particle QME for the time evolution of the single-particle density matrix. If we assume that the dissipation processes are sufficiently weak (the weak-coupling or Born approximation) and memoryless or Markovian (one collision is completed before the next one starts, so that collisions do not depend on their history or initial conditions), then we can consider that the transport consists of periods of “free flights” (generalized “free flights” generated by the single particle Hamiltonian) and temporally and spatially very localized

collisions described by a linear collision operator. In this way we can obtain a Boltzmann like QME for the time evolution of the single-particle density matrix  $\rho(t)$  [3]

$$\frac{d\rho}{dt} = \frac{1}{i\hbar}\mathcal{L}\rho + \mathcal{C}\rho, \quad (4.6)$$

where  $\mathcal{C}$  is the collision superoperator, which is usually used to describe electron/phonon or electron/impurity interactions, and  $\mathcal{L}$  is a commutator superoperator (4.4) generated by the single-particle Hamiltonian  $H$ .  $H$ , for noninteracting particles of the same kind (usually we are interested in electrons), is a sum of the kinetic energy operator and the potential energy due to any external potential  $V_{ext}(\mathbf{r})$ , but if we couple the transport equation (4.6) with the Poisson equation it will also include the Hartree potential  $V_H(\mathbf{r})$  (mean-field approximation). So, we have in total

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}). \quad (4.7)$$

Equation (4.6) is a limiting case of a density matrix completely reduced down to the single-particle states, with the additional assumptions about the nature of interactions in the system, stated above. The consequence of this derivation is the introduction of the time-irreversibility into the evolution of the single-particle density matrix  $\rho$  in (4.6), starting from the time-reversible (4.4).

So far we have considered a closed physical system for which  $\mathcal{L}$  in (4.6) is hermitian, i.e. with real eigenvalues. Therefore it will contribute with complex oscillatory solutions for  $\rho$  in (4.6). The collision operator  $\mathcal{C}$  will introduce negative real parts of eigenvalues which will cause an exponential decay of  $\rho$ . Therefore, this time-irreversible system is stable and behaves in an expected way.  $\mathcal{L}$  is hermitian as a consequence of the hermiticity of the single-particle Hamiltonian for a closed system, where the hermiticity is defined through [3, 24]

$$\begin{aligned} \int_V [\psi^*(H\psi) - (H\psi)^*\psi] d^3r &= 0 \\ &= \int_S \left( \psi^* \frac{d\psi}{dn} - \frac{d\psi^*}{dn} \psi \right) d^2r = \int_S \mathbf{J} ds, \end{aligned} \quad (4.8)$$

where Green's identity was used,  $\psi$  is the wavefunction,  $H$  the single-particle Hamiltonian and  $\mathbf{J}$  the current density. We see that, when the number of particles is conserved in the volume  $V$  (closed system), the current density flux given by the last term in (4.8) is zero according to the current continuity equation and  $H$ , as well as  $\mathcal{L}$ , are hermitian.

If, on the other hand, the system is open, so that it exchanges particles with the environment, the number of particles is not conserved in general and both  $H$  and  $\mathcal{L}$  are non-hermitian. Therefore, the eigenvalues of  $\mathcal{L}$  will have imaginary parts and only non-positive imaginary parts are permissible in order to avoid having growing exponentials. To ensure this, it was shown by Frenslley [3] that the boundary conditions have to be carefully chosen. In particular it is necessary to use time-irreversible boundary conditions, which can be easily defined only in phase space.

For example, if we have a 1D problem with two contacts and a region of interest (open system) in between we can choose different boundary conditions at  $(x_L, p_x)$  than at  $(x_R, -p_x)$ , where  $x_L$  and  $x_R$  are the left and right spatial boundaries of our open system. Now, under the time inversion those boundary conditions will apply to  $(x_L, -p_x)$  and  $(x_R, p_x)$ , respectively, and the problem will not be the same anymore. These BCs mean that the occupations of positive and negative propagating states are fixed by the left and right contacts, respectively. Even if we disregard the fact that the time-irreversible BCs are needed to achieve stability, they are a natural choice in the context of the following statement in [3] “if one’s objective is to develop useful models of physical systems with many dynamical variables, rather than to construct a rigorously deductive mathematical system, it is clearly most profitable to adopt the view that irreversibility is a fundamental law of nature.” The BCs of this form are naturally to be used with the Wigner function method. To include this kind of boundary conditions in (4.6) we can formally specify a contribution to the time evolution of the density matrix due to the injection/extraction through the contacts, a source term, the form of which can be determined phenomenologically

$$\frac{d\rho}{dt} = \frac{1}{i\hbar} \mathcal{L}\rho + C\rho + \left( \frac{\partial\rho}{\partial t} \right)_{\text{inj/extr}}. \quad (4.9)$$

### 2.3 The Pauli Master Equation

As already mentioned in Sect. 1, the PME describes the time evolution of the probabilities of occupation of the single-particle Hamiltonian’s eigenstates. With  $p_n(t) \equiv \rho_{nn}(t)$  and for a closed system it is given by

$$\frac{d}{dt} p_n(t) = \sum_m [A_{nm} p_m(t) - A_{mn} p_n(t)]. \quad (4.10)$$

Equation (4.10) is easily justifiable at a phenomenological level, in situations when the exact Hamiltonian is not known, or when it is too complicated [15]. Then, we can always set up a master equation of the previous form, to describe the dissipative transport in the system. Coefficients  $A_{mn}$  represent transition rates between the levels and they can be found in a standard way, by using the quantum mechanical perturbation theory (Fermi’s golden rule), or from experimental data. Alternatively, the PME follows from (4.6) by using Fermi’s golden rule for the collision superoperator and a basis that diagonalizes the single-particle Hamiltonian that generates  $\mathcal{L}$ , since then the term  $\mathcal{L}\rho$  vanishes and there is only the collision operator, which corresponds to the right-hand side of (4.10). So, the PME is a closed equation for the diagonal elements of the single-particle density matrix in the eigenbasis of the single-particle Hamiltonian, obtained from (4.6) by using Fermi’s golden rule to describe scattering. It will be a complete description of the problem in the case the off-diagonal elements in (4.6) can be neglected. We will say more on the conditions to satisfy that requirement in the following.

The simplicity of the PME (4.10) makes it attractive for applications to real problems of quantum transport in electronic devices. However, the major disadvantage of the PME is that it violates the current continuity, as shown by Frensley [3]. The reason for this is that open systems are inhomogeneous, making the eigenstates have different spatial distributions. Mathematically, if we combine the PME and the current continuity equation, with  $\rho(x, x; t)$  being the electron density, we can obtain for the rate of change of the electron density due to transitions between two eigenstates  $\psi_m$  and  $\psi_n$  [3]

$$\begin{aligned} \frac{\partial}{\partial t} \rho(x, x; t) &= \frac{\partial p_m}{\partial t} |\psi_m(x)|^2 + \frac{\partial p_n}{\partial t} |\psi_n(x)|^2 \\ &= [A_{nm} p_m(t) - A_{mn} p_n(t)] \times [|\psi_n(x)|^2 - |\psi_m(x)|^2]. \end{aligned} \quad (4.11)$$

The left-hand side of (4.11) must be zero, because the divergence of an eigenstate's current density is zero. Since the second term on the right-hand side is non-zero, due to different spatial distributions of different eigenstates, we need the first term on the right-hand side to be zero, which is true only in equilibrium when detailed balance is satisfied. The conclusion is that the PME alone (i.e. without considering the off-diagonal terms) may be used at or very near equilibrium and in steady state, when  $\partial p_{m,n}/\partial t = 0$  and therefore  $\partial \rho(x, x; t)/\partial t = 0$ , as it should be because  $\nabla \cdot \mathbf{J}_m = \nabla \cdot \mathbf{J}_n = 0$ .

A good example of using the PME in modeling small electronic devices is the work done by Fischetti [16, 17]. There, the PME application to small devices was justified and the results of steady state simulations with [16] and without [17] the full band structure were compared with those obtained by using the BTE. Set-up is such that contacts to the device as well as phonons and other particles important for scattering belong to the environment, while the device region with electrons is the open system. The justification and conditions for using the PME go as follows:

- As shown by Van Hove [25] and Kohn and Luttinger [26], if one starts from a quasideagonal initial state and in the weak-scattering limit the off-diagonal terms remain negligible. Quasideagonal states satisfy the condition that the off-diagonal terms are nonvanishing only when mixing states with energy difference  $\delta E_{th} \ll \delta E_D$ , where  $\delta E_{th}$  is the thermal broadening of the states and  $\delta E_D$  is the energy scale over which the matrix elements of perturbing interactions are constant.
- If the size of the device is comparable or smaller than the dephasing length of the incoming electrons from the contacts,  $L \ll \lambda_\phi$  ( $\lambda_\phi \approx 30\text{--}50\text{ nm}$  for Si at 300K), then they appear as plane waves, i.e. the density matrix is diagonal in the momentum representation. Assuming the weak-scattering limit in the open system (device), we can say, with respect to the previous statement, that neither are off-diagonal elements injected from the contacts nor do they form in the device region, so that the PME is applicable.
- The PME is unable to model the femtosecond time dynamics, because that is a genuinely off-diagonal problem on time-scales of the order of collision durations and strong-scattering effects beyond Fermi's golden rule. The PME's areas of



applicability are steady state with the weak-scattering and long-time limits and “adiabatic” transients, when the number of particles in the system changes very slowly with time.

The PME with Fermi’s golden rule can only be used to find occupation probabilities governed by scattering in the system, but not due to the coupling to the contacts. Following the work of Fischetti [16, 17] this coupling can be introduced at a phenomenological level through a source term in the PME. The form of that source term for a general multiterminal configuration is given by [17]

$$\left( \frac{\partial \rho_\mu^{(s)}}{\partial t} \right)_{\text{res}} = |C_\mu^{(s)}|^2 v_\perp(\mathbf{k}_{\mu s}) \left[ f^{(s)}(\mathbf{k}_{\mu s}) - \rho_\mu^{(s)} \right], \quad (4.12)$$

where  $s$  indicates the contact/terminal,  $v_\perp$  is the injecting velocity,  $f^{(s)}$  the  $s$ -th contact distribution function,  $\mu$  the full set of quantum numbers describing the eigenstates in the open system/device and  $C_\mu^{(s)}$  takes care of the proper normalization of the states. Additional assumption is that the injecting distributions are given by the drifted Fermi–Dirac distribution  $f^{(s)}(\mathbf{k}_\mu^{(s)} - \mathbf{k}_d^s)$ , where  $\mathbf{k}_d^s$  is calculated from the semiclassical current in the contact  $s$ . This takes into account the fast relaxation in the contacts and ensures the charge neutrality near the contacts/device boundaries as well as the current continuity. With this source term we can write the final steady state equation of motion for populations as

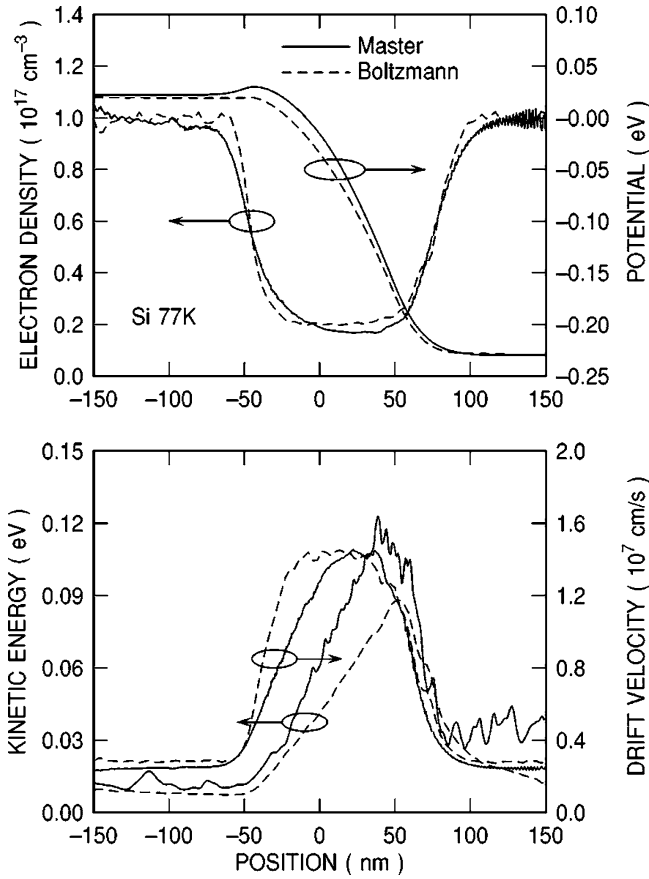
$$\begin{aligned} \sum_{\mu'r} \left[ A_{\mu s; \mu'r} \rho_{\mu'}^{(r)} - A_{\mu'r; \mu s} \rho_\mu^{(s)} \right] + |C_\mu^{(s)}|^2 v_\perp(\mathbf{k}_{\mu s}) \rho_\mu^{(s)} \\ = |C_\mu^{(s)}|^2 v_\perp(\mathbf{k}_{\mu s}) f^{(s)}(\mathbf{k}_\mu^{(s)} - \mathbf{k}_d^s). \end{aligned} \quad (4.13)$$

This is a set of equations over  $\mu$  that has to be solved self-consistently with  $\mathbf{k}_d$  by applying the condition of current continuity at the contact/device boundaries.

