

Chapter 4

Technical Tools

Abstract This chapter provides tools that are useful for the solution and handling of master equations. We start with simple analytic approaches including the equation of motion technique and the quantum regression theorem. As numerical techniques, we investigate a Runge–Kutta solver applied to a master equation and introduce the stochastic Schrödinger equation. For rate equations obeying local detailed balance, we treat the evolution of the Shannon entropy and connect it to the full counting statistics. We show how the statistics of energy and matter transfers can be extracted from the master equation. In particular, we demonstrate how the moments and cumulants of the corresponding distributions can be obtained. Finally, we relate symmetries in the respective generating functions with the fluctuation theorem for entropy production. The methods in this chapter may also be applied to Markovian master equations that are not in Lindblad form; only constant coefficients and a time-local evolution equation for the density matrix are required.

4.1 Analytic Techniques for Solving Master Equations

Trivially, as the superoperator notation in Sect. 1.6 allows us to write master equations as systems of ordinary coupled differential equations with constant coefficients, we may obtain the solution of the master equation by exponentiating the Liouvillian superoperator

$$\rho(t) = e^{\mathcal{L}t} \rho_0. \tag{4.1}$$

This is usually quite difficult and constrained to very small dimensions of \mathcal{L} . In addition, since the Liouville superoperator \mathcal{L} is not hermitian, it need not even have a spectral decomposition.

Exercise 4.1 (Single resonant level) Calculate the matrix exponential of the Liouvillian superoperator for a single resonant level tunnel-coupled to a single junction

$$\mathcal{L} = \begin{pmatrix} -\Gamma f & +\Gamma(1-f) \\ +\Gamma f & -\Gamma(1-f) \end{pmatrix}$$

when the dot level is much lower than the Fermi edge ($f \rightarrow 1$) and when it is much larger than the Fermi edge $f \rightarrow 0$.

Thus, solving the master equation by brute force is usually not advisable.

4.1.1 Laplace Transform

If one is only interested in stationary properties, it is often useful to obtain the formal solution by performing a Laplace transform, $\tilde{\rho}(z) = \int_0^\infty \rho(t)e^{-zt} dt$. In frequency space, the master equation is then reduced to an algebraic problem, which may readily be solved by

$$\tilde{\rho}(z) = \frac{1}{z \cdot \mathbf{1} - \mathcal{L}} \rho_0, \quad (4.2)$$

where ρ_0 is just the initial state. This just requires the computation of the inverse of $z \cdot \mathbf{1} - \mathcal{L}$, which is significantly less demanding than exponentiating a matrix. The main obstacle however is the calculation of the inverse Laplace transform, which requires one to identify the poles of $[z \cdot \mathbf{1} - \mathcal{L}]^{-1}$. In cases where one is only interested in stationary values, it can be useful to compute the steady-state values of observables by exploiting properties of the Laplace transform: the long-time limit of a function in the time domain can be obtained from a small- z limit in the frequency domain, $\lim_{t \rightarrow \infty} f(t) = \lim_{z \rightarrow 0} z \tilde{f}(z)$. Applied to an observable, this yields

$$\langle \bar{A} \rangle = \text{Tr}\{A\bar{\rho}\} = \lim_{z \rightarrow 0} z \text{Tr}\{A\tilde{\rho}(z)\} = \lim_{z \rightarrow 0} z \text{Tr}\left\{A \frac{1}{z \cdot \mathbf{1} - \mathcal{L}} \rho_0\right\}, \quad (4.3)$$

such that the trace can be performed in frequency space, which may sometimes yield significant simplifications.

4.1.2 Equation of Motion Technique

Instead of solving the master equation for the density matrix, it may be more favorable to derive a related linear set of first-order differential equations for observables $\langle B_i \rangle(t)$ of interest instead. In fact, for infinitely large system Hilbert space dimensions such a procedure might even be necessary:

$$\begin{aligned} \langle \dot{B}_i(t) \rangle &= \text{Tr}\{B_i \mathcal{L} \rho(t)\} \\ &= -i \text{Tr}\{B_i [H, \rho(t)]\} + \sum_{\alpha} \gamma_{\alpha} \text{Tr}\left\{B_i \left(L_{\alpha} \rho(t) L_{\alpha}^{\dagger} - \frac{1}{2} \{L_{\alpha}^{\dagger} L_{\alpha}, \rho(t)\}\right)\right\} \end{aligned}$$

$$\begin{aligned}
&= \text{Tr} \left\{ \left(+i[H, B_i] + \sum_{\alpha} \gamma_{\alpha} \left[L_{\alpha}^{\dagger} B_i L_{\alpha} - \frac{1}{2} \{ L_{\alpha}^{\dagger} L_{\alpha}, B_i \} \right] \right) \rho(t) \right\} \\
&= \text{Tr} \left\{ \left[\sum_j G_{ij} B_j \right] \rho(t) \right\} = \sum_j G_{ij} \langle B_j(t) \rangle,
\end{aligned} \tag{4.4}$$

where in the last line we have used the fact that there is for a finite-dimensional system Hilbert space only a finite set of linearly independent operators. The linear coefficients G_{ij} have to be found for each master equation separately. The advantage is that, for well-chosen sets of operators, one can hope to end up with a much smaller set of equations than are necessary for solving the complete master equation. For example, this is the case when the matrix G_{ij} has a block structure.

Exercise 4.2 (Equation of motion for the harmonic oscillator) Calculate the expectation value of $a + a^{\dagger}$ for a cavity in a vacuum bath

$$\dot{\rho} = -i[H, \rho] + \gamma \left[a \rho a^{\dagger} - \frac{1}{2} \{ a^{\dagger} a, \rho \} \right]. \tag{4.5}$$

4.1.3 Quantum Regression Theorem

As with the Heisenberg picture for closed quantum systems, it may be favorable to keep the density matrix as constant and to shift the complete time dependence to the operators. From Eq. (4.4) we can conclude for the operators that

$$\begin{aligned}
\dot{B}_i(t) &= \mathcal{L}^{\dagger} B_i(t) = +i[H, B_i(t)] + \sum_{\alpha} \gamma_{\alpha} \left[L_{\alpha}^{\dagger} B_i(t) L_{\alpha} - \frac{1}{2} \{ L_{\alpha}^{\dagger} L_{\alpha}, B_i(t) \} \right] \\
&= \sum_j G_{ij} B_j(t),
\end{aligned} \tag{4.6}$$

where we have introduced the adjoint Liouvillian \mathcal{L}^{\dagger} . For open quantum systems, it is however often important to calculate the expectation values of operators at different times, which may be facilitated with the help of the quantum regression theorem. We find directly from properties of the matrix exponential that

$$\frac{d}{d\tau} B_i(t + \tau) = \mathcal{L}^{\dagger} B_i(t + \tau) = \sum_j G_{ij} B_j(t + \tau). \tag{4.7}$$

Using this relation, we find the quantum regression theorem for two-point correlation functions.

Definition 4.1 (Quantum regression) Let single observables follow the closed equation $\langle \dot{B}_i \rangle = \sum_j G_{ij} \langle B_j \rangle$. Then, the two-point correlation functions obey the equation

tions

$$\frac{d}{d\tau} \langle B_i(t + \tau) B_\ell(t) \rangle = \sum_j G_{ij} \langle B_j(t + \tau) B_\ell(t) \rangle \quad (4.8)$$

with exactly the same coefficient matrix G_{ij} .

The advantage of the quantum regression theorem is that it enables the calculation of expressions for two-point correlation functions just from the evolution of single-operator correlation functions.

Let us consider the example of a single electron transistor (SET) at infinite bias ($f_L \rightarrow 1$ and $f_R \rightarrow 0$). The single-operator expectation values obey

$$\frac{d}{dt} \begin{pmatrix} \langle dd^\dagger(t) \rangle \\ \langle d^\dagger d(t) \rangle \end{pmatrix} = \begin{pmatrix} -\Gamma_L & +\Gamma_R \\ +\Gamma_L & -\Gamma_R \end{pmatrix} \begin{pmatrix} \langle dd^\dagger(t) \rangle \\ \langle d^\dagger d(t) \rangle \end{pmatrix}, \quad (4.9)$$

such that the quantum regression theorem tells us that

$$\frac{d}{d\tau} \begin{pmatrix} \langle dd^\dagger(t + \tau) d^\dagger d(t) \rangle \\ \langle d^\dagger d(t + \tau) d^\dagger d(t) \rangle \end{pmatrix} = \begin{pmatrix} -\Gamma_L & +\Gamma_R \\ +\Gamma_L & -\Gamma_R \end{pmatrix} \begin{pmatrix} \langle dd^\dagger(t + \tau) d^\dagger d(t) \rangle \\ \langle d^\dagger d(t + \tau) d^\dagger d(t) \rangle \end{pmatrix}. \quad (4.10)$$

4.2 Numerical Techniques for Solving Master Equations

Numerical techniques are applicable when analytic methods fail or would require comparably large efforts. We will just discuss two popular approaches here.

