

## Appendix 7.A Derivation of the Quantum Master Equation

It is instructive to formally derive the quantum master equation [Eq. (7.4)] and see how the irreversible dynamics of the reduced system emerges from the reversible dynamics generated by the Hamiltonian of a macroscopic total system. In this appendix, we provide such a derivation and explicitly show the approximations involved in deriving the quantum master equation.

We start from the quantum Liouville equation ( $\hbar = 1$ ) that describes the density matrix  $\rho(t)$  of a total system with Hamiltonian  $H$

$$\begin{aligned}\dot{\rho}(t) &= -i[H, \rho(t)] \\ &= -i\mathcal{L}\rho(t),\end{aligned}\tag{7.17}$$

where we have defined the Liouville superoperator as the commutator of the Hamiltonian with an arbitrary operator  $\mathcal{O}$ ,  $\mathcal{L}\mathcal{O} = [H, \mathcal{O}]$ . In the Laplace space ( $t \rightarrow s$ ), the Liouville equation is

$$s\tilde{\rho}(s) = \rho(0) - i\mathcal{L}\tilde{\rho}(s),\tag{7.18}$$

where  $\tilde{\rho}(s)$  is the Laplace transform of  $\rho(t)$ , and  $\rho(0)$  is the initial condition of the total system. Equation (7.18) provides the formal solution of the Liouville equation in the Laplace space,  $\tilde{\rho}(s) = \frac{1}{s+i\mathcal{L}}\rho(0)$ . Note that  $\frac{1}{s+i\mathcal{L}}$  is a superoperator and should be interpreted as the inverse of  $(s + i\mathcal{L})$ .

In most physical applications, we are only interested in properties that are determined by states in a subspace of the total Hilbert space. Using a projection operator  $\mathcal{P}$ , we divide the density matrix of the total system into a relevant part  $\rho_1(t) = \mathcal{P}\rho(t)$ , and an irrelevant part  $\rho_2(t) = (1 - \mathcal{P})\rho(t) \equiv \mathcal{Q}\rho(t)$ , so that  $\rho(t) = \rho_1(t) + \rho_2(t)$ . Note

that by definition, projectors  $\mathcal{P}$  and  $\mathcal{Q}$  must satisfy  $\mathcal{P}\mathcal{P}\dots\mathcal{P} = \mathcal{P}$ ,  $\mathcal{Q}\mathcal{Q}\dots\mathcal{Q} = \mathcal{Q}$ , and  $\mathcal{P}\mathcal{Q} = \mathcal{Q}\mathcal{P} = 0$ . Applying  $\mathcal{P}$  and  $\mathcal{Q}$  to both sides of Eq. (7.18), we obtain two coupled linear equations:

$$\begin{aligned} s\tilde{\rho}_1(s) - \rho_1(0) &= -i\mathcal{P}\mathcal{L}[\tilde{\rho}_1(s) + \tilde{\rho}_2(s)], \\ s\tilde{\rho}_2(s) - \rho_2(0) &= -i\mathcal{Q}\mathcal{L}[\tilde{\rho}_1(s) + \tilde{\rho}_2(s)]. \end{aligned}$$

These equations can be solved to obtain the formal solution for the relevant part of the density matrix in the Laplace space,

$$s\tilde{\rho}_s(s) - \rho_s(0) = -i\mathcal{P}\mathcal{L}\tilde{\rho}_s(s) - i\mathcal{P}\mathcal{L}\frac{1}{s+i\mathcal{Q}\mathcal{L}}\rho_b(0) - \mathcal{P}\mathcal{L}\frac{1}{s+i\mathcal{Q}\mathcal{L}}\mathcal{Q}\mathcal{L}\tilde{\rho}_s(s). \quad (7.19)$$

The inverse Laplace transform of Eq. (7.19) yields the following differential-integral equation that describes the time evolution of  $\rho_1(t)$ :

$$\dot{\rho}_1(t) = -i\mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}t}\rho_2(0) - i\mathcal{P}\mathcal{L}\rho_1(t) - \int_0^t d\tau\mathcal{K}(\tau)\rho_1(t-\tau), \quad (7.20)$$

where we have defined the memory kernel

$$\mathcal{K}(\tau) = \mathcal{P}\mathcal{L}e^{-i\mathcal{Q}\mathcal{L}\tau}\mathcal{Q}\mathcal{L}. \quad (7.21)$$