Some of the results of the full-band calculations with (4.13) are given in Fig. 4.1 for an *nin* Si diode at 77 K, biased at 0.25 V [17]. For comparison purposes, alongside them are the results of the simulation with the Monte Carlo BTE.

## 2.4 A Single-Particle QME Beyond the Born–Markov Approximation

A somewhat different QME to study semiconductors in a uniform electric field can be constructed using the perturbation expansion of the single-electron/many-phonon Liouville–von Neumann equation [18–20]. The difference with the previous one is that it was applied to homogeneous bulk problems (not devices), but on the other hand it makes no assumption about the electron–phonon coupling (it is beyond the Born–Markov or weak-scattering/long-time limit of the PME) and is able to simulate energy-nonconserving transitions, multiple collisions and intracollisonal field effects [27, 28].



**Fig. 4.1** *Top frame* – the electron charge density and potential energy for an *nin* Si diode at 77 K, biased at 0.25 V, where the *solid lines* are results of using the master equation (4.13), while the *dashed lines* are results of using the Monte Carlo BTE. *Bottom frame* – similar as the *top frame*, but with results for the average kinetic energy and drift velocity. Reprinted with permission from [17], M. V. Fischetti, Phys. Rev. B **59**, 4901 (1999). ©1999 The American Physical Society

The perturbation expansion to the Liouville–von Neumann equation for bulk semiconductors in a uniform electric field can be constructed as follows [18]. The Hamiltonian of this system in the effective mass approximation and with parabolic energy bands is a sum of several contributions

$$H = H_e + H_E + H_p + H_{e-ph} = H_0 + H_{e-ph}, \quad (4.14)$$

where

$$H_e = -\frac{\hbar^2}{2m^*} \nabla^2, \quad H_E = e\mathbf{E}\mathbf{r}, \quad H_p = \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a_{\mathbf{q}}^\dagger a_{\mathbf{q}} \quad (4.15)$$

and  $H_{e-ph}$  is a standard Hamiltonian describing electron–phonon coupling and consisting of absorption and emission parts.  $H_0$ , describing the free and non-interacting electron gas, the equilibrium phonon distribution and the external homogeneous electric field is used to solve the time-dependent Schrödinger equation. Approximate solutions are the tensor products of the time-dependent accelerated plane waves (they would be accelerated Bloch waves beyond the effective mass approximation) normalized to 1 over the crystal volume  $V$  [29], and the many-body phonon states  $|n_{\mathbf{q}}, t\rangle$

$$|\mathbf{k}_0, n_{\mathbf{q}}, t\rangle = \frac{1}{\sqrt{V}} e^{i\mathbf{k}(t)\mathbf{r}} e^{-i\int_0^t ds \omega(\mathbf{k}(s))} |n_{\mathbf{q}}, t\rangle, \quad (4.16)$$

where  $\mathbf{k}(t) = \mathbf{k}_0 - e\mathbf{E}t/\hbar$  and  $\omega(\mathbf{k}(t)) = \hbar k^2/2m^*$ .

If we use this basis set (whose time evolution is generated by  $H_0$ ) for the density matrix, the Liouville–von Neumann equation contains only the interaction Hamiltonian

$$i\hbar \frac{\partial}{\partial t} \rho(\mu, \mu', t) = [H_{e-ph}(t), \rho(t)]_{\mu, \mu'}, \quad (4.17)$$

where  $\mu \equiv (\mathbf{k}_0, n_{\mathbf{q}})$ . Upon the formal integration and perturbation expansion we obtain the following Dyson series for the diagonal elements of the density matrix  $\rho(\mu, t) = \rho(\mu, \mu, t)$

$$\begin{aligned} \rho(\mu, t) &= \rho(\mu, 0) + \int_0^t dt_1 \left[ \tilde{H}_{e-ph}(t_1), \rho(0) \right]_{\mu, \mu} \\ &\quad + \int_0^t dt_1 \int_0^{t_1} dt_2 \left[ \tilde{H}_{e-ph}(t_1), \left[ \tilde{H}_{e-ph}(t_2), \rho(0) \right] \right]_{\mu, \mu} + \dots \\ &= \rho^{(0)}(\mu, t) + \rho^{(1)}(\mu, t) + \rho^{(2)}(\mu, t) + \dots, \end{aligned} \quad (4.18)$$

where  $\tilde{H}_{e-ph} = (1/i\hbar)H_{e-ph}$  and the initial condition is assumed to be diagonal and uncoupled,  $\rho(\mu, \mu', 0) = \rho(\mu, 0) = \rho^{(0)}(\mu, t) = f_0(\mathbf{k}_0)P_{eq}(n_{\mathbf{q}})$ , where  $f_0$  and  $P_{eq}$  are the initial distribution functions of electrons and phonons, respectively.

We are only interested in the diagonal elements, whose time-evolution is given by (4.18), since, first, we want to evaluate expectation values of electronic quantities only and, second, they are diagonal in the electronic part of the wave function. Furthermore, (4.18) is a closed equation for the diagonal elements of  $\rho(t)$ , which is a consequence of a diagonal initial condition and the fact that there are only initial values of  $\rho$  at the right hand side of the perturbation expansion. Remember that we have mentioned a similar effect in a somewhat different context in Sect. 2.3, i.e. that the closed equation for the diagonal elements of the PME can be obtained from the general form of the single-particle QME (4.6) by working in the basis of the single-particle Hamiltonian and by approximating the collision superoperator with Fermi’s golden rule. The fact that each term in the perturbation expansion starts from a diagonal state and have to end up in some other (or the same) diagonal state means

that only even order terms in the expansion will survive. This can be explained by the fact that each interaction Hamiltonian (being linear in creation/destruction operators) will either create or destroy a phonon in that state (left or right) of the initial diagonal outer product of states (since in general  $\rho = \sum |\alpha\rangle\langle\alpha|$ ) that is on the same side as that interaction Hamiltonian, after we expand the commutation relations. So to maintain the diagonalization we have to balance each absorption/emission at one of the sides by either the opposite process (emission/absorption) on the same side, or by the same process (absorption/emission) at the opposite side. This can only be achieved by having an even number of interaction Hamiltonians in a particular term in the perturbation expansion.

Equation (4.18) has several advantages over the steady state PME with Fermi's golden rule (of course within the limits of its applicability), beside the fact it can actually handle the transient regime. It is able to model quantum transitions of a finite duration and, because of the basis used, the acceleration of the plane waves during that time. The former ensures that the processes where the subsequent scattering effects begin before the previous ones have finished are accounted for (multiple collisions), while the latter ensures that the intracollisional field effect is not neglected. This approach also relaxes the constraint of the strict energy conservation during collisions, especially at short timescales. One of the disadvantages is that the trace over many-phonon degrees of freedom has to be taken in (4.18) [18].

## 2.5 Monte Carlo Solution to the QME

Using the Monte Carlo stochastic technique to solve the semiclassical BTE [30–33] is very common today, since it provides very accurate results (without using extensive approximations to make the problem numerically tractable), while the computational time is no more a bottleneck considering the availability of computing resources. The same idea of solving the semi-classical transport equation stochastically, instead of directly numerically, can be applied to the QME. In this section we will give a brief review of the ways this can be done in the case of a single-electron QME where we seek solutions (steady state and transient) to the diagonal elements of the density matrix. They will be algorithmically compared with the semiclassical Monte Carlo and shown to bear many similar characteristics, as far as the implementation is concerned.

### 2.5.1 The Steady-State PME for Inhomogeneous Devices

As has been shown in Sect. 2.3, the PME can be successfully applied to a certain class of problems which nowadays have high importance due to the down-scaling of electronic devices. The main equation of that section (4.13), which is a linear steady state equation for the occupations of levels with source terms modeling injection/extraction from the contacts, can be solved by using the Monte Carlo method [16]. For comparison purposes, let us write the standard BTE [33]

$$\frac{df(\mathbf{k}, \mathbf{r}, t)}{dt} + \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k}) \nabla_{\mathbf{r}} f(\mathbf{k}, \mathbf{r}, t) + \frac{\mathbf{F}}{\hbar} \cdot \nabla_{\mathbf{k}} f(\mathbf{k}, \mathbf{r}, t) = \left. \frac{\partial f(\mathbf{k}, \mathbf{r}, t)}{\partial t} \right|_{\text{Coll}}. \quad (4.19)$$

Diagonal elements of the density matrix from the PME (4.10),  $p_n(t) = \rho_{n,n}(t)$  ( $n$  is a full set of basis quantum numbers), correspond to the distribution function  $f(\mathbf{k}, \mathbf{r}, t)$  in (4.19), while the right hand side of (4.10) corresponds to the right hand side of (4.19). The main difference is in the drift and diffusion terms (due to the external field and spatial inhomogeneity) present in (4.19). Their absence from (4.10) is a consequence of a specific basis chosen for the density matrix, which diagonalizes the total potential consisting of the Hartree potential and the potential due to the external field. Although the BTE is most often used in the form given by (4.19), it can also be cast in the form without those two terms by a change in coordinates, from the phase space variables  $(\mathbf{r}, \mathbf{k})$  into the collision-free trajectories (path variables) [34]. So, to solve the PME we can use the conventional Monte Carlo procedure, used to solve the standard BTE (4.19), but without the free-flight part.

To better understand the relationship between (4.10) and (4.19) it can be shown that they are both limiting cases, but at the opposite ends of the domain [16]. As already mentioned in Sect. 2.3, the PME, being diagonal and therefore neglecting the off-diagonal elements, is justified for the quasidiagonal initial state. As shown by Van Hove [25], it is the state obtained by mixing the eigenstates of the unperturbed Hamiltonian, but only in a very narrow energy range (amplitudes are non-zero only for a very narrow range of energies of the states being mixed). Therefore, those states are highly delocalized. This physically corresponds to our assumption of devices much smaller than the dephasing length in the contacts, such that injecting electrons appear to them as spatially delocalized (but energetically very localized) wave packets, plane waves being the limiting case. There is one more group of states for which the diagonal form of the transport equation is justified and they are spatially very localized states, formed by linear combinations of eigenstates of the unperturbed Hamiltonian with amplitudes varying slowly with the energy. This opposite limit is satisfied by the BTE, which is therefore diagonal in the real space (the PME is diagonal in the wave vector space).

Finally, the implementation procedure would go as follows [16]:

- Electrons are initialized into the eigenstates  $|\mu\rangle$ , where  $\mu$  is a full set of quantum numbers for the open system considered, according to the thermal equilibrium occupations as determined by the solution to the ballistic problem (no scattering).
- The time step is chosen and all transition probabilities are calculated. Scattering probability  $P_{\text{scatter}}$  is proportional to the transition rates determined by Fermi's golden rule, while injection/extraction probabilities (the processes that can change the number of particles in the open system)  $P_{\text{in/out}}$  are proportional to the injection/extraction rates. Scattering or extraction events are selected according to the generated random number.
- If scattering is selected then the final state is chosen according to the final density of states and the matrix elements connecting the initial and final states, just like in the conventional Monte Carlo procedure. If extraction (exit through a contact)

is selected, the electron is simply removed. After all particles are processed, new particles are added to the states according to  $P_{\text{in}}$  and the drifted Fermi–Dirac distribution in the injecting contacts.

- After a few Monte Carlo steps the occupations of states, obtained from the Monte Carlo, are used to update the potential and wave functions with the Schrödinger/Poisson solver. The frequency of this update is determined by the plasma frequency of the whole device. The new potential is treated as a sudden perturbation which redistribute electrons from the old states  $|\mu^{(old)}\rangle$  to the new states  $|\mu^{(new)}\rangle$  according to the probability given by  $|\langle\mu^{(new)}|\mu^{(old)}\rangle|^2$ .