4.2.1 Numerical Integration

Numerical integration is generally performed by discretizing time into sufficiently small steps. Note that there are different discretization schemes, e.g., explicit ones,

$$\frac{\rho(t + \Delta t) - \rho(t)}{\Delta t} = \mathcal{L} \rho(t), \quad (4.11)$$

where the right-hand side depends on time t , and implicit ones, such as

$$\frac{\rho(t + \Delta t) - \rho(t)}{\Delta t} = \mathcal{L} \frac{1}{2} [\rho(t) + \rho(t + \Delta t)]. \quad (4.12)$$

Whereas it is straightforward to solve the explicit scheme for $\rho(t + \Delta t)$, in the implicit scheme this would require matrix inversion. Thus, the differential equation is mapped to an iteration equation that maps the density matrix from time t to time $t + \Delta t$. As a rule of thumb, explicit schemes are easy to implement but may be

numerically unstable (i.e., an adaptive stepsize may be required to prevent the solution from exploding) [1]. In contrast, implicit schemes are usually more stable but require a lot of effort to propagate the solution. Here, we will just discuss a fourth-order Runge–Kutta solver [2].

In order to propagate a density matrix ρ_n at time t to the density matrix ρ_{n+1} at time $t + \Delta t$, the fourth-order Runge–Kutta scheme requires the evaluation of four intermediate values $\sigma_{n,1}$, $\sigma_{n,2}$, $\sigma_{n,3}$, and $\sigma_{n,4}$ that can be successively computed from ρ_n by applying a single multiplication with the Liouvillian \mathcal{L} . The density matrix at time $t + \Delta t$ is then obtained from these auxiliary intermediate values. Explicitly, the Runge–Kutta algorithm is given by

$$\begin{aligned}
 \sigma_{n,1} &= \Delta t \mathcal{L} \rho_n, \\
 \sigma_{n,2} &= \Delta t \mathcal{L} \left(\rho_n + \frac{1}{2} \sigma_{n,1} \right), \\
 \sigma_{n,3} &= \Delta t \mathcal{L} \left(\rho_n + \frac{1}{2} \sigma_{n,2} \right), \\
 \sigma_{n,4} &= \Delta t \mathcal{L} (\rho_n + \sigma_{n,3}), \\
 \rho_{n+1} &= \rho_n + \frac{1}{6} \sigma_{n,1} + \frac{1}{3} \sigma_{n,2} + \frac{1}{3} \sigma_{n,3} + \frac{1}{6} \sigma_{n,4} + \mathcal{O}\{\Delta t^5\}.
 \end{aligned} \tag{4.13}$$

This explicit scheme requires four matrix-vector multiplications per time step. It should always be used in combination with an adaptive stepsize, which can be controlled by comparing (e.g., by computing the norm of the difference) the result from two successive propagations with stepsize Δt with the result of a single propagation with stepsize $2\Delta t$. If the difference exceeds a predefined error bound, the stepsize must be reduced (and the intermediate result should be discarded). If it is not too large, the result can always be accepted. If the error estimate is much smaller than the error bound, one can cautiously increase the time step. In particular when the matrix-vector multiplication is costly, this will save precious computation time. Thus, the required computational overhead of 50 % for an adaptive stepsize is well justified.

Exercise 4.3 (Order of the Runge–Kutta scheme) Acting with the Liouville superoperator performs the time derivative of the density matrix. Show that the presented scheme (4.13) is of fourth order in Δt , i.e., that

$$\rho_{n+1} = \left[\mathbf{1} + \mathcal{L} \Delta t + \mathcal{L}^2 \frac{\Delta t^2}{2!} + \mathcal{L}^3 \frac{\Delta t^3}{3!} + \mathcal{L}^4 \frac{\Delta t^4}{4!} \right] \rho_n + \mathcal{O}\{\Delta t\}^5.$$

If the Liouvillian \mathcal{L} does not have a special structure, the Runge–Kutta scheme requires one to store the $N \times N$ density matrix completely. Since N scales exponentially with the size of the system, this may be quite demanding—if not impossible for larger quantum systems.

4.2.2 Simulation as a Piecewise Deterministic Process (PDP)

Suppose we would like to solve the Lindblad form master equation (in diagonal representation)

$$\dot{\rho} = -i[H, \rho] + \sum_{\alpha} \gamma_{\alpha} \left[L_{\alpha} \rho L_{\alpha}^{\dagger} - \frac{1}{2} \{ \rho, L_{\alpha}^{\dagger} L_{\alpha} \} \right] \quad (4.14)$$

numerically, but we are not able to store the N^2 matrix elements of the density matrix nor to write the master equation in a simpler (e.g., rate equation or block structure) representation.

If it is possible to store at least N states, the master equation can be unraveled to a piecewise deterministic process (PDP) for a pure quantum state. The advantage here lies in the fact that a pure state requires only N complex observables to be evolved.

Consider the nonlinear but deterministic equation

$$|\dot{\Psi}\rangle = -i \left[H - \frac{i}{2} \sum_{\alpha} \gamma_{\alpha} L_{\alpha}^{\dagger} L_{\alpha} \right] |\Psi\rangle + \frac{1}{2} \left[\sum_{\alpha} \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle \right] |\Psi\rangle. \quad (4.15)$$

Although this is nonlinear in $|\Psi(t)\rangle$, one can show that the solution is given by

$$|\Psi\rangle = \frac{e^{-iMt} |\Psi_0\rangle}{\langle \Psi_0 | e^{+iM^{\dagger}t} e^{-iMt} | \Psi_0 \rangle^{1/2}}, \quad (4.16)$$

where we have used the operator $M = H - \frac{i}{2} \sum_{\alpha} \gamma_{\alpha} L_{\alpha}^{\dagger} L_{\alpha}$, which is also often termed the non-hermitian Hamiltonian.

Exercise 4.4 (Norm for continuous evolution) Calculate the norm of the state vector $\langle \Psi(t) | \Psi(t) \rangle$ from Eq. (4.16).

We show the validity of the solution by differentiation

$$\begin{aligned} |\dot{\Psi}\rangle &= -iM|\Psi\rangle - \frac{1}{2} \frac{e^{-iMt} |\Psi_0\rangle}{\langle \Psi_0 | e^{+iM^{\dagger}t} e^{-iMt} | \Psi_0 \rangle^{3/2}} \\ &\quad \times i \left[\langle \Psi_0 | e^{+iM^{\dagger}t} M^{\dagger} e^{-iMt} | \Psi_0 \rangle - \langle \Psi_0 | e^{+iM^{\dagger}t} M e^{-iMt} | \Psi_0 \rangle \right] \\ &= -iM|\Psi\rangle - \frac{1}{2} \frac{e^{-iMt} |\Psi_0\rangle}{\langle \Psi_0 | e^{+iM^{\dagger}t} e^{-iMt} | \Psi_0 \rangle^{3/2}} i \langle \Psi_0 | e^{+iM^{\dagger}t} [M^{\dagger} - M] e^{-iMt} | \Psi_0 \rangle \\ &= -iM|\Psi\rangle + \frac{1}{2} \frac{e^{-iMt} |\Psi_0\rangle}{\langle \Psi_0 | e^{+iM^{\dagger}t} e^{-iMt} | \Psi_0 \rangle^{3/2}} \sum_{\alpha} \gamma_{\alpha} \langle \Psi_0 | e^{+iM^{\dagger}t} L_{\alpha}^{\dagger} L_{\alpha} e^{-iMt} | \Psi_0 \rangle \\ &= -iM|\Psi\rangle + \frac{1}{2} |\Psi\rangle \sum_{\alpha} \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle. \end{aligned} \quad (4.17)$$

However, the name PDP already suggests that the process is only piecewise deterministic. To reproduce the original Lindblad dynamics, the continuous evolution (4.16) must be interrupted by stochastic events. The total probability that a jump of the wave function will occur in the infinitesimal interval $[t, t + \Delta t]$ is given by

$$P_{\text{jump}} = \Delta t \sum_{\alpha} \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle. \quad (4.18)$$

That is, if a jump has occurred, one still has to decide which jump. Choosing a particular jump

$$|\Psi\rangle \rightarrow \frac{L_{\alpha} |\Psi\rangle}{\sqrt{\langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle}} \quad (4.19)$$

is performed randomly with conditional probability

$$P_{\alpha} = \frac{\gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle}{\sum_{\alpha} \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle}, \quad (4.20)$$

where the normalization is obvious. This recipe for deterministic (continuous) and jump evolutions may also be written as a single stochastic differential equation, which is often called the stochastic Schrödinger equation [3].