The first term in the right hand side of Eq. (7.20) explicitly depends on the initial condition of the irrelevant part of the total system  $\rho_2(0)$ . However, by choosing an initial condition so that  $\mathcal{P}\rho(0) = \rho(0)$ , we can make  $\rho_2(0) = 0$ , and the  $\rho_2(0)$  term will vanish identically. For example, the projection operator defined in Eq. (7.1) and the product state initial condition defined in Eq. (7.3) satisfy this condition. Hence, by selecting a proper combination of projector and initial conditions, Eq. (7.20) can be simplified to

$$\dot{\rho}_1(t) = -i\mathcal{P}\mathcal{L}\rho_1(t) - \int_0^t d\tau \mathcal{K}(\tau)\rho_1(t-\tau). \quad (7.22)$$

Equation (7.22) has a non-Markovian memory kernel, and is in the form of a generalized Fokker-Planck equation. The first term in Eq. (7.22) represents the unitary evolution governed by the Hamiltonian of the system, and the second term represents the dissipative dynamics of the relevant part of the total system. Note that total system still undergoes unitary evolution [Eq. (7.17)], it is the reduced system degrees of freedom (after tracing out the environment degrees of freedom) that have to be described by a non-unitary evolution. Clearly, the non-unitary evolution is a result of the separation of the total system into the system part and the bath part.

To derive the dynamics of a reduced system, we separate the total Hamiltonian  $H$  into the system part  $H_S$ , the bath part  $H_B$ , and the system-bath interaction part  $\lambda H_{SB}$ . We also require that  $H_S$  and  $H_B$  operate in two different Hilbert spaces, so that their commutator vanishes,  $[H_S, H_B] = 0$ . The corresponding Liouville operator can be decomposed accordingly:

$$\mathcal{L} = \mathcal{L}_S + \mathcal{L}_B + \lambda\mathcal{L}_{SB}. \quad (7.23)$$

In addition, we also define the projection operators  $\mathcal{P}$  and  $\mathcal{Q} = 1 - \mathcal{P}$  using

$$\mathcal{P}\rho = \rho_b^{eq} \text{Tr}_B \rho. \quad (7.24)$$

Note that the projector in Eq. (7.24) not only defines the relevant part of the total system by tracing out the irrelevant part, it also provides a definition for the temperature of the system. Eq. (7.24) is a convenient choice of projector, but this form is not required. Other projection operators can be chosen [23, 24]. With the definition in Eq. (7.24), the projector  $\mathcal{P}$  and the Liouville operators satisfy the equalities  $\mathcal{L}_B\mathcal{P} = \mathcal{P}\mathcal{L}_B = 0$ ,  $\mathcal{P}\mathcal{L}_S\mathcal{Q} = \mathcal{Q}\mathcal{L}_S\mathcal{P} = 0$ , and  $\mathcal{P}\mathcal{L}_{SB}\mathcal{P} = 0$ . The last equality is true if the thermal average of  $H_{SB}$  over the equilibrium bath states is zero,  $\langle H_{SB} \rangle_{eq} = 0$

(where  $\langle \dots \rangle_{eq}$  denotes  $\text{Tr}_B\{\dots\rho_b^{eq}\}$ ). Note that for any Hamiltonian with  $\langle H_{SB} \rangle_{eq} \neq 0$ , we can always absorb the average into  $H_S$  and obtain a new interaction term with vanishing average,  $H'_{SB} = H_{SB} - \langle H_{SB} \rangle_{eq}$ , therefore, the condition to establish the equality  $\mathcal{P}\mathcal{L}_{SB}\mathcal{P} = 0$  can always be achieved. For simplicity, we assume  $\langle H_{SB} \rangle_{eq} = 0$  hereafter. Plugging Eq. (7.23) into Eq. (7.22) and applying the equalities, we obtain the equation of motion for the reduced system after tracing out the irrelevant bath degrees of freedom:

$$\begin{aligned} \dot{\sigma}(t) &= \text{Tr}_B \dot{\rho}_1(t) \\ &= -i\mathcal{L}_s\sigma(t) - \lambda^2 \int_0^t d\tau \text{Tr}_B \{ \mathcal{L}_{SB} e^{-i\mathcal{Q}\mathcal{L}\tau} \mathcal{Q}\mathcal{L}_{SB}\rho_b^{eq} \} \sigma(t-\tau). \end{aligned} \quad (7.25)$$

Equation (7.25) describes the dynamics of the reduced system under the initial condition  $\rho(0) = \sigma(0) \otimes \rho_b^{eq}$ , and is often called the “generalized master equation” [3]. Note that Eq. (7.22) is still exact, provided that the proper projectors and equilibrium bath initial conditions are used. In fact, up to this point we did nothing but reformulating the Liouville equation. Equation (7.25) is of little use because solving the propagator  $e^{-i\mathcal{Q}\mathcal{L}\tau}$  in the memory kernel is as difficult as solving the original Liouville equation, but this equation is a convenient starting point for the derivations of many useful quantum master equations.