## 2.5.2 A Single-Electron QME in Homogeneous Bulk

The explanation of the similarity of (4.18) with the BTE can proceed by remembering what we said in Sect. 2.5.1, about the BTE written in the path variables, when it has the following form (after the drift-diffusion terms have disappeared)

$$f(t) = f(0) + P_i f - P_o f = f_0 + P_i f_0 - P_o f_0 + P_i P_i f_0 - P_i P_o f_0 - P_o P_i f_0 + P_o P_o f_0 + \dots, \quad (4.20)$$

where  $P_i$  and  $P_o$  are the integral operators for scattering “in” and “out”. This equation is of the same general form as (4.18) and so similar Monte Carlo procedures can again be used to solve both equations, as will be outlined below.

The Monte Carlo algorithm to solve (4.18) has several novelties comparing to the one explained in Sect. 2.5.1 [20]. Beside the initialization and the standard random selections of the type of the scattering process (in/out scattering and the type of scattering) like in the conventional Monte Carlo, here we have several new random selections due to the perturbation expansion. First, there is a selection of the perturbative order (just the even ones, as shown previously), second, the selection of  $n/2$  times where the first interaction Hamiltonians of each quantum process (a quantum process is defined as a pair of  $\tilde{H}_{e-ph}$ 's for a distinct  $\mathbf{q}$ ) are to be evaluated and, third, as already pointed out the average over the phonon variables  $\mathbf{q}$  have to be performed (equivalent of taking the trace over the phonon degrees of freedom), for which a separate random number is reserved. So far, this is the same for both (4.18) and (4.20). The additional steps for the quantum case would be to select the side of  $\rho(0)$  where each process starts and the time for the second  $\tilde{H}_{e-ph}$  in the process.

The restoration of this quantum Monte Carlo algorithm to the standard one, consisting of periods of free flights interrupted by scattering events, can be achieved by introducing a quantum analog of the self-scattering in the standard Monte Carlo algorithm, that makes scattering rates constant [35, 36]. That can be achieved by the following transformation [19, 20]

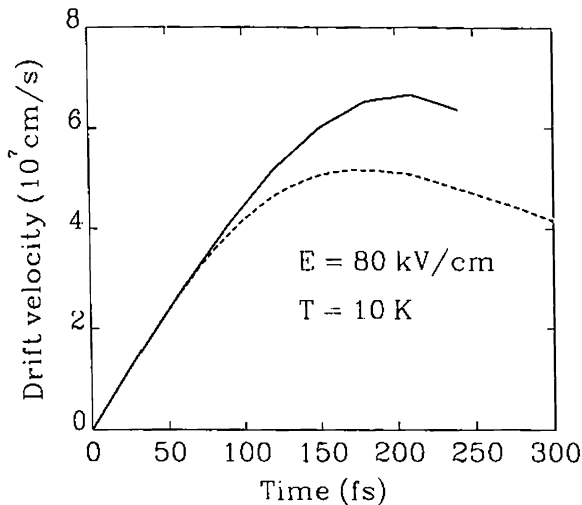
$$\rho(t) \rightarrow \exp\left(\int_{t_0}^t \gamma(t_1) dt_1\right) \rho(t), \quad (4.21)$$

where  $\rho$  is understood to represent diagonal elements  $\rho_\mu$  as before. For constant  $\gamma = 1/\tau$  and  $t_0 = 0$  we have  $\rho \rightarrow e^{(t/\tau)}\rho$ , which gives the following equation instead of (4.18)

$$\rho(t) = e^{-(t/\tau)} \left[ \rho_0 + \left( \tilde{H}\tilde{H} + \frac{1}{2\tau} \right) \rho_0 - \tilde{H}\rho_0\tilde{H} - \tilde{H}\rho_0\tilde{H} + \rho_0 \left( \tilde{H}\tilde{H} + \frac{1}{2\tau} \right) + \dots \right]. \quad (4.22)$$

In this concise notation the integral signs as well as argument lists and subscripts are dropped, and the commutation relations are expanded. This equation is actually equal to (4.18), since the damping factor  $e^{-(t/\tau)}$  is going to cancel with all the factors  $1/2\tau$  when all the integration and summations are performed. Nevertheless, this form makes the quantum Monte Carlo very similar to the standard ensemble Monte Carlo, consisting of periods of free flights interrupted by scattering events. The change to the previously explained algorithm is that the times selected for the first  $\tilde{H}$  in each process is separated by a constant time  $\tau$ , the “free-flight” time, but only a few events will actually be quantum processes (scattering events) with a definite  $\mathbf{q}$ . Although this procedure does not really contribute to the physical side of the problem, the fact that it is made similar to the semiclassical approach makes comparison with it much more transparent.

A representative result of the application of this algorithm and a comparison with the semiclassical Monte Carlo is shown in Fig. 4.2 [20]. We see a clear discrepancy



**Fig. 4.2** Drift velocity overshoot in silicon. The result of the quantum Monte Carlo technique is shown with the *solid line*, while the semiclassical result is shown with the *dashed line*. Reprinted with permission from [20], C. Jacoboni, *Semicond. Sci. Technol.* 7, B6 (1992). ©1992 IOP Publishing Ltd

in the drift velocity overshoot between the two techniques, which is attributed to the intracollisional field effect favoring transitions oriented along the field direction, comparing with the standard isotropic cross section.

### 3 Reduced Many-Particle QMEs

The reduced many-particle density matrix and the corresponding QME by its complexity fall between the single-particle and the full many-particle cases. This contributes to its flexibility, allowing us to find the optimal balance between the accuracy of modeling important physical processes in the open system and the computational complexity that results from including a large number of degrees of freedom. In this section we will first derive the formal, exact equation of motion for the reduced density matrix, the Nakajima–Zwanzig equation, and then introduce several approaches that make this equation more tractable for practical applications.

#### 3.1 The Nakajima–Zwanzig Equation

Here, we will formally derive the Nakajima–Zwanzig equation for an exact reduced many-particle system. As already mentioned in Sect. 1 we are only interested in the time evolution of *the system*. Therefore, starting from (4.4) we need to trace out all *the environmental* degrees of freedom. This can be formally done by introducing a projection superoperator pair  $\mathcal{P}$  and  $\mathcal{Q}$

$$\mathcal{P}\rho(t) = \rho_E \otimes \text{Tr}_E(\rho(t)) = \rho_E \otimes \rho_S(t), \quad \mathcal{Q}\rho(t) = \rho(t) - \mathcal{P}\rho(t), \quad (4.23)$$

where  $\rho(t)$  is the total density matrix,  $\rho_S(t)$  the density matrix of the system and  $\rho_E(t)$  represents the density matrix of the environment. Accordingly, we can split the Hamiltonian and the Liouvillian of the total system into three parts

$$H = H_S + H_E + H_I, \quad \mathcal{L} = \mathcal{L}_S + \mathcal{L}_E + \mathcal{L}_I, \quad (4.24)$$

where by index  $I$  we represent the interaction between the system and environment. Here, it is to be understood that each part acts in its corresponding Hilbert space (or Liouville space, for  $\mathcal{L}$ ), e.g.

$$H = I_E \otimes H_S + H_E \otimes I_S + H_I, \quad H_I = \sum_i A_i \otimes B_i, \quad (4.25)$$

where  $I_\alpha$  is the identity operator in the  $\alpha$ -subspace, and  $A$  and  $B$  are operators that act on the environment and system Hilbert spaces, respectively. The form of interaction in (4.25) is the most general one. By acting with projection operators (4.23) on (4.4) we get a system of two equations, one for  $\mathcal{P}\rho$  and one for  $\mathcal{Q}\rho$ . Upon formally solving



it for the relevant part  $\mathcal{P}\rho$  we arrive at the formally exact equation of motion for the density matrix, the Nakajima–Zwanzig equation<sup>2</sup> [14, 37, 38]

$$\begin{aligned} \frac{d}{dt}\mathcal{P}\rho(t) &= -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - \int_0^t ds\mathcal{K}(t,s)\mathcal{P}\rho(s) \\ &\quad - i\mathcal{P}\mathcal{L}(t)\mathcal{G}(t,0)\mathcal{Q}\rho(0), \end{aligned} \quad (4.26)$$

where the convolution or memory kernel  $\mathcal{K}$  is

$$\mathcal{K}(t,s) = \mathcal{P}\mathcal{L}(t)\mathcal{G}(t,s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}, \quad \mathcal{G}(t,s) = T_{\leftarrow} \exp \left[ -i \int_s^t ds' \mathcal{Q}\mathcal{L}(s') \right], \quad (4.27)$$

with  $T_{\leftarrow}$  being the time ordering operator which sorts the operators to the right of it according to increasing time argument from right to left.

Equation (4.26) is not very useful for practical applications in this form because it is very complex. It contains all orders of interaction  $H_I$  and some memory terms, which makes it an exact non-Markovian QME. Memory terms are incorporated through the non-local memory kernel, the integral over past times  $[0, t]$  and through the explicit dependence on the initial conditions in the second and third term. In the next section we will show some common approximations that are used to derive an approximate (to the second order in interaction) Markovian QME. Further modification to (4.26) that is commonly done is to choose the projection operator  $\mathcal{P}$  such that the third term is canceled in the situations when the initial state of the total system is uncoupled  $\rho(0) = \rho_E(0) \otimes \rho_S(0)$ . This is achieved if  $\mathcal{P}\rho$  is induced by  $\rho_E(0)$  in (4.23) because

$$\mathcal{Q}\rho(0) = \rho(0) - \mathcal{P}\rho(0) = \rho(0) - \rho_E(0) \otimes \rho_S(0) = 0. \quad (4.28)$$

Now (4.26) is just

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - \int_0^t ds\mathcal{K}(t,s)\mathcal{P}\rho(s). \quad (4.29)$$

To finally obtain the reduced dynamics described by  $\rho_S(t)$  we have to take the trace over environmental variables  $Tr_E(\mathcal{P}\rho(t))$ .

### 3.2 The Born–Markov Approximation

Now, we will briefly sketch how to derive an approximate Markovian QME that ultimately lead to a QME whose time-evolution generator (equivalent to  $\mathcal{L}$  in (4.4))

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<sup>2</sup> In the following we set  $\hbar = 1$ .

satisfies the quantum dynamical semigroup property, meaning that if we define a dynamical map  $\mathcal{W}(t)$  as

$$\rho_S(t) = \mathcal{W}(t)\rho_S(0), \quad (4.30)$$

its property is

$$\mathcal{W}(t_1)\mathcal{W}(t_2) = \mathcal{W}(t_1 + t_2). \quad (4.31)$$

This defines a Markovian evolution and the necessary microscopic conditions for it will be stated in the following. The generator of this dynamical map can be defined as

$$\begin{aligned} \mathcal{W}(t) &= \exp(\mathcal{F}t), \\ \frac{d}{dt}\rho_S(t) &= \mathcal{F}\rho_S(t), \end{aligned} \quad (4.32)$$

from which it follows that the time evolution generator must be time-independent in order to have a Markovian QME.

The Born approximation is justified for weak coupling. This coupling is characterized by the interaction Hamiltonian  $H_I$ , which may refer to the coupling to reservoirs, phonons and everything else that can be encountered in real electronic devices. Since we assume that the coupling is weak we can keep only terms up to the second order in  $H_I$  in (4.29). Higher order interactions are contained in the memory term  $\mathcal{K}$  in the integral in (4.29) and in order to keep just the second order term we need to have  $\mathcal{L}_I$  in  $\mathcal{K}$  appearing twice at most. To achieve that we can approximate the propagator  $\mathcal{G}(t, s)$  with

$$\mathcal{G}(t, s) = T_{\leftarrow} \exp \left[ \int_s^t ds' \mathcal{Q}(\mathcal{L}_S(s') + \mathcal{L}_E(s')) \right], \quad (4.33)$$

which corresponds to leaving only zeroth order term in  $\mathcal{L}_I(t)$ . The Born approximation may be restated in several equivalent ways, depending on the way of derivation of final equations. The most obvious way, just mentioned, is to explicitly keep terms only up to the second order in interaction [15]. Equivalently, we can assume that, due to the weak-coupling, the density matrix of the system is always factorized during the evolution as [14]

$$\rho_S(t) = \rho_E \otimes \rho_S(t) \quad (4.34)$$

and that the density matrix of the reservoir is only negligibly affected by the interaction. The third way is somewhat less formal and is connected to the quantum mechanical scattering theory [22]. A variation of the Neumann series method, known as the Born series in this context, is used to approximate the form of the wave function after the scattering. This is also used in Fermi's golden rule, to calculate the transition rates which are valid in the weak-coupling and long-time limits.