Definition 4.2 (Stochastic Schrödinger equation) A Lindblad-type master equation of the form

$$\dot{\rho} = -i[H, \rho] + \sum_{\alpha} \gamma_{\alpha} \left[L_{\alpha} \rho L_{\alpha}^{\dagger} - \frac{1}{2} \{ \rho, L_{\alpha}^{\dagger} L_{\alpha} \} \right] \quad (4.21)$$

can be effectively modeled by the stochastic differential equation

$$\begin{aligned} |d\Psi\rangle = & \left[-iH - \frac{1}{2} \sum_{\alpha} \gamma_{\alpha} L_{\alpha}^{\dagger} L_{\alpha} + \frac{1}{2} \sum_{\alpha} \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle \right] |\Psi\rangle dt \\ & + \sum_{\alpha} \left(\frac{L_{\alpha} |\Psi\rangle}{\sqrt{\langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle}} - |\Psi\rangle \right) dN_{\alpha}, \end{aligned} \quad (4.22)$$

where the Poisson increments dN_{α} satisfy

$$dN_{\alpha} dN_{\beta} = \delta_{\alpha\beta} dN_{\alpha}, \quad \mathcal{E}(dN_{\alpha}) = \gamma_{\alpha} \langle \Psi | L_{\alpha}^{\dagger} L_{\alpha} | \Psi \rangle dt \quad (4.23)$$

and $\mathcal{E}(x)$ denotes the classical expectation value (ensemble average).

The last two equations simply mean that at most a single jump can occur at once (practically we have $dN_{\alpha} \in \{0, 1\}$) and that the probability for a jump at time t is

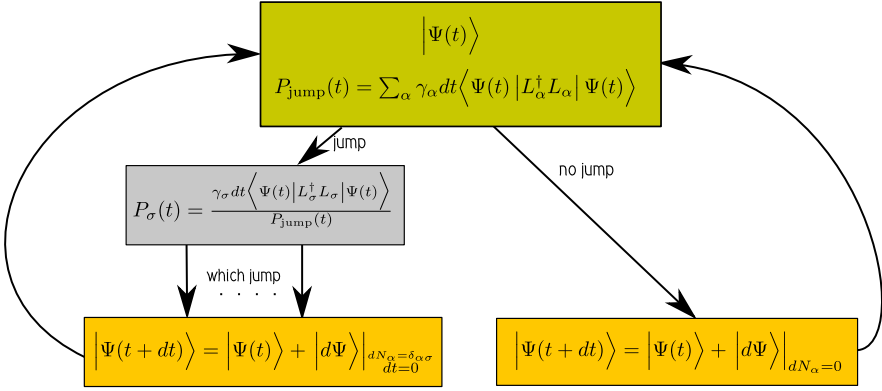


Fig. 4.1 Recipe for propagating the stochastic Schrödinger equation in Definition 4.2. At time t , one calculates the total probability of a jump P_{jump} occurring during the interval $[t, t + \Delta t]$. A random number generator is used to determine whether a jump should occur or not. Given that a jump occurs, one determines which type of jump by drawing another random number: setting the particular $dN_\alpha = 1$ and $dt = 0$, one solves the stochastic Schrödinger equation for $|\Psi(t + \Delta t)\rangle = |\Psi(t)\rangle + |d\Psi(t)\rangle \stackrel{\alpha}{=} L_\alpha |\Psi(t)\rangle / \sqrt{\langle \Psi(t) | L_\alpha^\dagger L_\alpha | \Psi(t) \rangle}$ and proceeds with the next time step. Given that no jump occurs, one sets $dN_\alpha = 0$ for all α , solves the stochastic Schrödinger equation for $|\Psi(t + \Delta t)\rangle = |\Psi(t)\rangle + |d\Psi(t)\rangle$, and proceeds with the next time step

given by $P_\alpha = \gamma_\alpha \langle \Psi | L_\alpha^\dagger L_\alpha | \Psi \rangle dt$. Numerically, it constitutes a simple recipe; see Fig. 4.1. Altogether, the description in terms of a stochastic differential equation in Definition 4.2 simply combines the smooth evolution according to the nonlinear Schrödinger equation (4.15) with stochastic jumps. The concept can be extended beyond Lindblad master equations [4, 5].

It remains to be shown that this PDP is actually an unraveling of the master equation; i.e., that the expectation value of the operator $\hat{\pi} = |\Psi\rangle\langle\Psi|$, also called the covariance matrix,

$$\rho = \mathcal{E}(\hat{\pi}) = \mathcal{E}(|\Psi\rangle\langle\Psi|), \quad (4.24)$$

fulfills the original Lindblad-type master equation. Then, ensemble averages of all trajectories will also obey the Lindblad dynamics. To show this, we first note that $\langle \Psi | L_\alpha^\dagger L_\alpha | \Psi \rangle = \text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\}$. The change of the covariance matrix is given by

$$d\hat{\pi} = |d\Psi\rangle\langle\Psi| + |\Psi\rangle\langle d\Psi| + |d\Psi\rangle\langle d\Psi|. \quad (4.25)$$

Note that the last term cannot be neglected completely, since the term $\mathcal{E}(dN_\alpha dN_\beta)$ is not necessarily small. Making everything explicit, we obtain

$$\begin{aligned} d\hat{\pi} = & +dt \left\{ -i[H, \hat{\pi}] - \frac{1}{2} \sum_\alpha \gamma_\alpha \{L_\alpha^\dagger L_\alpha, \hat{\pi}\} + \sum_\alpha \gamma_\alpha \hat{\pi} \text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\} \right\} \\ & + \sum_\alpha dN_\alpha \left[\frac{L_\alpha \hat{\pi} L_\alpha^\dagger}{\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\}} - \hat{\pi} \right] + \mathcal{O}\{dt^2, dt dN_\alpha\}. \end{aligned} \quad (4.26)$$

We now use the general relation

$$\mathcal{E}(dN_\alpha g(\hat{\pi})) = \gamma_\alpha dt \mathcal{E}(\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\} g(\hat{\pi})) \quad (4.27)$$

for arbitrary functions $g(\hat{\pi})$ of the projector. This relation can be understood by binning all K values of the actual state $\hat{\pi}^{(k)}(t)$ in the expectation value into L equal-sized compartments where $\hat{\pi}^{(k)} \approx \hat{\pi}^{(\ell)}$. In each compartment, we have N_ℓ realizations of $dN_\alpha^{\ell m}$ with $1 \leq m \leq N_\ell$ and $\sum_\ell N_\ell = K$, of which we can compute the average first:

$$\begin{aligned} \mathcal{E}(dN_\alpha g(\hat{\pi})) &= \lim_{K \rightarrow \infty} \frac{1}{K} \sum_k dN_\alpha^{(k)}(t) g(\hat{\pi}^{(k)}(t)) \\ &= \lim_{L, N_\ell \rightarrow \infty} \frac{\sum_\ell N_\ell \frac{1}{N_\ell} \sum_m dN_\alpha^{(\ell m)} g(\hat{\pi}^{(\ell)}(t))}{\sum_\ell N_\ell} \\ &= \lim_{L, N_\ell \rightarrow \infty} \frac{\sum_\ell N_\ell \gamma_\alpha dt \text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}^{(\ell)}\} g(\hat{\pi}^{(\ell)}(t))}{\sum_\ell N_\ell} \\ &= \lim_{L, N_\ell \rightarrow \infty} \frac{\sum_\ell N_\ell \gamma_\alpha dt \mathcal{E}(\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}^{(\ell)}\} g(\hat{\pi}^{(\ell)}(t)))}{\sum_\ell N_\ell} \\ &= \gamma_\alpha dt \mathcal{E}(\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\} g(\hat{\pi}^{(\ell)}(t))), \end{aligned} \quad (4.28)$$

where we have used the relation that $\bar{x} = \frac{\sum_i N_i \bar{x}_i}{\sum_i N_i}$ when \bar{x}_i represent averages of disjoint subsets of the complete set. Specifically, we apply it on the expressions

$$\begin{aligned} \mathcal{E}\left(dN_\alpha \frac{\hat{\pi}}{\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\}}\right) &= \gamma_\alpha dt \mathcal{E}\left(\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\} \frac{\hat{\pi}}{\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\}}\right) = \gamma_\alpha dt \rho, \\ \mathcal{E}(dN_\alpha \hat{\pi}) &= \gamma_\alpha dt \mathcal{E}(\text{Tr}\{L_\alpha^\dagger L_\alpha \hat{\pi}\} \hat{\pi}). \end{aligned} \quad (4.29)$$

This implies that

$$d\rho = dt \left\{ -i[H, \rho] + \sum_\alpha \gamma_\alpha \left[L_\alpha \rho L_\alpha^\dagger - \frac{1}{2} \{L_\alpha^\dagger L_\alpha, \rho\} \right] \right\}, \quad (4.30)$$

i.e., the average of trajectories from the stochastic Schrödinger equation yields the same solution as the master equation.

This may be of great numerical use: simulating the full master equation for an N -dimensional system Hilbert space may involve the storage of $\mathcal{O}\{N^4\}$ real variables in the Liouvillian, whereas for the generator of the stochastic Schrödinger equation one requires only $\mathcal{O}\{N^2\}$ real variables. This is of course weakened, since in order to get a realistic estimate of the expectation value, one has to compute K different trajectories, but since typically $K \ll N^2$, the stochastic Schrödinger equation is a useful tool in the numeric modeling of a master equation.