To derive Eq. (7.4), we need to apply two approximations. The first one is to replace the full propagator  $e^{-i\mathcal{Q}\mathcal{L}\tau}$  in the memory kernel with the zeroth order propagator  $e^{-i\mathcal{Q}(\mathcal{L}_S + \mathcal{L}_B)\tau}$ , which effectively neglects terms beyond second order in  $\lambda$  in  $\mathcal{K}(\tau)$ . This approximation is similar to the Born approximation usually used in the scattering theory. The second one is to replace  $\sigma(t-\tau)$  in the integral with  $e^{iH_S\tau}\sigma(t)e^{-iH_S\tau}$ , which makes the integral time-convolutionless and is effectively the partial ordering prescription (POP) used in the generalized cumulant expansion methods [5, 6]. If the second approximation is not made, then the integral retains the time-convolution  $\rho(t-\tau)$  term, which is sometimes called the chronological ordering prescription (COP) [4, 6]. Note that the two approximations both assume weak system-bath interactions,

i.e.  $\lambda \ll 1$ . In the  $\lambda \ll 1$  limit, both approximations are valid and we obtain from Eq. (7.25)

$$\dot{\sigma}(t) = -i[H_S, \sigma(t)] - \lambda^2 \int_0^t d\tau \text{Tr}_B \{ [H_{SB}, [H_{SB}(-\tau), \sigma(t) \otimes \rho_b^{eq}]] \}. \quad (7.26)$$

To explicitly evaluate the trace over the bath degrees of freedoms, we consider a generic product form for  $H_{SB}$ :

$$H_{SB} = \sum_{n,\alpha} S_n \otimes B_\alpha,$$

where  $S_n$  are an system operators, and  $B_\alpha$  are bath operators, so that  $[S_n, B_\alpha] = 0$ . Substitution of  $H_{SB}$  in Eq. (7.26) yields

$$\begin{aligned} \dot{\sigma}(t) = & -i[H_S, \sigma(t)] \\ & - \frac{1}{2} \lambda^2 \int_0^t d\tau \sum_{n,n',\alpha,\alpha'} \{ [\langle B_{\alpha'}(-\tau) B_\alpha \rangle_{eq} + \langle B_\alpha B_{\alpha'}(-\tau) \rangle_{eq}] [S_n, [e^{-iH_S\tau} S_{n'} e^{iH_S\tau}, \sigma(t)]] \\ & - [\langle B_{\alpha'}(-\tau) B_\alpha \rangle_{eq} - \langle B_\alpha B_{\alpha'}(-\tau) \rangle_{eq}] [S_n, [e^{-iH_S\tau} S_{n'} e^{iH_S\tau}, \sigma(t)]_+] \}. \end{aligned} \quad (7.27)$$

where  $[...]_+$  denotes the anticommutator.

Finally, we define bath correlation functions

$$C_{\alpha'\alpha}(\tau) = \langle B_{\alpha'}(\tau) B_\alpha \rangle_{eq} = \Gamma_r^{\alpha'\alpha}(\tau) + i\Gamma_i^{\alpha'\alpha}(\tau), \quad (7.28)$$

where  $\Gamma_r^{\alpha'\alpha}(\tau)$  and  $\Gamma_i^{\alpha'\alpha}(\tau)$  are real functions representing the real part and the imaginary part of the correlation functions, respectively. Using the definitions in Eq. (7.28) and the symmetry properties of quantum correlation functions,

$$\langle B_\alpha B_{\alpha'}(\tau) \rangle_{eq} = \langle B_{\alpha'}(\tau) B_\alpha \rangle_{eq}^* = \Gamma_r^{\alpha'\alpha}(\tau) - i\Gamma_i^{\alpha'\alpha}(\tau),$$

we obtain

$$\begin{aligned} \dot{\sigma}(t) = & -i[H_S, \sigma(t)] - \lambda^2 \int_0^t d\tau \sum_{n, n', \alpha, \alpha'} \left\{ \Gamma_r^{\alpha' \alpha}(-\tau) [S_n, [e^{-iH_S \tau} S_{n'} e^{iH_S \tau}, \sigma(t)]] \right. \\ & \left. - i\Gamma_i^{\alpha' \alpha}(-\tau) [S_n, [e^{-iH_S \tau} S_{n'} e^{iH_S \tau}, \sigma(t)]_+] \right\}, \end{aligned} \quad (7.29)$$

which is the non-Markovian quantum master equation shown in Eq. (7.4). This is an equation for  $\sigma(t)$  along, and the influence of the bath on the system is formulated through the bath correlation functions. The bath correlation functions, which are equilibrium properties of the bath, determine the non-equilibrium dynamics of the system. Note that no fast bath relaxation time has been assumed yet; the only assumptions made in deriving Eq. (7.4) are the equilibrium bath at the initial time and the weak system-bath interaction.