The Markovian approximation would proceed by first replacing  $\mathcal{P}\rho(s)$  by  $\mathcal{P}\rho(t)$  in (4.29), thus removing any dependence at time  $t$  on the past states, for  $s < t$ ,

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - \int_0^t ds\mathcal{K}(t,s)\mathcal{P}\rho(t). \quad (4.35)$$

This equation (in other forms and/or specific basis) is called the Redfield equation [14, 15, 39]. Second, there is an integral left which depends on the initial conditions, or in other words the interval between the present and initial states. To get rid of this we make a simple substitution  $s \rightarrow t - s$  and let the upper limit of integration go to infinity, which gives us

$$\frac{d}{dt}\mathcal{P}\rho(t) = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - \int_0^\infty ds\mathcal{K}(t,t-s)\mathcal{P}\rho(t). \quad (4.36)$$

These two approximations, that make up the Markovian approximation, are possible provided  $\tau_E \ll \tau_S$ , where  $\tau_E$  is the environmental relaxation rate and  $\tau_S$  the open system relaxation rate. This means that the time evolution can be coarse-grained such that  $\rho_S(t)$  is almost constant during  $\tau_E$ , while the integral in (4.36) vanishes fast with decreasing  $t - s$  and, therefore, the Markovian approximation is justified.

Proceeding with some further less significant modifications to (4.36) we arrive at the most general form of the generator of the quantum dynamical semigroup [14, 15]. It constitutes the Lindblad form of the QME for an open system [40]

$$\frac{d}{dt}\rho_S(t) = -i[H, \rho_S(t)] + \sum_k \gamma_k \left( A_k \rho_S A_k^\dagger - \frac{1}{2} A_k^\dagger A_k \rho_S - \frac{1}{2} \rho_S A_k^\dagger A_k \right), \quad (4.37)$$

where  $H$  is the Hamiltonian that generates a unitary evolution, consisting of the system Hamiltonian and corrections due to the system–environment coupling, and  $A_k$ 's are the Lindblad operators that describe the interaction with the environment in the Born–Markov limit.

### 3.3 The Conventional Time-Convolutionless Equation of Motion

The Nakajima–Zwanzig equation (4.26), that relies upon the use of the projection-operator technique, has several shortcomings that are the motivation for the following sections. Various variants of the projection-operators have been used in the past to study a range of physical systems. Argyres and Kelley [41] applied it to a theory of linear response in spin-systems, Barker and Ferry [42] to quantum transport in very small devices, Kassner [43] to relaxation in systems with initial system-bath coupling, Sparpaglione and Mukamel [44] to electron transfer in polar media, followed by a study of condensed phase electron transfer by Hu and Mukamel [45], while Romero-Rochin and Oppenheim [46] studied relaxation of two-level systems

weakly coupled to a bath. However, this approach is limited by two computationally intensive operations needed to arrive at the final, reduced, density matrix of the open system: the time-convolution integral containing the memory kernel and the partial trace over environmental variables,  $\text{Tr}_E(\mathcal{P}\rho)$ . Specifically, these limits would be lifted by applying the Markov and Born approximations of Sect. 3.2, respectively, because then the time-convolution disappears and the trace is a trivial operation since the equation for  $\mathcal{P}\rho$  is already well factorized into the environmental and system parts.

Going beyond the Born–Markov approximation we have to think of different methods of leveraging the computational burden. In line with that, Tokuyama and Mory [47] proposed a time-convolutionless equation of motion in the Heisenberg picture. This was extended to the Schrödinger picture by Shibata et al. [48, 49] after which a stream of research appeared. Saeki analyzed the linear response of an externally driven systems coupled to a heat bath [50] and systems coupled to a stochastic reservoir [51, 52]. Ahn extended the latter to formulate the quantum kinetic equations for semiconductors [53], and a theory of optical gain in quantum-well lasers [54]. Later, he treated noisy quantum channels [55] and quantum information processing [56]. Chang and Skinner [57] applied the time-convolutionless approach to analyze relaxation of a two-level system strongly coupled to a harmonic bath, while Golosov and Reichmann [58] analyzed condensed-phase charge-transfer process. In the following, we will give a brief derivation of the time-convolutionless equation of motion and point out some of its shortcomings, resulting from the fact that it is still based on the projection-operator technique.

Let us choose some arbitrary, but proper and constant in time, environmental density matrix  $\tilde{\rho}_E$  as a generator for the time-independent projection operator (4.23). This means that  $\text{Tr}_E(\tilde{\rho}_E) = 1$  and therefore

$$\text{Tr}_E(\mathcal{P}\rho) = \text{Tr}_E(\tilde{\rho}_E) \cdot \text{Tr}_E(\rho) = \text{Tr}_E(\rho) = \rho_S. \quad (4.38)$$

The two equations for the projection operators  $\mathcal{P}$  and  $\mathcal{Q}$  are

$$\frac{d}{dt}(\mathcal{P}\rho(t)) = -i\mathcal{P}\mathcal{L}(t)\rho(t) = -i\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho(t) - i\mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho(t), \quad (4.39)$$

$$\frac{d}{dt}(\mathcal{Q}\rho(t)) = -i\mathcal{Q}\mathcal{L}(t)\rho(t) = -i\mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho(t) - i\mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho(t). \quad (4.40)$$

A formal solution of (4.40) is

$$\mathcal{Q}\rho(t) = -i \int_0^t dt' \mathcal{G}(t, t') \mathcal{Q}\mathcal{L}(t') \mathcal{P}\mathcal{U}(t', t) \rho(t) + \mathcal{G}(t, 0) \mathcal{Q}\rho(0), \quad (4.41)$$

where for  $t > t'$

$$\begin{aligned} \mathcal{G}(t, t') &= T_{\leftarrow} \exp \left( -i \int_{t'}^t ds \mathcal{Q}\mathcal{L}(s) \mathcal{Q} \right), \\ \mathcal{U}(t', t) &= T_{\rightarrow} \exp \left( i \int_{t'}^t ds \mathcal{L}(s) \right). \end{aligned} \quad (4.42)$$

The superoperator  $\mathcal{U}(t, t')$  is defined by

$$\begin{aligned} \rho(t) &= \mathcal{U}(t, t_0)\rho(t_0), \\ \mathcal{U}(t, t') &= \Theta(t-t')T_{\leftarrow} \exp\left(-i \int_{t'}^t ds \mathcal{L}(s)\right) + \Theta(t'-t)T_{\rightarrow} \exp\left(i \int_t^{t'} ds \mathcal{L}(s)\right). \end{aligned} \quad (4.43)$$

By using it we make (4.41) time-local, which is the essence of this approach. Equation (4.41) can be rearranged in the following way

$$\mathcal{D}(t; 0)\mathcal{Q}\rho(t) = [1 - \mathcal{D}(t; 0)]\mathcal{P}\rho(t) + \mathcal{G}(t, 0)\mathcal{Q}\rho(0), \quad (4.44)$$

where  $\mathcal{D}(t; 0)$  is defined as

$$\mathcal{D}(t; 0) = 1 + i \int_0^t dt' \mathcal{G}(t, t')\mathcal{Q}\mathcal{L}(t')\mathcal{P}\mathcal{U}(t', t). \quad (4.45)$$

Assuming that  $\mathcal{D}(t; 0)$  is invertible, (4.41) finally becomes

$$\mathcal{Q}\rho(t) = [\mathcal{D}(t; 0)^{-1} - 1]\mathcal{P}\rho(t) + \mathcal{D}(t; 0)^{-1}\mathcal{G}(t, 0)\mathcal{Q}\rho(0). \quad (4.46)$$

Using the last equation in (4.39) we obtain

$$\frac{d}{dt}(\mathcal{P}\rho(t)) = -i\mathcal{P}\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{P}\rho(t) - i\mathcal{P}\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{G}(t, 0)\mathcal{Q}\rho(0). \quad (4.47)$$

The last step that is left to obtain the conventional time-convolutionless equation of motion is to take the trace over environmental variables of (4.47), which gives us

$$\begin{aligned} \frac{d}{dt}\rho_S(t) &= -i\text{Tr}_E [\mathcal{P}\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{P}\rho(t)] - i\text{Tr}_E [\mathcal{P}\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{G}(t, 0)\mathcal{Q}\rho(0)] \\ &= -i\text{Tr}_E [\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\tilde{\rho}_E \otimes \rho_S(t)] - i\text{Tr}_E [\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{G}(t, 0)\mathcal{Q}\rho(0)] \\ &= -i\text{Tr}_E [\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\tilde{\rho}_E] \rho_S(t) - i\text{Tr}_E [\mathcal{L}(t)\mathcal{D}(t; 0)^{-1}\mathcal{G}(t, 0)\mathcal{Q}\rho(0)]. \end{aligned} \quad (4.48)$$

This conventional form of the time-convolutionless equation of motion has three shortcomings. First, it explicitly depends on the choice of  $\tilde{\rho}_E$  that induces the projection operator, although the final result will not depend on it. Second, we have to evaluate complicated matrices  $\mathcal{U}$ ,  $\mathcal{G}$  and  $\mathcal{D}$  involving all the degrees of freedom in the system+environment, but at the end we will extract only those degrees

belonging to the system, by taking the trace. Third, this approach depends on invertibility of  $\mathcal{D}$ , which might be difficult to fulfill. These issues will be addressed in the following sections.

### 3.4 The Eigenproblem of the Projection Operator

The projection operator, as defined in (4.38), is idempotent ( $\mathcal{P}^2 = \mathcal{P}$ ) because

$$\begin{aligned} \mathcal{P}^2 \rho &= \mathcal{P}(\mathcal{P}\rho) = \tilde{\rho}_E \otimes \text{Tr}_E [\tilde{\rho}_E \otimes \text{Tr}_E (\rho)] \\ &= \tilde{\rho}_E \otimes \text{Tr}_E (\tilde{\rho}_E) \text{Tr}_E [\text{Tr}_E (\rho)] = \tilde{\rho}_E \otimes \text{Tr}_E (\rho) = \mathcal{P}\rho. \end{aligned} \quad (4.49)$$

Therefore, it has two eigenvalues, 0 and 1, and since they are both real we can conclude that  $\mathcal{P}$  is also hermitian,  $\mathcal{P} = \mathcal{P}^\dagger$ . In analogy with the notion that system states are members of the respective Hilbert space, while operators (like  $\rho$ ) act on it, we can introduce a Liouville space whose members are operators acting on the Hilbert space, while superoperators (like  $\mathcal{L}$ ) act on it. To complete the definition we have to define the inner product which is conveniently done as  $(A, B) = \text{Tr}(A^\dagger B)$ , where  $A$  and  $B$  are some operators belonging to the Liouville space. So, if the Hilbert spaces are  $\mathcal{H}_S$ ,  $\mathcal{H}_E$  and the composite space  $\mathcal{H}_{S+E} = \mathcal{H}_E \otimes \mathcal{H}_S$ , the respective Liouville spaces are  $\mathcal{H}_S^2$ ,  $\mathcal{H}_E^2$  and  $\mathcal{H}_{S+E}^2$ , where the dimensionality of Liouville spaces with respect to that of the corresponding Hilbert spaces is obvious. It follows that  $\mathcal{P}$  is a superoperator acting on  $\mathcal{H}_{S+E}^2$ , which is  $d_E^2 d_S^2$ -dimensional. By construction (4.23) the image space of  $\mathcal{P}$  corresponds to  $\mathcal{H}_S^2$ , so that the subspace of  $\mathcal{P}$  spanned by the degenerate eigenvalue 1 is isomorphic to  $\mathcal{H}_S^2$ . We can write

$$\mathcal{H}_{S+E}^2 = (\mathcal{H}_{S+E}^2)_{\mathcal{P}=1} \oplus (\mathcal{H}_{S+E}^2)_{\mathcal{P}=0}, \quad (4.50)$$

where  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=1}$  is the  $d_S^2$ -dimensional unit subspace and  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=0}$  is the  $d_S^2 (d_E^2 - 1)$ -dimensional zero subspace of the eigenspace of  $\mathcal{H}_{S+E}^2$ .