4.2.2.1 Example: Cavity in a Thermal Bath

As an example, we study the cavity in a thermal bath. We have the Lindblad-type master equation describing the interaction of a cavity mode with a thermal bath,

$$\begin{aligned} \dot{\rho}_S = & -i[\Omega a^\dagger a, \rho_S] + \gamma(1 + n_B) \left[a \rho_S a^\dagger - \frac{1}{2} a^\dagger a \rho_S - \frac{1}{2} \rho_S a^\dagger a \right] \\ & + \gamma n_B \left[a^\dagger \rho_S a - \frac{1}{2} a a^\dagger \rho_S - \frac{1}{2} \rho_S a a^\dagger \right]. \end{aligned} \quad (4.31)$$

We can immediately identify the jump operators

$$L_1 = a \quad \text{and} \quad L_2 = a^\dagger \quad (4.32)$$

and the corresponding rates

$$\gamma_1 = \gamma(1 + n_B) \quad \text{and} \quad \gamma_2 = \gamma n_B. \quad (4.33)$$

From the master equation, we obtain for the occupation number $n = \langle a^\dagger a \rangle$ the evolution equation $\frac{d}{dt}n = -\gamma n + \gamma n_B$, which is solved by

$$n(t) = n_0 e^{-\gamma t} + n_B [1 - e^{-\gamma t}]. \quad (4.34)$$

The corresponding stochastic differential equation reads

$$\begin{aligned} |d\Psi\rangle = & \left\{ -i\Omega a^\dagger a - \frac{1}{2} [\gamma(1 + 2n_B) a^\dagger a + \gamma n_B] \right. \\ & \left. + \frac{1}{2} [\gamma(1 + 2n_B) \langle \Psi | a^\dagger a | \Psi \rangle + \gamma n_B] \right\} | \Psi \rangle dt \\ & + \left(\frac{a | \Psi \rangle}{\sqrt{\langle \Psi | a^\dagger a | \Psi \rangle}} - | \Psi \rangle \right) dN_1 \\ & + \left(\frac{a^\dagger | \Psi \rangle}{\sqrt{\langle \Psi | a a^\dagger | \Psi \rangle}} - | \Psi \rangle \right) dN_2. \end{aligned} \quad (4.35)$$

When the initial state is not a superposition of different Fock basis states, the above equation becomes particularly simple. For example, for a Fock number state $| \Psi \rangle = | n \rangle$ we obtain

$$\begin{aligned} |dn\rangle = & \left\{ -i\Omega n - \frac{1}{2} [\gamma(1 + 2n_B)n + \gamma n_B] + \frac{1}{2} [\gamma(1 + 2n_B)n + \gamma n_B] \right\} | n \rangle dt \\ & + (| n - 1 \rangle - | n \rangle) dN_1 + (| n + 1 \rangle - | n \rangle) dN_2 \\ = & -i\Omega n dt | n \rangle + (| n - 1 \rangle - | n \rangle) dN_1 + (| n + 1 \rangle - | n \rangle) dN_2 \end{aligned} \quad (4.36)$$

such that, provided we start in a single energy eigenstate, superpositions are never created during the evolution. The total probability of having a jump in the system during the interval dt is given by

$$\begin{aligned} P_{\text{jump}} &= \gamma dt \left[(1 + n_B) \langle n | a^\dagger a | n \rangle + n_B \langle n | a a^\dagger | n \rangle \right] \\ &= \gamma \left[(1 + n_B)n + n_B(n + 1) \right] dt. \end{aligned} \quad (4.37)$$

If no jump occurs, the system evolves only oscillatory behavior, which has no effect on the expectation value of $a^\dagger a$. However, if a jump occurs, the respective conditional probability of jumping out of the system reads

$$P_1 = \frac{(n_B + 1)n}{(n_B + 1)n + n_B(n + 1)} \quad (4.38)$$

and that of jumping into the system consequently reads (these must add up to one)

$$P_2 = \frac{n_B(n + 1)}{(n_B + 1)n + n_B(n + 1)}. \quad (4.39)$$

Computing trajectories with a suitable random number generator and averaging the trajectories, we find convergence to the master equation result as expected; see Fig. 4.2. The plots in Fig. 4.2 could with the same effort have been obtained by a Monte Carlo solution of the rate equation corresponding to Eq. (4.31),

$$\begin{aligned} \dot{\rho}_{nn} &= -\gamma \left[n(1 + n_B) + (n + 1)n_B \right] \rho_{nn} + \gamma(n + 1)(1 + n_B) \rho_{n+1, n+1} \\ &\quad + \gamma n n_B \rho_{n-1, n-1}. \end{aligned} \quad (4.40)$$

The rate equation alone however is not sufficient to describe the decay of initial superpositions to a statistical mixture; thus, the stochastic Schrödinger equation is a more general tool.

4.3 Shannon's Entropy Production

We assume that in some favorable basis (e.g., the system energy eigenbasis) the populations of the density matrix $P_i = \rho_{ii}$ obey a rate equation dynamics

$$\dot{P}_i = \sum_j \mathcal{L}_{ij} P_j = \sum_j \sum_v \mathcal{L}_{ij}^{(v)} P_j, \quad (4.41)$$

where the rates \mathcal{L}_{ij} from state j to state i are additively decomposable into contributions from different reservoirs v . Such rate equations are commonly obtained for the quantum optical master equation in Definition 2.4 when nondegenerate system energies are assumed. Furthermore, the assumption of additively entering rates is quite naturally related to the weak coupling limit: it is always possible for an inter-

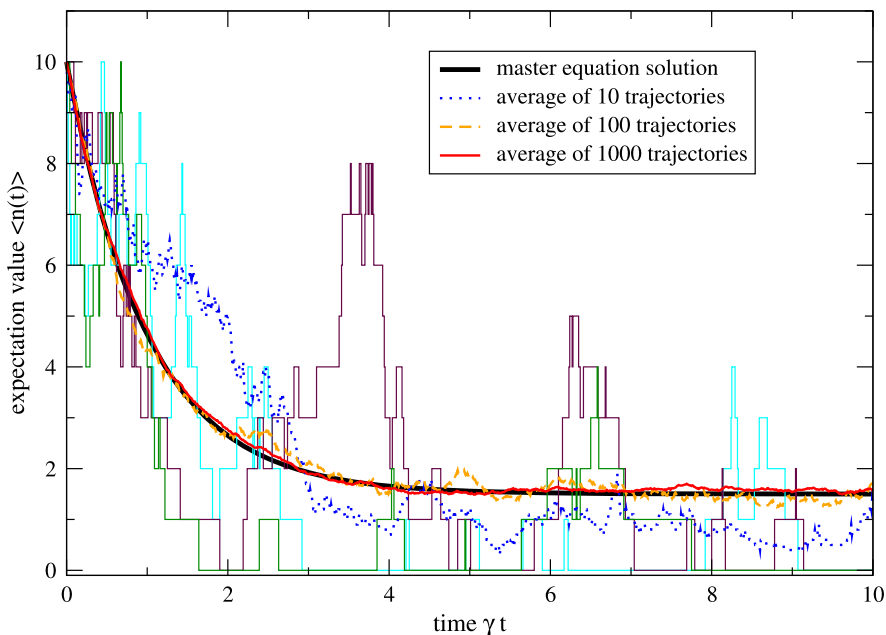


Fig. 4.2 Single trajectories of the stochastic Schrödinger equation (*curves with integer jumps*). The averages of 10, 100, and 1000 trajectories (*thin dotted, dashed, and solid curves, respectively*) converge to the prediction from the associated master equation (*thick solid curve*). Parameters have been chosen as $\gamma dt = 0.01$, $n_B = 1.5$

action of the form $H_I = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha}$ with system and bath operators A_{α} and B_{α} , respectively, to choose $\langle B_{\alpha} \rangle = 0$. For L multiple reservoirs kept at different equilibrium states, the stationary density matrix is given by a tensor product of different equilibrium states

$$\bar{\rho} = \frac{e^{-\beta_1(H_B^{(1)} - \mu_1 N_B^{(1)})}}{Z_1} \otimes \cdots \otimes \frac{e^{-\beta_L(H_B^{(L)} - \mu_L N_B^{(L)})}}{Z_L}, \quad (4.42)$$

where β_{ν} and μ_{ν} represent the temperature and chemical potential of the ν -th reservoir described by the Hamiltonian $H_B^{(\nu)}$ and with total particle number operator $N_B^{(\nu)}$.

Exercise 4.5 (Additivity of rates) Show that for an interaction Hamiltonian of the form $H_I = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha} = \sum_a \sum_{\nu} A_{a\nu} \otimes B_{a\nu}$, where ν labels the reservoir and where $\langle B_{a\nu} \rangle = 0$ holds, different reservoirs do not interfere, such that the rates can be calculated additively:

$$C_{\alpha\beta}(\tau) = C_{a\nu, b\mu}(\tau) = \langle B_{a\nu}(\tau) B_{b\nu} \rangle \delta_{\mu\nu}.$$

4.3.1 Balance Equation Far from Equilibrium

Keeping in mind that each reservoir is kept at a certain equilibrium, we postulate the existence of a local detailed balance condition for each reservoir. This implies that the ratio of forward and backward transition rates between states i and j that are triggered by reservoir ν obey

$$\frac{\mathcal{L}_{ji}^{(\nu)}}{\mathcal{L}_{ij}^{(\nu)}} = e^{-\beta_\nu[(\varepsilon_j - \varepsilon_i) - \mu_\nu(n_j - n_i)]}, \quad (4.43)$$

where β_ν and μ_ν denote the inverse temperature and chemical potential of the corresponding reservoir, and ε_i and n_i denote the energy and particle number of the state i , respectively. The above relation follows naturally from the extension of the Kubo–Martin–Schwinger (KMS) condition (2.51) to systems with chemical potentials and is automatically fulfilled for a large number of microscopically derived models, as we shall see later.

Then, the Shannon entropy of the system, $S = -\sum_i P_i(t) \ln P_i(t)$, obeys a balance equation,

$$\begin{aligned} \dot{S} &= -\frac{d}{dt} \sum_i P_i \ln P_i = -\sum_i \dot{P}_i \ln P_i \\ &= -\sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j \ln \left(P_i \frac{\mathcal{L}_{ji}^{(\nu)}}{P_j \mathcal{L}_{ij}^{(\nu)}} \frac{P_j \mathcal{L}_{ij}^{(\nu)}}{\mathcal{L}_{ji}^{(\nu)}} \right) \\ &= +\sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j \ln \left(\frac{\mathcal{L}_{ij}^{(\nu)} P_j}{\mathcal{L}_{ji}^{(\nu)} P_i} \right) + \sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j \ln \left(\frac{\mathcal{L}_{ji}^{(\nu)}}{\mathcal{L}_{ij}^{(\nu)}} \frac{1}{P_j} \right) \\ &= +\sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j \ln \left(\frac{\mathcal{L}_{ij}^{(\nu)} P_j}{\mathcal{L}_{ji}^{(\nu)} P_i} \right) + \sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} P_j \ln \left(\frac{\mathcal{L}_{ji}^{(\nu)}}{\mathcal{L}_{ij}^{(\nu)}} \right) \\ &\stackrel{t \rightarrow \infty}{\rightarrow} + \underbrace{\sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} \bar{P}_j \ln \left(\frac{\mathcal{L}_{ij}^{(\nu)} \bar{P}_j}{\mathcal{L}_{ji}^{(\nu)} \bar{P}_i} \right)}_{\geq 0} + \sum_{ij} \sum_\nu \mathcal{L}_{ij}^{(\nu)} \bar{P}_j \underbrace{\ln \left(\frac{\mathcal{L}_{ji}^{(\nu)}}{\mathcal{L}_{ij}^{(\nu)}} \right)}_{-\beta_\nu[(\varepsilon_j - \varepsilon_i) - \mu_\nu(n_j - n_i)]}. \end{aligned} \quad (4.44)$$

In the above lines, we have simply used trace conservation $\sum_i \mathcal{L}_{ij}^{(\nu)} = 0$ and finally the local detailed balance property (4.43). This property enables us to identify in the long-term limit the second term as energy and matter currents. When multiplied by the inverse temperature of the corresponding reservoir, they combine to the entropy change rate of the reservoirs, which motivates the definition below.

Definition 4.3 (Entropy flow) For a rate equation of the type (4.41), the entropy flow from reservoir ν is defined as

$$\begin{aligned}\dot{S}_e^{(\nu)} &= + \sum_{ij} \mathcal{L}_{ij}^{(\nu)} \bar{P}_j [-\beta_\nu [(\varepsilon_j - \varepsilon_i) - \mu_\nu (n_j - n_i)]] \\ &= \beta_\nu (I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}),\end{aligned}\quad (4.45)$$

where energy currents $I_E^{(\nu)}$ and matter currents $I_M^{(\nu)}$ associated to reservoir ν count positive when entering the system.

The remaining contribution corresponds to a production term [6]. We note that it is always positive, which can be deduced from the formal similarity to the Kullback–Leibler divergence of two probability distributions or, more directly, by using the logarithmic sum inequality.

Exercise 4.6 (Logarithmic sum inequality) Show that for non-negative a_i and b_i ,

$$\sum_{i=1}^n a_i \ln \frac{a_i}{b_i} \geq a \ln \frac{a}{b}$$

with $a = \sum_i a_i$ and $b = \sum_i b_i$.

Its positivity is perfectly consistent with the second law of thermodynamics, and we therefore identify the remaining contribution as entropy production.

Definition 4.4 (Entropy production) For a rate equation of the type (4.41), the average entropy production is defined as

$$\dot{S}_i = \sum_{ij} \sum_{\nu} \mathcal{L}_{ij}^{(\nu)} \bar{P}_j \ln \left(\frac{\mathcal{L}_{ij}^{(\nu)} \bar{P}_j}{\mathcal{L}_{ji}^{(\nu)} \bar{P}_i} \right) \geq 0. \quad (4.46)$$

It is always positive and at steady state balanced by the entropy flow.

When the dimension of the system's Hilbert space is finite and the rate equation (4.41) approaches a stationary state, its Shannon entropy will also approach a constant value $\dot{S} = 0$. Therefore, at steady state the entropy production in the system must be balanced by the entropy flow through its terminals

$$\dot{S}_i = -\dot{S}_e = - \sum_{\nu} \beta_\nu (I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}). \quad (4.47)$$

The above formula conveniently relates the entropy production to energy and matter currents from the terminals into the system. Evidently, the entropy production is thus related to heat currents $\dot{Q}^{(\nu)} = I_E^{(\nu)} - \mu_\nu I_M^{(\nu)}$, which can be determined from a master equation by means of the full counting statistics.

We note here that identifying the entropy production in a system is not a purely academic exercise: in the long term, it is additive in the respective entropy flows, and their identification allows, e.g., for the definition of thermodynamically meaningful (and bounded) efficiencies of thermoelectric nanoscale devices.

4.3.2 Linear Response for Two Terminals

As an example, we consider a system coupled to two terminals S and D obeying a rate equation dynamics as discussed before. In the long-time limit, entropy production will be balanced by the entropy flow, and assuming that both energy and matter currents are conserved, $I_E^{(D)} + I_E^{(S)} = 0$ and $I_M^{(D)} + I_M^{(S)} = 0$, we can express the entropy production solely using the currents entering the system from the source $\dot{S}_i = (\beta_D - \beta_S)I_E^{(S)} + (\mu_S\beta_S - \mu_D\beta_D)I_M^{(S)}$. In the linear response regime we assume that the differences of temperatures and chemical potentials are small. Rewriting these parameters in terms of mean and differences $\beta_S = \beta - \Delta\beta/2$, $\beta_D = \beta + \Delta\beta/2$, $\mu_S = \mu + \Delta\mu/2$, and $\mu_D = \mu - \Delta\mu/2$, the entropy production can be expanded in $\Delta\beta$ and $\Delta\mu$, which to lowest order yields

$$\dot{S}_i = \Delta\beta(I_E^{(S)} - \mu I_M^{(S)}) + \beta\Delta\mu I_M^{(S)} = \Delta\beta\dot{Q} + \beta\Delta\mu I_M, \quad (4.48)$$

where \dot{Q} represents the heat current and I_M the matter current from S to D , respectively. This equation has the characteristic affinity-flux form [7], where the affinity to the heat current is given by $\Delta\beta = \beta_D - \beta_S = \Delta T/T^2 + \mathcal{O}\{\Delta T^2\}$, and the affinity for the matter current is given by $\beta\Delta\mu = \beta(\mu_S - \mu_D)$. In the linear response regime, the fluxes are linearly related to the affinities,

$$\begin{pmatrix} \dot{Q} \\ I_M \end{pmatrix} = \begin{pmatrix} L_{QQ} & L_{QM} \\ L_{MQ} & L_{MM} \end{pmatrix} \begin{pmatrix} \Delta\beta \\ \beta\Delta\mu \end{pmatrix}, \quad (4.49)$$

with the Onsager matrix L . Consequently, the entropy production can—in the linear response—be expressed as a quadratic form of the affinities

$$\dot{S}_i = (\Delta\beta, \beta\Delta\mu) \begin{pmatrix} L_{QQ} & L_{QM} \\ L_{MQ} & L_{MM} \end{pmatrix} \begin{pmatrix} \Delta\beta \\ \beta\Delta\mu \end{pmatrix}. \quad (4.50)$$

Positivity of the entropy production requires positivity of the Onsager matrix.