We can always arrange the eigenbasis of  $\mathcal{P}$ ,  $\{|n\rangle | n = 1, \dots, d_E^2 d_S^2\}$ , such that the first  $d_S^2$  basis vectors span  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=1}$  and therefore

$$\mathcal{P} = \sum_{n=1}^{d_S^2} |n\rangle \langle n|. \quad (4.51)$$

The eigenstates of the composite space  $\mathcal{H}_{S+E}$  are constructed as  $|i\alpha\rangle = |i\rangle \otimes |\alpha\rangle$ , from which follows that the eigenstates  $|n\rangle$  of  $\mathcal{H}_{S+E}^2$  can be written by using four quantum numbers, i.e. as linear combinations of  $|i\alpha, j\beta\rangle$ . Here, states  $|i\rangle$  belong to the environment, while states  $|\alpha\rangle$  to the system. Furthermore, if we define  $\mathcal{P}$  by using a uniform density matrix

$$\bar{\rho}_E = d_E^{-1} \cdot \mathbf{1}_{d_E \times d_E}, \quad (4.52)$$

we can avoid mixing states with different  $\alpha$  and  $\beta$  to obtain a given  $|n\rangle$  [59]. One finds that the states defined as

$$|\overline{\alpha\beta}\rangle = \frac{1}{\sqrt{d_E}} \sum_{i=1}^{d_E} |i\alpha, i\beta\rangle \quad (4.53)$$

constitute an orthonormal basis within the unit subspace of  $\mathcal{P}$ , i.e.

$$\mathcal{P} |\overline{\alpha\beta}\rangle = |\overline{\alpha\beta}\rangle, \quad \langle \overline{\alpha\beta} | \overline{\sigma\gamma} \rangle = \delta_{\alpha\sigma} \delta_{\beta\gamma}. \quad (4.54)$$

Finally, we can write

$$\mathcal{P} = \sum_{\alpha, \beta=1}^{d_S} |\overline{\alpha\beta}\rangle \langle \overline{\alpha\beta}| = \frac{1}{d_E} \sum_{\alpha, \beta=1}^{d_S} \left( \sum_{i=1}^{d_E} |i\alpha, i\beta\rangle \right) \left( \sum_{j=1}^{d_E} \langle j\alpha, j\beta| \right). \quad (4.55)$$

Since

$$\rho = \sum_{i, j=1}^{d_E} \sum_{\alpha, \beta=1}^{d_S} \rho_{j\beta}^{i\alpha} |i\alpha\rangle \langle j\beta| = \sum_{i, j=1}^{d_E} \sum_{\alpha, \beta=1}^{d_S} \rho^{i\alpha, j\beta} |i\alpha, j\beta\rangle, \quad (4.56)$$

we now have representations for both  $\mathcal{P}$  and  $\rho$ , which allows us to explicitly calculate  $\mathcal{P}\rho$  (with the help of  $\langle i\alpha, j\beta | p\sigma, q\nu \rangle = \delta_{ip} \delta_{jq} \delta_{\alpha\sigma} \delta_{\beta\nu}$ ) as

$$\mathcal{P}\rho = \frac{1}{\sqrt{d_E}} \sum_{\alpha, \beta=1}^{d_S} (\text{Tr}_E \rho)^{\alpha\beta} |\overline{\alpha\beta}\rangle = \sum_{\alpha, \beta=1}^{d_S} (\mathcal{P}\rho)^{\overline{\alpha\beta}} |\overline{\alpha\beta}\rangle, \quad (4.57)$$

where

$$(\mathcal{P}\rho)^{\overline{\alpha\beta}} = \frac{(\text{Tr}_E \rho)^{\alpha\beta}}{\sqrt{d_E}}. \quad (4.58)$$

Equation (4.58) defines an isomorphism between  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=1}$  and  $\mathcal{H}_S^2$  that allows us to calculate the trace over environmental variables by effectively doing the basis transformation (4.53).

The conclusion of the previous paragraph is that by working in the eigenbasis of  $\mathcal{P}$ , as one of the possible eigenbasis of  $\mathcal{H}_{S+E}^2$  (4.50), from the beginning we can avoid explicitly taking the trace over environmental variables at the end. In that eigenbasis, given by (4.53) and completed for  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=0}$  (details in [59]), the total density operator can be written as a  $d_S^2 d_E^2$ -dimensional column vector

$$\rho = \begin{bmatrix} \rho_1 \\ \rho_2 \end{bmatrix}, \quad (4.59)$$

where  $\rho_1$  is  $d_S^2$ -dimensional and  $\rho_2$  is  $d_S^2(d_E^2 - 1)$ -dimensional, while the projection operators as  $d_S^2 d_E^2 \times d_S^2 d_E^2$  matrices

$$\begin{aligned} \mathcal{P} &= \begin{bmatrix} \mathbf{1}_{d_S^2 \times d_S^2} & \mathbf{0}_{d_S^2 \times d_S^2 (d_E^2 - 1)} \\ \mathbf{0}_{d_S^2 (d_E^2 - 1) \times d_S^2} & \mathbf{0}_{d_S^2 (d_E^2 - 1) \times d_S^2 (d_E^2 - 1)} \end{bmatrix}, \\ \mathcal{Q} &= \begin{bmatrix} \mathbf{0}_{d_S^2 \times d_S^2} & \mathbf{0}_{d_S^2 \times d_S^2 (d_E^2 - 1)} \\ \mathbf{0}_{d_S^2 (d_E^2 - 1) \times d_S^2} & \mathbf{1}_{d_S^2 (d_E^2 - 1) \times d_S^2 (d_E^2 - 1)} \end{bmatrix}. \end{aligned} \quad (4.60)$$

We see that  $\rho_S = \text{Tr}_E(\rho)$  is given just by (using (4.58))

$$\rho_S = \sqrt{d_E} \cdot \rho_1. \quad (4.61)$$

Similarly, any superoperator  $\mathcal{A}$  acting on  $\mathcal{H}_{S+E}^2$  is represented by

$$\mathcal{A} = \begin{bmatrix} \mathcal{A}_{11} & \mathcal{A}_{12} \\ \mathcal{A}_{21} & \mathcal{A}_{22} \end{bmatrix}. \quad (4.62)$$

Additionally, if an operator is a system operator, i.e.  $\mathcal{A}_{\text{sys}} = \mathbf{1}_E \otimes \mathcal{A}_S$ , then it commutes with  $\mathcal{P}$

$$\mathcal{P} \mathcal{A}_{\text{sys}} \rho = \bar{\rho}_E \otimes \text{Tr}_E[(\mathbf{1}_E \otimes \mathcal{A}_S) \rho] = \bar{\rho}_E \otimes \mathcal{A}_S \text{Tr}_E \rho \quad (4.63)$$

$$= (\mathbf{1}_E \otimes \mathcal{A}_S) (\bar{\rho}_E \otimes \text{Tr}_E \rho) = \mathcal{A}_{\text{sys}} \mathcal{P} \rho, \quad (4.64)$$

which means that it is block-diagonal in the eigenbasis of  $\mathcal{P}$ . Furthermore, it is easily shown that the upper left block matrix is just  $\mathcal{A}_S$  (see Appendix B of [61]), so that

$$\mathcal{A} = \begin{bmatrix} \mathcal{A}_S & \mathbf{0} \\ \mathbf{0} & \mathcal{A}_2 \end{bmatrix}. \quad (4.65)$$

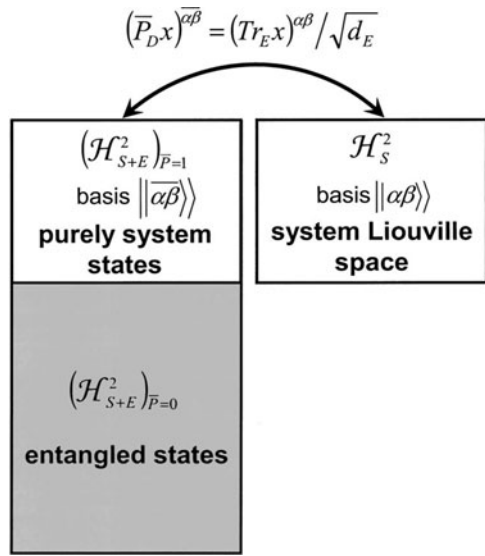
The above mentioned isomorphism between  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=1}$  and  $\mathcal{H}_S^2$  and the decomposition of  $\mathcal{H}_{S+E}^2$  according to (4.50) are graphically shown in Fig. 4.3. Because of the isomorphism (4.58, 4.61) density matrices of the form

$$\rho = \begin{bmatrix} \rho_1 \\ \mathbf{0} \end{bmatrix} \quad (4.66)$$

are called “purely system states”, because they are completely determined by the state of the system S and depend on the environment only in an average sense (through the trace operation). On the other hand, density matrices for which  $\rho_1 = 0$  and  $\rho_2 \neq 0$  we call “entangled states” because they carry microscopic connections to the environmental states, beyond the point of easy separability like in the case of “purely system states”. This can be seen by explicitly deriving the part of the basis for  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=0}$ , with the help of the Gram-Schmidt procedure (see Appendix of [59] and, for more compact and explicit form, Appendix A of [62]).



**Fig. 4.3** Decomposition of the total Liouville space  $\mathcal{H}_{S+E}^2$  into the subspaces of the projection operator  $\mathcal{P}$  and the isomorphism between the unit subspace  $(\mathcal{H}_{S+E}^2)_{\mathcal{P}=1}$  and  $\mathcal{H}_S^2$  for an operator  $x$  acting on  $\mathcal{H}_{S+E}$ . Reprinted with permission from [60], I. Knezevic and D. K. Ferry, Phys. Rev. A **69**, 012104 (2004). ©2004 The American Physical Society



### 3.5 A Partial-Trace-Free Equation of Motion

We proceed by writing the conventional time-convolutionless equation of motion from Sect. 3.3 in the basis of  $\mathcal{P}$  derived in Sect. 3.4. The Liouville operator and the time-evolution operator are given by the following block forms

$$\mathcal{L}(t) = \begin{bmatrix} \mathcal{L}_{11}(t) & \mathcal{L}_{12}(t) \\ \mathcal{L}_{21}(t) & \mathcal{L}_{22}(t) \end{bmatrix}, \quad \mathcal{U}(t, t') = \begin{bmatrix} \mathcal{U}_{11}(t, t') & \mathcal{U}_{12}(t, t') \\ \mathcal{U}_{21}(t, t') & \mathcal{U}_{22}(t, t') \end{bmatrix}. \quad (4.67)$$

The Liouville–von Neumann and equation for the time-evolution now have the following forms

$$\begin{aligned} \frac{d\rho_1}{dt} &= -i\mathcal{L}_{11}(t)\rho_1(t) - i\mathcal{L}_{12}(t)\rho_2(t), \\ \frac{d\rho_2}{dt} &= -i\mathcal{L}_{21}(t)\rho_1(t) - i\mathcal{L}_{22}(t)\rho_2(t) \end{aligned} \quad (4.68)$$

and

$$\begin{aligned} \rho_1(t) &= \mathcal{U}_{11}(t, t')\rho_1(t') + \mathcal{U}_{12}(t, t')\rho_2(t'), \\ \rho_2(t) &= \mathcal{U}_{21}(t, t')\rho_1(t') + \mathcal{U}_{22}(t, t')\rho_2(t'). \end{aligned} \quad (4.69)$$

The block matrix forms of  $\mathcal{G}$  and  $\mathcal{D}$  from (4.42) and (4.45) are

$$\mathcal{G}(t, t') = T_{\leftarrow} \exp \left( -i \int_{t'}^t ds \mathcal{Q} \mathcal{L}(s) \mathcal{Q} \right) = \begin{bmatrix} 1 & 0 \\ 0 & T_{\leftarrow} \exp \left( -i \int_{t'}^t ds \mathcal{L}_{22}(s) \right) \end{bmatrix}, \quad (4.70)$$

$$\begin{aligned}
\mathcal{D}(t;0) &= 1 + i \int_0^t dt' \begin{bmatrix} 1 & 0 \\ 0 & \mathcal{G}_{22}(t,t') \end{bmatrix} \begin{bmatrix} 0 & 0 \\ \mathcal{L}_{21}(t') & 0 \end{bmatrix} \begin{bmatrix} \mathcal{U}_{11}(t',t) & \mathcal{U}_{12}(t',t) \\ \mathcal{U}_{21}(t',t) & \mathcal{U}_{22}(t',t) \end{bmatrix} \\
&= \begin{bmatrix} 1 & 0 \\ i \int_0^t dt' \mathcal{G}_{22}(t,t') \mathcal{L}_{21}(t') \mathcal{U}_{11}(t',t) & 1 + i \int_0^t dt' \mathcal{G}_{22}(t,t') \mathcal{L}_{21}(t') \mathcal{U}_{12}(t',t) \end{bmatrix}.
\end{aligned} \tag{4.71}$$