Considering, e.g., an SET with the matter current in the weak coupling regime approaching Eq. (3.50), and assuming tight coupling between energy and matter currents, such that $\dot{Q} = (\varepsilon - \mu)I_M$ (compare also Sect. 5.1), the Onsager relations become

$$\begin{pmatrix} \dot{Q} \\ I_M \end{pmatrix} = \frac{\Gamma_S\Gamma_D}{\Gamma_S + \Gamma_D} f(1-f) \begin{pmatrix} (\varepsilon - \mu)^2 & (\varepsilon - \mu) \\ (\varepsilon - \mu) & 1 \end{pmatrix} \begin{pmatrix} \Delta\beta \\ \beta\Delta\mu \end{pmatrix} \quad (4.51)$$

with $f = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$,

which fulfills the Onsager relation $L_{QM} = L_{MQ}$ and has a positive definite Onsager matrix. Due to the tight coupling property we note that the determinant of the Onsager matrix vanishes.

Exercise 4.7 (SET Onsager relations) Confirm the validity of Eq. (4.51).

4.4 Full Counting Statistics: Phenomenological Introduction

Having successfully derived a rate equation of the form (4.41), one can very often interpret the process associated with the rate $\mathcal{L}_{ij}^{(v)}$ as a jump of $(|n_i - n_j|)$ particles from the bath v into the system (when $n_i > n_j$) or out of the system into the bath v (when $n_i < n_j$). Typically, the weak coupling limit assumed during the derivation of the rate equation leads to sequential transport only; i.e., only terms $\mathcal{L}_{ij}^{(v)}$ with $n_i - n_j \in \{-1, 0, +1\}$ will be nonvanishing. Such a jump may also transfer the energy $|E_i - E_j|$ from the bath v into the system ($E_i > E_j$) or out of the system into the bath v ($E_i < E_j$), even if no particles are transferred ($n_i = n_j$). A straightforward observation is that even though on average a matter or energy current may be directed in a certain direction, there is for a given initial state a finite probability that a jump will occur in the opposite direction. Such trajectories would actually decrease the entropy of the system and must—since they are not completely forbidden—somehow be suppressed to obey the second law on average. Fortunately, one may calculate the statistics of these events in a straightforward manner, as will be discussed in the following subsections.

4.4.1 Discrete Particle Counting Statistics

We denote the probability that the system is in the state i and simultaneously n particles have tunneled into reservoir σ by $P_i^{(n)}(t)$. Obviously, we have $-\infty < n < +\infty$ (unless transport is unidirectional) and $P_i(t) = \sum_n P_i^{(n)}(t)$. However, the rate equation (4.41) can now be written as

$$\dot{P}_i^{(n)} = \sum_{v \neq \sigma} \sum_j \mathcal{L}_{ij}^{(v)} P_j^{(n)} + \mathcal{L}_{ii}^{(\sigma)} P_i^{(n)} + \sum_{j \neq i} \mathcal{L}_{ij}^{(\sigma)} P_j^{(n+n_i-n_j)}, \quad (4.52)$$

where we have separated the jumps triggered by other reservoirs than σ and also the trace-preserving diagonal term proportional to $\mathcal{L}_{ii}^{(\sigma)}$. We note that one can interpret the term $\mathcal{L}_{ij}^{(\sigma)} P_j^{(n+n_i-n_j)}$ as follows: before the jump, the system is in state j with n_j particles in the system and $n + n_i - n_j$ particles in reservoir σ . After the jump, the system is in state i with n_i particles in the system and n particles in reservoir σ . Thus, the combined particle number $n + n_i$ in both system and reservoir is conserved during the jump.

For ease of notation, we write the conditioned rate equation (4.52) as a conditioned density vector $\rho^{(n)} = (P_1^{(n)}, \dots, P_d^{(n)})^T$ and assume that at most one particle can be transferred at once to and from the bath. This is the standard case arising in most microscopic derivations; however, for a counter-example we refer the reader to Sect. 5.8. Then, Eq. (4.52) becomes

$$\dot{\rho}^{(n)} = \mathcal{L}_0 \rho^{(n)} + \mathcal{L}_- \rho^{(n+1)} + \mathcal{L}_+ \rho^{(n-1)}, \quad (4.53)$$

and the translational invariance in n (the rates contained in $\mathcal{L}_{0/\pm}$ do not depend on n themselves) suggests that we simplify the coupled system via a discrete Fourier transformation,

$$\rho(\chi, t) = \sum_n \rho^{(n)}(t) e^{in\chi}, \quad (4.54)$$

which yields a d -dimensional ordinary differential equation similar to a rate equation but now with complex-valued rates, since we have introduced the counting field χ :

$$\dot{\rho}(\chi, t) = [\mathcal{L}_0 + e^{-i\chi} \mathcal{L}_- + e^{+i\chi} \mathcal{L}_+] \rho(\chi, t) = \mathcal{L}(\chi) \rho(\chi, t). \quad (4.55)$$

Thus, we have reduced the dimension at the price of introducing a dimensionless counting field, but the resulting generalized master equation can now be formally solved as

$$\rho(\chi, t) = e^{\mathcal{L}(\chi)t} \rho(\chi, 0) = e^{\mathcal{L}(\chi)t} \rho_0, \quad (4.56)$$

where we have used the convention that at time $t = 0$ no particles should have entered the reservoir $\rho^{(n)}(0) = \rho_0 \delta_{n,0}$.

If we disregard the state of the system and only consider the number of tunneled particles, the corresponding probability becomes

$$P_n(t) = \sum_i P_i^{(n)}(t) = \text{Tr}\{\rho^{(n)}(t)\} = \frac{1}{2\pi} \int_{-\pi}^{+\pi} \text{Tr}\{e^{\mathcal{L}(\chi)t} \rho_0\} e^{-in\chi} d\chi, \quad (4.57)$$

where we have simply inserted the inverse of the discrete Fourier transform (4.54). By tracing over Eq. (4.54) and taking suitable derivatives with respect to the counting field χ , we note that the moments of this probability distribution can be conveniently calculated by taking derivatives:

$$\begin{aligned} \langle n^k \rangle &\equiv \sum_n n^k P_n(t) = (-i\partial_\chi)^k \text{Tr}\{\rho(\chi, t)\} \Big|_{\chi=0} \\ &= (-i\partial_\chi)^k \text{Tr}\{e^{\mathcal{L}(\chi)t} \rho_0\} \Big|_{\chi=0}. \end{aligned} \quad (4.58)$$

This directly motivates us to define a moment-generating function.

Definition 4.5 (Moment-generating function) With a particle-counting-field dependent Liouvillian $\mathcal{L}(\chi)$, the moment-generating function corresponding to the distribution $P_n(t)$ is defined as

$$M(\chi, t) = \text{Tr}\{e^{\mathcal{L}(\chi)t} \rho_0\} \xrightarrow{t \rightarrow \infty} \text{Tr}\{e^{\mathcal{L}(\chi)t} \bar{\rho}\} \quad (4.59)$$

with the initial state ρ_0 and the stationary state defined by $\mathcal{L}(0)\bar{\rho} = \mathbf{0}$.

Given the moment-generating function, moments of the distribution $P_n(t)$ may be calculated conveniently via

$$\langle n^k \rangle(t) = (-i\partial_\chi)^k M(\chi, t)|_{\chi=0}, \quad (4.60)$$

whereas the calculation of the full distribution requires one to calculate the full inverse Fourier transform of the moment-generating function,

$$P_n(t) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} M(\chi, t) e^{-in\chi} d\chi. \quad (4.61)$$

The latter is, except for some specific cases, only numerically possible.

4.4.2 Continuous Energy Counting Statistics

Similarly, we may extract the statistics of energy transfers from the rate equation (4.41). One possible way [8] is to treat transitions occurring with a certain energy transfer ω_i with a separate particle number counting n_i and a separate dimensionless counting field χ_i . The total transferred energy can then later be deduced from the specific particle transitions via $E = \sum_i \omega_i n_i$. In this case, the energy-resolved distribution function would then be given by

$$\rho^{(E)}(t) = \sum_{n_1, \dots, n_k} \rho^{(n_1 \dots n_k)}(t) \delta\left(E - \sum_i \delta E_i n_i\right). \quad (4.62)$$

Here however, we would like avoid introducing too many counting fields and therefore decide to count the transferred energy directly [9]. Obviously, when the transition frequencies of the system ω_i are incommensurate, the total transferred energy E will become a continuous variable.

Denoting the density vector conditioned on energy E contained in the reservoir σ by $\rho^{(E)} = (P_1^{(E)}, \dots, P_d^{(E)})^T$ with $-\infty < E/\Omega < \infty$ (for any energy scale Ω) and $\rho(t) = \int \rho^{(E)}(t) dE$, we may write the rate equation (4.41) as

$$\dot{\rho}^{(E)} = \mathcal{L}_0 \rho^{(E)} + \sum_{\Delta E} \mathcal{L}_{\Delta E} \rho^{(E-\Delta E)}, \quad (4.63)$$

where \mathcal{L}_0 does not induce energy transfers with reservoir σ and $\mathcal{L}_{\Delta E}$ describes the transfer of energy ΔE from the system to reservoir σ ; negative ΔE simply implies the opposite direction. Here, one usually has multiple energy differences $|\Delta E|$. Only very simple systems admit only a single transition frequency, and then energy and particle currents are tightly coupled. Now, we have to choose a continuous Fourier transform

$$\rho(\xi, t) = \int \rho^{(E)}(t) e^{iE\xi} dE, \quad (4.64)$$

where the dual field ξ now has the dimension of inverse energy. The Fourier-transformed master equation becomes

$$\dot{\rho}(\xi, t) = \left[\mathcal{L}_0 + \sum_{\Delta E} \mathcal{L}_{\Delta E} e^{i\xi \Delta E} \right] \rho(\xi, t) = \mathcal{L}(\xi) \rho(\xi, t), \quad (4.65)$$

and the field ξ is now allowed to range over the complete real axis. With the convention that initially no energy has been transferred, $\rho^{(E)}(0) = \delta(E) \rho_0$, we may similarly write the solution as $\rho(\xi, t) = e^{\mathcal{L}(\xi)t} \rho_0$.

The moments of the energy-transfer distribution

$$\langle E^k \rangle = \int E^k \text{Tr}\{\rho^{(E)}(t)\} dE \quad (4.66)$$

can now be similarly obtained—compare Eq. (4.64)—by differentiation of the moment-generating function

$$M(\xi, t) = \text{Tr}\{e^{\mathcal{L}(\xi)t} \rho_0\} \quad (4.67)$$

with respect to the dimensioned counting field ξ . Similarly, the full distribution can be obtained by calculating the inverse Fourier transform of the moment-generating function

$$P_E(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} M(\xi, t) e^{-in\xi} d\xi. \quad (4.68)$$

4.4.3 Moments and Cumulants

It is often more convenient to characterize distributions by cumulants instead of moments, since higher cumulants are invariant against translations of the distribution (in the following discussion we treat dimensionless particle counting and dimensioned energy counting similarly).

Definition 4.6 (Cumulant-generating function) The cumulant-generating function is defined as the logarithm of the moment-generating function:

$$C(\chi, t) = \ln \text{Tr}\{e^{\mathcal{L}(\chi)t} \rho_0\}. \quad (4.69)$$

The cumulants of the distribution $P_n(t)$ are obtained by differentiation with respect to the counting field

$$\langle\langle n^k \rangle\rangle(t) = (-i\partial_\chi)^k C(\chi, t)|_{\chi=0}, \quad (4.70)$$

and similarly for cumulants of the energy distribution function. Cumulants and moments are therefore obviously related. Considering for example particle counting, the first few cumulants can be expressed by the moments as

$$\begin{aligned} \langle\langle n^1 \rangle\rangle &= \langle n^1 \rangle, \\ \langle\langle n^2 \rangle\rangle &= \langle n^2 \rangle - \langle n \rangle^2, \\ \langle\langle n^3 \rangle\rangle &= \langle n^3 \rangle - 3\langle n \rangle \langle n^2 \rangle + 2\langle n \rangle^3, \\ \langle\langle n^4 \rangle\rangle &= \langle n^4 \rangle - 4\langle n \rangle \langle n^3 \rangle - 3\langle n^2 \rangle^2 + 12\langle n \rangle^2 \langle n^2 \rangle - 6\langle n \rangle^4, \end{aligned} \quad (4.71)$$

and they geometrically correspond to the mean, width, skewness, and kurtosis of a distribution, respectively. It should be noted however that such simple geometric interpretations only hold for unimodal distributions.

The true advantage of considering cumulants instead of moments becomes visible for master equations admitting only a single stationary state. Then, the cumulant-generating function in the large-time limit scales approximately linearly in time,

$$C(\chi, t) \rightarrow \lambda(\chi)t, \quad (4.72)$$

where $\lambda(\chi)$ is the eigenvalue of the generalized Liouvillian $\mathcal{L}(\chi)$ with the largest real part.

We show this by using the decomposition of the Liouvillian in Jordan block form,

$$\mathcal{L}(\chi) = Q(\chi)\mathcal{L}_J(\chi)Q^{-1}(\chi), \quad (4.73)$$

where $Q(\chi)$ is a (in general nonunitary) similarity matrix and $\mathcal{L}_J(\chi)$ contains the eigenvalues of the Liouvillian on its diagonal, distributed in blocks with a size corresponding to the eigenvalue multiplicity. We assume that there exists only one stationary state $\bar{\rho}$, i.e., only one eigenvalue $\lambda(\chi)$ with $\lambda(0) = 0$, and that all other eigenvalues have a nonvanishing negative real part near $\chi = 0$. Then, we use this decomposition in the matrix exponential to estimate its long-term evolution:

$$\begin{aligned} \mathcal{M}(\chi, t) &= \text{Tr}\{e^{\mathcal{L}(\chi)t}\rho_0\} = \text{Tr}\{e^{Q(\chi)\mathcal{L}_J(\chi)Q^{-1}(\chi)t}\rho_0\} \\ &= \text{Tr}\{Q(\chi)e^{\mathcal{L}_J(\chi)t}Q^{-1}(\chi)\rho_0\} \\ &\rightarrow \text{Tr}\left\{Q(\chi)\begin{pmatrix} e^{\lambda(\chi)\cdot t} & & & \\ & 0 & & \\ & & \ddots & \\ & & & 0 \end{pmatrix}Q^{-1}(\chi)\rho_0\right\} \end{aligned}$$

$$\begin{aligned}
&= e^{\lambda(\chi)t} \text{Tr} \left\{ Q(\chi) \begin{pmatrix} 1 & & & \\ & 0 & & \\ & & \ddots & \\ & & & 0 \end{pmatrix} Q^{-1}(\chi) \rho_0 \right\} \\
&= e^{\lambda(\chi)t} c(\chi)
\end{aligned} \tag{4.74}$$

with some polynomial $c(\chi)$ depending on the matrix $Q(\chi)$ and on the initial state ρ_0 . This implies that the cumulant-generating function

$$\mathcal{C}(\chi, t) = \ln \mathcal{M}(\chi, t) = \lambda(\chi)t + \ln c(\chi) \approx \lambda(\chi)t \tag{4.75}$$

becomes linear in $\lambda(\chi)$ for large times, up to a small correction. This small correction is usually negligible, particularly when one is interested in time derivatives such as the current. We note here that this simple limit only holds when there is a unique stationary state. For bistable or multistable systems a more sophisticated theory applies [10, 11]. Note further, that when cumulants are to be obtained from the moments, the small constant correction may be important.

Exercise 4.8 (Cumulant-generating function) Calculate the long-term cumulant-generating function for current through the SET

$$\mathcal{L}(\chi) = \begin{pmatrix} -\Gamma_L f_L - \Gamma_R f_R & +\Gamma_L(1-f_L) + \Gamma_R(1-f_R)e^{+i\chi} \\ +\Gamma_L f_L + \Gamma_R f_R e^{-i\chi} & -\Gamma_L(1-f_L) - \Gamma_R(1-f_R) \end{pmatrix}.$$

What are the first two long-term cumulants for the current, i.e., current $I = \frac{d}{dt} \langle n \rangle$ and noise $S = \frac{d}{dt} \langle n^2 \rangle = \frac{d}{dt} (\langle n^2 \rangle - \langle n \rangle^2)$?

4.4.4 Convenient Calculation of Lower Cumulants

To calculate moments and/or cumulants, it is not always necessary to exponentiate the Liouvillian or to calculate its dominant eigenvalue.

If one is just interested in the long-term current, e.g., the time derivative of the mean energy or particle number transferred (first moment/cumulant), the calculations are considerably simplified, since we can insert the stationary state as initial condition:

$$\begin{aligned}
I = \langle \dot{n}(t) \rangle &= -i \partial_\chi \left. \frac{d}{dt} \text{Tr} \{ e^{-\mathcal{L}(\chi)t} \bar{\rho} \} \right|_{\chi=0} = -i \partial_\chi \text{Tr} \{ \mathcal{L}(\chi) e^{-\mathcal{L}(\chi)t} \bar{\rho} \} \Big|_{\chi=0} \\
&= -i \text{Tr} \{ \mathcal{L}'(0) e^{-\mathcal{L}(0)t} \bar{\rho} \} - i \text{Tr} \{ \mathcal{L}(0) \partial_\chi e^{-\mathcal{L}(\chi)t} \Big|_{\chi=0} \bar{\rho} \} \\
&= -i \text{Tr} \{ \mathcal{L}'(0) \bar{\rho} \},
\end{aligned} \tag{4.76}$$

where we have used $\mathcal{L}(0)\bar{\rho} = 0$ and also $\text{Tr}\{\mathcal{L}(0)S\} = 0$ for all operators S (trace conservation). Therefore, to compute the current, the only challenge is to calculate the stationary state of the rate matrix at vanishing counting fields.