Since we need  $\mathcal{D}^{-1}(t;0)$ , from (4.71) we obtain

$$\mathcal{D}^{-1}(t;0) = \begin{bmatrix} 1 & 0 \\ -\mathcal{D}_{22}^{-1}(t;0) \mathcal{D}_{21}(t;0) & \mathcal{D}_{22}^{-1}(t;0) \end{bmatrix}. \tag{4.72}$$

As a final step we use all previously defined block forms of necessary operators and superoperators, along with the equation of motion for  $\mathcal{P}\rho$  (4.47) and the isomorphism (4.58) to obtain

$$\begin{aligned}
\frac{d\rho_S(t)}{dt} &= -i [\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t) \mathcal{D}_{22}^{-1}(t;0) \mathcal{D}_{21}(t;0)] \rho_S(t) \\
&\quad - i \sqrt{d_E} \mathcal{L}_{12}(t) \mathcal{D}_{22}^{-1}(t;0) \mathcal{G}_{22}(t,0) \rho_2(0).
\end{aligned} \tag{4.73}$$

Equation (4.73) is a partial-trace-free time-convolutionless equation of motion for the reduced density matrix  $\rho_S(t)$ . It describes the evolution of the representation basis of  $\rho_S$ . Working with representation matrices is a necessary condition of this method and might help in the case when one is interested in numerical implementation. The increased transparency of working with representation forms may also help when introducing various approximations in the exact equation of motion. Out of those three problems, mentioned at the end of Sect. 3.3, there is still one remaining. Namely, we still have the problem of evaluating the inverse of potentially large matrix  $\mathcal{D}_{22}^{-1}(t;0)$  (if it exists at all). The solution to that problem will be discussed, among other things, in the next section.

### 3.6 Memory Dressing

Let us explicitly write the equations of motion for the density operator  $\rho$  in the eigenbasis of  $\mathcal{P}$  from the previous section, i.e. within the partial-trace-free approach. By using (4.47) and (4.46), or directly (4.73) for  $\rho_1$ , we obtain

$$\begin{aligned}
\frac{d\rho_1(t)}{dt} &= -i [\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t) \mathcal{D}_{22}^{-1}(t;0) \mathcal{D}_{21}(t;0)] \rho_1(t) \\
&\quad - i \mathcal{L}_{12}(t) \mathcal{D}_{22}^{-1}(t;0) \mathcal{G}_{22}(t,0) \rho_2(0), \\
\rho_2(t) &= -\mathcal{D}_{22}^{-1}(t;0) \mathcal{D}_{21}(t;0) \rho_1(t) + \mathcal{D}_{22}^{-1}(t;0) \mathcal{G}_{22}(t,0) \rho_2(0),
\end{aligned} \tag{4.74}$$

where from (4.70) and (4.71) and by formally differentiating  $\mathcal{D}(t;0)$ 's submatrices with respect to time we have

$$\begin{aligned} \mathcal{G}_{22}(t,0) &= T_- \exp \left( -i \int_0^t ds \mathcal{L}_{22}(s) \right), \\ \frac{d\mathcal{D}_{21}(t;0)}{dt} &= -i\mathcal{L}_{22}(t)\mathcal{D}_{21}(t;0) + i\mathcal{D}_{21}(t;0)\mathcal{L}_{11}(t) + i\mathcal{D}_{22}(t;0)\mathcal{L}_{21}(t), \\ \frac{d\mathcal{D}_{22}(t;0)}{dt} &= -i\mathcal{L}_{22}(t)\mathcal{D}_{22}(t;0) + i\mathcal{D}_{22}(t;0)\mathcal{L}_{22}(t) + i\mathcal{D}_{21}(t;0)\mathcal{L}_{12}(t), \\ \mathcal{D}_{21}(0;0) &= 0, \quad \mathcal{D}_{22}(0;0) = 1, \end{aligned} \tag{4.75}$$

where in the last line the initial conditions are given. Taking the time derivative of the equation of motion for  $\rho_1(t)$  in (4.69) and comparing those two equations with (4.74) we obtain the following relations for the representation of time evolution operator  $\mathcal{U}(t,0)$

$$\begin{aligned} \frac{d\mathcal{U}_{11}(t,0)}{dt} &= -i [\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t)\mathcal{D}_{22}^{-1}(t;0)\mathcal{D}_{21}(t;0)] \mathcal{U}_{11}(t,0), \\ \frac{d\mathcal{U}_{12}(t,0)}{dt} &= -i [\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t)\mathcal{D}_{22}^{-1}(t;0)\mathcal{D}_{21}(t;0)] \mathcal{U}_{12}(t,0) \\ &\quad - i\mathcal{L}_{12}(t)\mathcal{D}_{22}^{-1}(t;0)\mathcal{G}_{22}(t,0), \\ \mathcal{U}_{21}(t,0) &= -\mathcal{D}_{22}^{-1}(t;0)\mathcal{D}_{21}(t;0)\mathcal{U}_{11}(t,0), \\ \mathcal{U}_{22}(t,0) &= \mathcal{D}_{22}^{-1}(t;0) [\mathcal{G}_{22}(t,0) - \mathcal{D}_{21}(t;0)\mathcal{U}_{12}(t,0)]. \end{aligned} \tag{4.76}$$

These are generic time-convolutionless equations of motions, the form of which results from using the specific basis within the partial-trace-free-approach. They have the general feature of time-convolutionless equations that  $\mathcal{U}_{21}$  and  $\mathcal{U}_{22}$  are expressed in terms of  $\mathcal{U}_{11}$  and  $\mathcal{U}_{12}$ . Formally, by solving (4.76) (for which we first have to solve (4.75)) we arrive at the final solution for the equation of motion of the reduced density operator  $\rho_S$ . However, this is a very difficult problem due to the sizes of the block matrices (the largest are at the position (2,2), being  $d_S^2(d_E^2 - 1) \times d_S^2(d_E^2 - 1)$ -dimensional) and because we need to evaluate the inverse of the matrix  $\mathcal{D}_{22}$  which is in turn the solution of coupled equations for  $\mathcal{D}_{21}$  and  $\mathcal{D}_{22}$ .

By inspection of (4.76) we see that we do not need all three large matrices  $\mathcal{G}_{22}$ ,  $\mathcal{D}_{21}$  and  $\mathcal{D}_{22}$  separately, but only the following combinations of them (we designate each of them with a new letter)

$$\begin{aligned} \mathcal{R}(t) &= \mathcal{D}_{22}^{-1}(t;0)\mathcal{D}_{21}(t;0), \\ \mathcal{S}(t;0) &= \mathcal{D}_{22}^{-1}(t;0)\mathcal{G}_{22}(t,0), \end{aligned} \tag{4.77}$$

where we left out the initial time in the argument list of  $\mathcal{R}(t;0)$  for convenience. By using (4.75) we can derive the equations of motion for the matrices  $\mathcal{R}$  and  $\mathcal{S}$

$$\begin{aligned} \frac{d\mathcal{R}(t)}{dt} &= -i\mathcal{L}_{22}(t)\mathcal{R}(t) - i\mathcal{R}(t)\mathcal{L}_{12}(t)\mathcal{R}(t) + i\mathcal{R}(t)\mathcal{L}_{11}(t) + i\mathcal{L}_{21}(t), \quad \mathcal{R}(0) = 0; \\ \frac{d\mathcal{S}(t;0)}{dt} &= -i[\mathcal{L}_{22}(t) + i\mathcal{R}(t)\mathcal{L}_{12}(t)]\mathcal{S}(t;0), \quad \mathcal{S}(0;0) = 1. \end{aligned} \quad (4.78)$$

Since we are really interested in the evolution of  $\rho_1$ , due to its direct connection with  $\rho_S$  via (4.61), we only need the time evolution matrices  $\mathcal{U}_{11}(t,0)$  and  $\mathcal{U}_{12}(t,0)$ . So, by starting from some initial state  $\rho(0) = [\rho_1(0) \quad \rho_2(0)]^T$ , we have a new system of equations completely describing the time evolution of the reduced density operator  $\rho_S$ , consisting of (4.78) and

$$\begin{aligned} \frac{d\mathcal{U}_{11}(t,0)}{dt} &= -i[\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t)\mathcal{R}(t)]\mathcal{U}_{11}(t,0), \quad \mathcal{U}_{11}(0,0) = 1; \\ \frac{d\mathcal{U}_{12}(t,0)}{dt} &= -i[\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t)\mathcal{R}(t)]\mathcal{U}_{12}(t,0) - i\mathcal{L}_{12}(t)\mathcal{S}(t;0), \quad \mathcal{U}_{12}(0,0) = 0. \end{aligned} \quad (4.79)$$

We see that by introducing  $\mathcal{R}(t)$  and  $\mathcal{S}(t;0)$  there is no more problem with the cumbersome inverse matrix  $\mathcal{D}_{22}^{-1}(t;0)$ . The equations for  $\mathcal{U}_{21}(t,0)$  and  $\mathcal{U}_{22}(t,0)$ , which we do not need here, but are sometimes important, for example in calculating two-time correlation functions in electronic transport where  $\mathcal{U}(t,t')$  for  $t' \neq 0$  are required [63–65], are

$$\mathcal{U}_{21}(t,0) = -\mathcal{R}(t)\mathcal{U}_{11}(t,0), \quad \mathcal{U}_{22}(t,0) = \mathcal{S}(t;0) - \mathcal{R}(t)\mathcal{U}_{12}(t,0). \quad (4.80)$$

The concept of memory dressing from the title of this section refers to  $\mathcal{R}(t)$ . This is because  $\mathcal{R}(t)$  always goes along with  $\mathcal{L}_{12}(t)$ , which is the term representing physical interaction (as follows from the representation form (4.68)), in the “quasi-Liouvillian”  $\mathcal{L}_{11}(t) - \mathcal{L}_{12}(t)\mathcal{R}(t)$ . So, it is a memory dressing of the physical interaction. The self-contained non-linear equation of motion for the memory dressing  $\mathcal{R}(t)$  (first of (4.78)) is a matrix Riccati equation, often encountered in control systems theory [66, 67]. It can be solved for  $\mathcal{R}$  to an arbitrary order by using the perturbation expansion, which also allows for a convenient diagrammatic representation [60].

## 4 Coarse-Graining for the Steady State Distribution Function

The purpose of this section is to derive the steady state distribution function for the open system, by solving for  $\rho_S(t)$  in a ballistic device (no scattering) that is attached to ideal contacts. We will show that, under these conditions, the distribution function

is of Landauer-type. It says that the occupation of incoming states is fixed by the respective contact, while that of outgoing states by the open system alone. Furthermore, since there is no scattering in the open system, the occupation will remain the one determined by the contacts. We will use a coarse-graining procedure to approximate the exact non-Markovian time evolution towards the steady state. At the end, an interaction Hamiltonian, suitable for ideal contacts, will be constructed and used to solve the approximate Markovian equation of motion.

#### 4.1 The Exact Dynamics and the Coarse-Graining Procedure

By using (4.61) and (4.77) in (4.74), we get the following form for the exact equation of motion for the reduced density matrix

$$\frac{d\rho_S(t)}{dt} = -i[\mathcal{L}_{11} - \mathcal{L}_{12}\mathcal{R}(t)]\rho_S(t) - i\sqrt{d_E}\mathcal{L}_{12}\mathcal{S}(t;0)\rho_2(0). \quad (4.81)$$

We will restrict our attention to the problems for which the initial density matrix is not correlated, i.e.

$$\rho(0) = \rho_E(0) \otimes \rho_S(0). \quad (4.82)$$

We see that when  $\rho_E(0) = \bar{\rho}_E$  then  $\rho_2(0) = 0$  and there exists a subdynamics ( $\rho_S$  does not depend on  $\rho_2(0)$ ). This is because  $\mathcal{P}$  is also generated by  $\bar{\rho}_E$ , so that  $\rho(0)$  is an eigenstate of  $\mathcal{P}$  and is of the form (4.66). Here, even though the environmental density matrix is not uniform, it can be proven that the following connecting relation holds

$$\rho_2(0) = \mathcal{M}\rho_1(0) = d_E^{-1/2}\mathcal{M}\rho_S(0), \quad (4.83)$$

where  $\mathcal{M}$  in the eigenbasis of  $\rho_E(0)$  is given by (see Appendix A of [62])

$$\mathcal{M}^i = \sqrt{\frac{d_E(d_E + 1 - i)}{d_E - 1}} \left( \rho_E^i(0) - \frac{1}{d_E + 1 - i} \sum_{j=1}^{d_E} \rho_E^j(0) \right). \quad (4.84)$$

So, in this more general case (for arbitrary  $\rho_E(0)$ ) there still exists the subdynamics in the following form

$$\rho_S(t) = [\mathcal{U}_{11}(t,0) + \mathcal{U}_{12}(t,0)\mathcal{M}]\rho_S(0) = \mathcal{W}(t,0)\rho_S(0), \quad (4.85)$$

which is in agreement with the statement made by Lindblad [68] that the subdynamics exists for an uncorrelated initial state. We can get a differential form of (4.85) by combining (4.74) and (4.83)

$$\frac{d\rho_S(t)}{dt} = -i[\mathcal{L}_{11} - \mathcal{L}_{12}\mathcal{R}(t)]\rho_S(t) - i\mathcal{L}_{12}\mathcal{S}(t)\mathcal{M}\rho_S(0). \quad (4.86)$$

In general we can write

$$\mathcal{W}(t, 0) = T_{\leftarrow} \exp \left[ \int_0^t \mathcal{F}(s) ds \right], \quad (4.87)$$

where  $\mathcal{F}(t)$  is the generator of  $\mathcal{W}(t, 0)$ .

It is very difficult to solve for the reduced system dynamics (4.85), because of the difficulties in obtaining  $\mathcal{W}(t, 0)$ . We can either be content with a Markovian approximation in the weak-coupling and van Hove limits [69], or by an expansion up to the second or fourth orders in the interaction if we need a non-Markovian approximation [14]. Although the weak-coupling limit has been used before to study tunneling structures in the Markovian approximation [70, 71], it is not generally applicable to nanostructures [70]. Here, we will apply an approximation beyond the weak-coupling limit, by approximating the exact reduced system dynamics using coarse-graining over the environmental relaxation time  $\tau$  [72, 73]. This limits the area of applicability to the open systems for which  $\tau \ll \tau_S$ , where  $\tau_S$  is the open system relaxation time, which is still a pretty wide area. For example, in typical small semiconductor devices (quasi-ballistic), with highly doped contacts at room temperature, the major energy relaxation mechanism is electron–electron scattering in the contacts (relaxation time for electron–electron scattering is about 10 fs for GaAs at  $10^{19} \text{ cm}^{-3}$  and room temperature [74], while about 150 fs for polar optical phonon scattering [36]). Electron–electron relaxation will drive the environmental distribution function to a drifted Fermi–Dirac distribution in a time interval  $\tau \approx 10\text{--}100$  fs, which is much shorter than the typical open system relaxation time for these devices  $\tau_S \approx 1\text{--}10$  ps.

The coarse-graining procedure proceeds by splitting the total evolution time interval  $[0, t]$  into segments of length  $\tau$ ,  $[1, 2, \dots, n] \times \tau$ , and defining the average of the generator of  $\mathcal{W}(t, 0)$  over each interval

$$\overline{\mathcal{F}}_j = \frac{1}{\tau} \int_{j\tau}^{(j+1)\tau} \mathcal{F}(s) ds. \quad (4.88)$$

This leads to the following connection between successive, discretized reduced density operators

$$\rho_{S,j+1} = \exp(\tau \overline{\mathcal{F}}_j) \rho_{S,j}, \quad (4.89)$$

which gives

$$\frac{\rho_{S,j+1} - \rho_{S,j}}{\tau} = \overline{\mathcal{F}}_j \rho_{S,j} \quad (4.90)$$

after expanding the exponent for small  $\tau$ . This is just a discretized version of the exact equation of motion.

There are three approximations applied in deriving (4.90). First, we don't have the information about the time evolution inside each  $\tau$ -interval, but only at its ends. Second, we cut the series after the first order in the expansion of  $\exp(\tau\overline{\mathcal{F}}_j)$  in order to get (4.90). Third, the time ordering from the exact equation (4.87) is violated at the  $\tau$  time scale, which can be shown explicitly by using the Dyson series to represent (4.87).

Finally, we will assume that the environmental state is nearly the same after every interval  $\tau$  during the transient, in other words  $\overline{\mathcal{F}}_0 = \overline{\mathcal{F}}_\tau \approx \overline{\mathcal{F}}_1 \approx \dots \approx \overline{\mathcal{F}}_n$ . This is also the most trivial way of ensuring that the coarse grained generators  $\overline{\mathcal{F}}_i$ 's commute (commute in an average sense). For this to be satisfied we have to ramp up the excitation (e.g. bias) to the system in small enough increments with sufficiently long time between two increments so that the open system is able to reach steady state, in the form of a drifted Fermi–Dirac distribution, after each small increment. This condition is more a thought experiment than a real constraint, because we are only interested in the steady state here. As the last step, we expand the discrete equation (4.90) to the continuum (since  $\tau$  is a small parameter) to obtain the final equation

$$\frac{d\rho_S}{dt} = \overline{\mathcal{F}}_\tau \rho_S(t). \quad (4.91)$$

This equation is an approximate Markovian (because the generator  $\overline{\mathcal{F}}_\tau$  is constant in time) QME for the reduced density matrix in the limit of small-increments/long-pauses kind of ramping up the bias and we will use it to obtain the steady state distribution function for arbitrarily large bias.

## 4.2 The Short-Time Expansion of $\overline{\mathcal{F}}_\tau$

The practical value of (4.91) is in the fact that  $\overline{\mathcal{F}}_\tau$  can be calculated using the expansion of  $\mathcal{F}(t)$  in the small parameter  $\tau$  around zero. By introducing a definition  $\mathcal{F}(t) = -i\mathcal{L}_{\text{eff}} - \mathcal{G}(t)$ , where  $\mathcal{L}_{\text{eff}}$  is an effective system Liouvillian and  $\mathcal{G}$  a correction due to the system-environment coupling, expanding (4.85) and (4.86) up to the second order in time and comparing coefficients it can be shown that (see Appendix B of [62])

$$\mathcal{F}(t) = -i\mathcal{L}_{\text{eff}} - 2\Lambda t + O(t^2), \quad (4.92)$$

where  $\mathcal{L}_{\text{eff}}$  is a commutator superoperator generated by  $H_S + \langle H_{\text{int}} \rangle$ , while  $\Lambda$  in the basis  $\alpha\beta$  of the system's Liouville space is given by

$$\Lambda_{\alpha'\beta'}^{\alpha\beta} = \frac{1}{2} \left\{ \langle H_{\text{int}}^2 \rangle_{\alpha'}^\alpha \delta_\beta^{\beta'} + \langle H_{\text{int}}^2 \rangle_\beta^{\beta'} \delta_{\alpha'}^\alpha - 2 \sum_{j,j'} (H_{\text{int}})_{j\alpha'}^{j'\alpha} \rho_E^j (H_{\text{int}})_{j'\beta}^{j\beta'} \right. \\ \left. - \left( \langle H_{\text{int}}^2 \rangle \right)_{\alpha'}^\alpha \delta_\beta^{\beta'} + 2 \langle H_{\text{int}} \rangle_{\alpha'}^\alpha \langle H_{\text{int}} \rangle_\beta^{\beta'} - \left( \langle H_{\text{int}} \rangle^2 \right)_\beta^{\beta'} \delta_{\alpha'}^\alpha \right\}, \quad (4.93)$$

where  $\rho_E^j$  are the eigenvalues of  $\rho_E(0)$  and  $\langle \cdots \rangle \equiv \text{Tr}_E(\rho_E(0) \cdots)$ .  $\Lambda$  contains important information on the directions of coherence loss. It has been implicitly defined previously [75], but only in the interaction (not Schrödinger) picture and for  $\langle H_{\text{int}} \rangle = 0$ .

If the following condition holds

$$\|\Lambda\| \tau \ll \|\mathcal{L}_{\text{eff}}\|, \quad (4.94)$$

then the short-time expansion of  $\mathcal{F}$  is valid and

$$\overline{\mathcal{F}}_\tau = -i\mathcal{L}_{\text{eff}} - \Lambda \tau, \quad (4.95)$$

which gives the final coarse-grained Markovian QME for the reduced density matrix

$$\frac{d\rho_S(t)}{dt} = (-i\mathcal{L}_{\text{eff}} - \Lambda \tau) \rho_S(t). \quad (4.96)$$

We have already said that this coarse-grained Markovian approximation is valid if the environmental relaxation time  $\tau$  is much smaller than the system relaxation time (corresponding to  $1/\|\Lambda\| \tau$ ), or

$$\|\Lambda\| \tau^2 \ll 1, \quad (4.97)$$

which, along with (4.94), gives in total

$$\|\Lambda\| \tau^2 \ll \min\{1, \|\mathcal{L}_{\text{eff}}\| \tau\}. \quad (4.98)$$

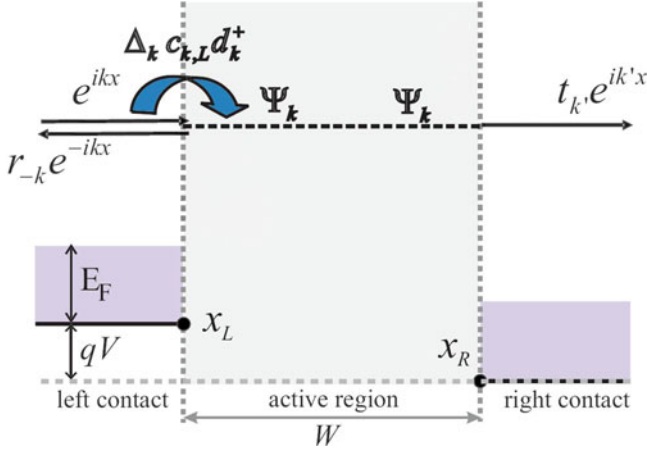
### 4.3 Steady State in a Two-Terminal Ballistic Nanostructure

In this section we will apply the main equation (4.96) to calculate the steady state distribution function for a two-terminal ballistic nanostructure attached to ideal contacts. By ideal contacts we mean contacts that behave like black bodies with respect to the emission/absorption of electrons. Therefore, they absorb all electrons coming from the open system. The consequence is that, as already mentioned, the occupation of states coming from the contacts is fixed by them, while the occupation of outgoing states is fixed by the open system. This gives a Landauer-type distribution function and specifically here, since the open system region is ballistic, the occupation of the incoming and outgoing states is the same and fixed by the injecting contact.

#### 4.3.1 The Open System Model

Schematic of our two-terminal nanostructure is shown in Fig. 4.4. The device is biased negatively such that the negative polarity is at the left contact. All open





**Fig. 4.4** Schematic of the two-terminal ballistic nanostructure, negatively biased at the *left* contact, with the boundaries between the open system and contacts shown at  $x_L$  and  $x_R$ , and with the graphical representation of the wave function injected from and the hoping type interaction with the *left* contact. It is similar for the wave function and interaction for the *right* contact

system eigenenergies  $\varepsilon_k$  above the bottom of the left contact have two eigenfunctions (double-degeneracy), one for the positive wave vector ( $\psi_k$ , injected from the left contact) and one for the negative wave vector ( $\psi_{-k}$ , injected from the right contact). The rest of the energy levels, made up of quasibound states that lay between the bottoms of the two contacts, have only one wave function for the states injected from the right contact and completely reflected. For doubly-degenerate scattering states we have the following asymptotic wave functions (assuming that the active region between  $x_L$  and  $x_R$  is wide enough)

$$\begin{aligned} \psi_k(x) &= \begin{cases} e^{ikx} + r_{-k,L}e^{-ikx}, & x < x_L \\ t_{k',L}e^{ik'x}, & x > x_R \end{cases}, \\ \psi_{-k}(x) &= \begin{cases} e^{-ik'x} + r_{k',L}e^{ik'x}, & x > x_R \\ t_{-k,L}e^{-ikx}, & x < x_L \end{cases}, \end{aligned} \quad (4.99)$$

where  $t$  and  $r$  are the transmission and reflection coefficients, respectively, while  $k$  and  $k'$  are the wave vectors for the same energy level  $\varepsilon_k$  measured from the bottom of the left and right contacts, respectively.

In the formalism of second quantization the non-interacting many-body Hamiltonian of the open system is given by (considering only scattering states in the following)

$$H_S = \sum_{k>0} \omega_k \left( d_k^\dagger d_k + d_{-k}^\dagger d_{-k} \right), \quad (4.100)$$

where  $\omega_k = \varepsilon_k/\hbar$  and  $d_{\pm k}$  and  $d_{\pm k}^\dagger$  are the destruction and creation operators, respectively, for the open system states  $\psi_{\pm k}$ . The many-body effect that this Hamiltonian is able to model is the Pauli exclusion principle. Considering that the contacts are ideal,

as explained above, the interaction Hamiltonian is modeled as a one-way coupling (for the particles that are injected only), while in the other way the electrons are free to propagate, because the contacts have ideal absorption characteristics. In other words, we do not have to enforce the Pauli exclusion principle (to “make room”) by explicitly creating one electron in the contacts after destroying it in the open system region. So, the interaction Hamiltonians are given by

$$\begin{aligned} H_{\text{int}}^L &= \sum_{k>0} \Delta_k d_k^\dagger c_{k,L} + \text{h.c.}, \\ H_{\text{int}}^R &= \sum_{k>0} \Delta_{-k} d_{-k}^\dagger c_{-k,R} + \text{h.c.}, \end{aligned} \quad (4.101)$$

where  $c_{\pm k,L/R}$  and  $c_{\pm k,L/R}^\dagger$  are the destruction and creation operators, respectively, for the  $\pm k$  states in the left/right contact and the injection rates are given by

$$\Delta_k = \frac{\hbar k}{m \|\psi_k\|^2}, \quad \Delta_{-k} = \frac{\hbar k'}{m \|\psi_{-k}\|^2}, \quad (4.102)$$

where  $\|\psi_k\|^2 = \int_{x_L}^{x_R} |\psi_k(x)|^2 dx$ .

In Fig. 4.4 there are only  $H_{\text{int}}^L$  and  $\psi_k$  graphically represented, but the situation is similar for the right contact.

### 4.3.2 Steady State Distribution Functions

Since the interaction Hamiltonians (4.101) are linear in the contact creation and destruction operators, we conclude that  $\langle H_{\text{int}}^{L/R} \rangle = 0$ , which gives us the following equations

$$\begin{aligned} \mathcal{L}_{\text{eff}} &= \mathcal{L}_S, \\ (\Lambda^{L/R})_{\alpha'\beta'}^{\alpha\beta} &= \frac{1}{2} \left[ \langle (H_{\text{int}}^{L/R})^2 \rangle_{\alpha'}^\alpha \delta_\beta^{\beta'} + \langle (H_{\text{int}}^{L/R})^2 \rangle_\beta^{\beta'} \delta_{\alpha'}^\alpha \right] \\ &\quad - \sum_{j,j'} (H_{\text{int}}^{L/R})_{j\alpha'}^{j'\alpha} \rho_{L/R}^j (H_{\text{int}}^{L/R})_{j'\beta}^{j\beta'}. \end{aligned} \quad (4.103)$$

The quantities that we need to evaluate first are (for the left contact)

$$\langle (H_{\text{int}}^L)^2 \rangle = \sum_{k>0} \Delta_k^2 \left[ f_k^L d_k d_k^\dagger + (1 - f_k^L) d_k^\dagger d_k \right], \quad (4.104)$$

which gives a contribution of the form  $\Lambda_{\alpha\beta}^{\alpha\beta}$ , and

$$\sum_{j,j'} (H_{\text{int}}^L)_{j\alpha'}^{j'\alpha} \rho_L^j (H_{\text{int}}^L)_{j'\beta}^{j\beta'} = \sum_{k>0} \Delta_k^2 \left[ (1 - f_k^L) (d_k^\dagger)_\beta^{\beta'} (d_k)_{\alpha'}^\alpha + f_k^L (d_k)_\beta^{\beta'} (d_k^\dagger)_{\alpha'}^\alpha \right], \quad (4.105)$$

which gives a contribution of the form  $\Lambda_{\beta\beta}^{\alpha\alpha}$ . It is similar for the right contact.

Quantities  $f_{\pm k}^{L/R}$  define the drifted Fermi–Dirac distribution function in the contacts, as a consequence of the current flowing through the device. They take into account the feedback of the device under applied bias on the contacts and ensure that the charge neutrality and current continuity are satisfied near the device/contacts boundaries [16, 17]. The left contact distribution function is given by

$$f_{\pm k}^L = \frac{1}{\exp\left\{\frac{\hbar^2[(\pm k - k_d)^2 - k_F^2]}{2mk_B T}\right\} + 1}, \quad (4.106)$$

where  $k_d$  is the drift wave vector. Here, there is a common  $k_d$  for both contacts (since they carry the same current), but in a more general multi-terminal case there will be one drift wave vector for each contact, defined by the current density  $J_l$  through the  $l$ -th contact by  $k_d^l = mJ_l/n_lq\hbar$ , where  $n_l$  is the charge density of the  $l$ -th contact. This is an additional parameter that has to be determined self-consistently, by an additional equation  $J_l^{dev} = J_l^{contact}$  that ensures the current continuity across the device/contacts boundaries (but not on a state-by-state basis). Here,  $J_l^{dev}$  is the current density due to the injection from the  $l$ -th contact only. There is a similar equation to (4.106) for the right contact with the following changes:  $k \rightarrow k'$  in the denominator and  $L \rightarrow R$ . Detailed Monte Carlo–molecular dynamics simulations in bulk semiconductors show that when electron–electron scattering is the dominant relaxation mechanism the distribution function is very close to the one given by (4.106) [74, 76, 77].

Since  $\Lambda = \sum_k \Lambda_k$ , according to (4.104) and (4.105), it is just a sum of independent modes. Each mode can be represented with a two-state basis: one state for a particle being in the state  $\psi_k$  (“+” state) and another state for a particle being absent from it (“−” state). The reduced density matrix in this basis is a column vector with four elements,  $\rho_{S,k} = (\rho_{S,k}^{++}, \rho_{S,k}^{+-}, \rho_{S,k}^{-+}, \rho_{S,k}^{--})^T$ , and the equation of motion is

$$\frac{d\rho_{S,k}}{dt} = [-i\mathcal{L}_{S,k} - \Lambda_k\tau] \rho_{S,k}, \quad (4.107)$$

where

$$\mathcal{L}_{S,k} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 2\omega_k & 0 & 0 \\ 0 & 0 & -2\omega_k & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}, \quad (4.108)$$

$$\Lambda_k = \begin{bmatrix} A_k & 0 & 0 & -B_k \\ 0 & C_k & 0 & 0 \\ 0 & 0 & C_k & 0 \\ -A_k & 0 & 0 & B_k \end{bmatrix}. \quad (4.109)$$

Quantities  $A_k = \Delta_k^2(1 - f_k^L)$ ,  $B_k = \Delta_k^2 f_k^L$  and  $C_k = (A_k + B_k)/2 = \Delta_k^2/2$  are calculated using (4.104) and (4.105).

The elements  $\rho_{S,k}^{+-}$  and  $\rho_{S,k}^{-+}$  are zero in the steady state, because they decay as  $\exp(\mp i2\omega_k - \tau C_k)t$ . The two remaining elements,  $\rho_{S,k}^{++} = f_k(t)$  and  $\rho_{S,k}^{--} = 1 - f_k(t)$ , give the following equation

$$\frac{f_k(t)}{dt} = -\tau(A_k + B_k)f_k(t) + \tau B_k = -\tau\Delta_k^2 f_k(t) + \tau\Delta_k^2 f_k^L, \quad (4.110)$$

where  $f_k(t)$  is the distribution function of  $+k$  states in the open system region. In the steady state, this gives just

$$\begin{aligned} f_k^\infty &= f_k^L, \\ f_{-k}^\infty &= f_{-k}^R, \end{aligned} \quad (4.111)$$

where  $f_{-k}^\infty$  is the steady state distribution function for  $-k$  states in the open system region, which can be derived in a similar way, starting by evaluating  $\langle (H_{\text{int}}^R)^2 \rangle$  and  $\sum_{j,j'} (H_{\text{int}}^R)_{j\alpha'}^{j'\alpha} \rho_{\text{int}}^j (H_{\text{int}}^R)_{j'\beta}^{j\beta'}$ . We see that the result is the distribution function for the scattering states of the ballistic open system determined by the injecting contact only, which is what it should be considering the problem that we were solving.

## 5 Conclusion

In this chapter we gave a review of several types of single-particle and reduced many-particle QMEs used in electronic transport. The density matrix is a quantum statistical concept introduced by John von Neumann in 1927 [21,22] and used to describe a mixed ensemble of states of some physical system. Since physical systems under consideration (electronic devices) are many-particle objects, it is extremely important to arrive at the form of the QME which is, on the one hand, sufficiently accurate in capturing important physical phenomena and, on the other hand, not too computationally complex for practical applications.

The single-particle QME of Sect. 2 is a special case of the reduced many-particle density matrix, where the reduction of the number of exactly described degrees of freedom is performed down to the single particle variables. It can be derived, similarly to the Boltzmann transport equation (BTE), by truncating the BBGKY chain of equations [2, 13]. In the case of electrons, this means that the transport is divided into periods of “free flight”, whose evolutions are determined by the single-particle Hamiltonian (usually including the kinetic energy and energies due to the external and Hartree potentials), and collisions with phonons and impurities in the Born–Markov approximation, represented by a linear collision superoperator (4.6). Within the context of the open system formalism the time-irreversible boundary conditions are required to maintain the stability of solutions (i.e. no growing exponentials) [3]. They can be incorporated through an explicit source term, that describes additional dynamics due to the coupling to the contacts/reservoirs, whose

form can only be determined phenomenologically (4.9). The PME (4.10), a closed single-particle QME for the diagonal elements of the density matrix in the basis of the single-particle Hamiltonian (with off-diagonal elements neglected), is applied to steady state transport in small devices [16, 17]. A single-electron/many-phonon QME within the perturbation expansion using the Dyson series (4.18), is applied to transients in bulk semiconductors beyond the Born–Markov approximation for scattering [18–20]. Because of the similarities between the single-particle QME and the BTE, the natural choice to solve the single-particle QME would be to use the Monte Carlo method, which is shown to be similar to the conventional ensemble Monte Carlo.

The reduced many-particle QME, as an equation of motion for the reduced many-particle density matrix within the open system formalism, provides a very good way to achieve the balance between the mathematical and physical rigor and practical applicability (computational complexity). The projection operator technique, applied to obtain the rigorous Nakajima–Zwanzig equation (4.26), is the starting point in this approach of Sect. 3. Several techniques are introduced that further modify the Nakajima–Zwanzig equation, making it more tractable. It is shown that in the Born–Markov approximation it yields the most general form of the generator of the quantum dynamical semigroup, the Lindblad form (4.37). The two most notable problems with the Nakajima–Zwanzig equation, the time-convoluted memory kernel and the need to carry all the degrees of freedom in the system through the calculation only to trace them out at the end, lead to the derivation of the conventional time-convolutionless equation of motion (4.48) and its further improvement, the partial-trace-free time-convolutionless equation of motion (4.73). The partial-trace-free approach is achieved at the expense of working in the specific basis, that diagonalizes the unity subspace of the projection operator, from the beginning. This is not a drawback since the numerical computation is our final goal. Using the partial-trace-free approach, at the end it was shown that by introducing the memory dressing  $\mathcal{R}(t)$  (4.77), which can be solved using the perturbation expansion [60], the final system of equations for the time evolution (4.78) and (4.79) are much more tractable.

Using the results of Sect. 3, it is shown in Sect. 4 how the Landauer-type steady state distribution functions can be obtained within the reduced many-particle density matrix formalism. Working within the limits of initially separable states [ $\rho(0) = \rho_E(0) \otimes \rho_S(0)$ ] and by using the coarse-graining procedure, the approximate Markovian QME (4.91) is derived. Since the steady state distribution functions are required, so that the exact transient behavior is not important, (4.91) provides an opportunity of deriving the generator of the time evolution in the limit of the short-time expansion, by assuming that the bias is ramped up in small increments separated by sufficiently long time intervals. The many-particle model Hamiltonian for coupling between the small ballistic open system and two large, ideal (“black-body”) reservoirs is developed and shown to yield the correct Landauer-type distribution functions for the open system, where the occupation of levels is set by the contacts only.

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