To calculate the long-term limit of higher cumulants, we may also use limits on the Laplace-transformed moment-generating function:

$$\begin{aligned}\tilde{M}(\chi, z) &= \int_0^\infty M(\chi, t)e^{-zt} dt = \text{Tr}\left\{\frac{1}{z\mathbf{1} - \mathcal{L}(\chi)}\rho_0\right\} \\ &\rightarrow \text{Tr}\left\{\frac{1}{z\mathbf{1} - \mathcal{L}(\chi)}\bar{\rho}\right\}.\end{aligned}\quad (4.77)$$

Having calculated the first moment $\langle n \rangle = It$, the time derivative of the second cumulant is, e.g., related to the first two moments via

$$C_2 = \lim_{t \rightarrow \infty} \frac{d}{dt} [\langle n^2 \rangle - \langle n \rangle^2] = \lim_{t \rightarrow \infty} \left[\frac{d}{dt} \langle n^2 \rangle - 2I^2 t \right]. \quad (4.78)$$

Performing a Laplace transform of this equation, we may use well-known properties of this transform,

$$\begin{aligned}f(t) \leftrightarrow \tilde{f}(z) &\implies \dot{f}(t) \leftrightarrow z\tilde{f}(z) - f(0), \\ \lim_{t \rightarrow \infty} f(t) &= \lim_{z \rightarrow 0} z\tilde{f}(z),\end{aligned}\quad (4.79)$$

to obtain an alternative formula for the time derivative of the second cumulant:

$$C_2 = \lim_{z \rightarrow 0} z \left[z(-i\partial_\chi)^2 \tilde{M}(\chi, z) - \frac{2I^2}{z^2} \right], \quad (4.80)$$

where we have used the fact that the initial value of the second moment vanishes. The evaluation of this expression requires only knowledge of the stationary current I and the inverse matrix occurring in the Laplace transform of the moment-generating function—which is much simpler to calculate than a matrix exponential. Keeping in mind that cumulants may have a constant contribution, one may extend the scheme to obtain formulae for higher cumulants.

4.4.5 Fluctuation Theorems

Representing the full energy or particle distributions, not in terms of the moment-generating function in Eqs. (4.61) and (4.68), but with the cumulant-generating

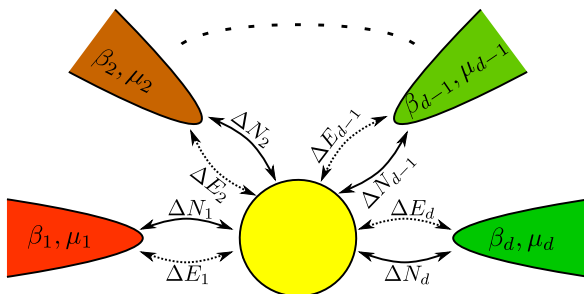


Fig. 4.3 Sketch of a system (yellow circle) that is coupled to d terminals, which admits the exchange of matter ΔN_i and energy ΔE_i between system and reservoirs. When these are in thermal equilibrium states described by temperatures and chemical potentials, one finds for sufficiently weak couplings a fluctuation theorem of energy and matter exchanges (Color figure online)

function $\mathcal{C}(\chi/\xi, t)$, we obtain

$$P_{\Delta n}(t) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} e^{\mathcal{C}(\chi, t)} e^{-i\Delta n \chi} d\chi, \quad (4.81)$$

$$P_{\Delta E}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{\mathcal{C}(\xi, t)} e^{-i\Delta E \xi} d\xi.$$

We will consider the general case here where all matter and energy transfers are monitored for a system with d junctions; see Fig. 4.3. Formally, simultaneous counting at all junctions requires introducing the multidimensional vectors $\Delta \mathbf{n} = (\Delta n_1, \dots, \Delta n_d)$ and $\Delta \mathbf{E} = (\Delta E_1, \dots, \Delta E_d)$, where Δn_ν and ΔE_ν denote the particles and energy exchanged with the ν th reservoir and the system (counted positive by construction when entering the system), respectively. The corresponding probability distribution reads

$$P_{+\Delta \mathbf{n}, +\Delta \mathbf{E}}(t) = \left(\frac{1}{2\pi}\right)^{2d} \int_{-\pi}^{+\pi} \cdots \int_{-\pi}^{+\pi} d^d \chi \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} d^d \xi \\ \times e^{\mathcal{C}(\chi, \xi, t)} e^{-i\Delta \mathbf{n} \cdot \chi} e^{-i\Delta \mathbf{E} \cdot \xi}, \quad (4.82)$$

such that the probability of the inverse process is

$$P_{-\Delta \mathbf{n}, -\Delta \mathbf{E}}(t) = \left(\frac{1}{2\pi}\right)^{2d} \int_{-\pi}^{+\pi} \cdots \int_{-\pi}^{+\pi} d^d \chi \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} d^d \xi \\ \times e^{\mathcal{C}(-\chi, -\xi, t)} e^{-i\Delta \mathbf{n} \cdot \chi} e^{-i\Delta \mathbf{E} \cdot \xi}, \quad (4.83)$$

where we have already transformed the integration variables $\chi \rightarrow -\chi$ and $\xi \rightarrow -\xi$. When now the cumulant-generating function obeys a symmetry of the form (typically, such symmetries arise in the long-term limit)

$$\mathcal{C}(-\chi, -\xi, t) = \mathcal{C}(\chi + i\Delta \chi, \xi + i\Delta \xi, t), \quad (4.84)$$

this implies a fluctuation theorem for the probabilities of matter and energy transfers

$$\frac{P_{+\Delta n, +\Delta E}}{P_{-\Delta n, -\Delta E}} = e^{\Delta n \cdot \Delta \chi} e^{\Delta E \cdot \Delta \xi}, \quad (4.85)$$

which can be demonstrated with a simple transformation of the integrand. Interpreted within the framework of stochastic thermodynamics [12], a transfer of Δn particles and energy ΔE from the reservoir to the system leads to the production of entropy of

$$\Delta_i S = \sum_{v=1}^d \beta_v \mu_v n_v - \sum_{v=1}^d \beta_v E_v, \quad (4.86)$$

where we have neglected contributions that arise from the change of the system's internal state: these contributions vanish anyway when identical initial and final states are considered, and for finite-sized systems they are negligibly small for large times, where the exchanged matter and energy contributions are dominating. For rate equations obeying local detailed balance (4.43), it can be shown quite generally that the characteristic polynomial of the rate matrix

$$\mathcal{D}(\chi, \xi) = |\mathcal{L}(\chi, \xi) - \lambda \mathbf{1}| \quad (4.87)$$

obeys the same symmetry, which then transfers to all eigenvalues of the Liouvillian and thus to the cumulant-generating function, too. Essentially, the proof [13] relies on analysis of the characteristic polynomial with Schnakenberg graph theory [14], but similar results may also be obtained with other methods [15, 16]. In particular, one obtains for d terminals with temperatures β_i and chemical potentials μ_i the shift relation (4.84) with

$$\Delta \chi = (\beta_1 \mu_1, \dots, \beta_d \mu_d), \quad \Delta \xi = (\beta_1, \dots, \beta_d). \quad (4.88)$$

In the long-term limit, the transfer of matter and energy to the terminals can be linked to the entropy flow in Definition 4.3, which at steady state is balanced by the entropy production in Definition 4.4. Therefore, the resulting fluctuation theorem describes the long-term statistics of entropy production:

$$\frac{P_{+\Delta n, +\Delta E}}{P_{-\Delta n, -\Delta E}} = \exp \left\{ \sum_v (\beta_v \mu_v n_v - \beta_v E_v) \right\} \Leftrightarrow \frac{P_{+\Delta_i S}}{P_{-\Delta_i S}} = e^{\Delta_i S} \quad (4.89)$$

and is a manifestation of the second law far from thermal equilibrium: trajectories with a negative entropy production are not completely forbidden but rather strongly suppressed, and it is straightforward to see that, on average, entropy production will

always be positive. We show this by averaging over all trajectories:

$$\begin{aligned} \langle \Delta_i S \rangle &= \sum_{\Delta_i S} \Delta_i S P_{\Delta_i S} = \sum_{\Delta_i S > 0} \Delta_i S (P_{+\Delta_i S} - P_{-\Delta_i S}) \\ &= \sum_{\Delta_i S > 0} \Delta_i S P_{-\Delta_i S} \underbrace{(e^{\Delta_i S} - 1)}_{\geq 0} \geq 0. \end{aligned} \quad (4.90)$$

Symmetries as in Eq. (4.87) hold in the rate equation (weak coupling) limit and imply of course that on average the second law is respected. The fluctuation relations have been verified, e.g., in an electronic setup [17, 18]. It turned out that slight modifications were visible, which can be explained by the interaction between system and detector. This interaction leads to further flows of information (physically connected to energy and matter flows) that modify the experimental signature.

It should be noted that when conservation laws exist, e.g. when the total particle current and/or the total energy current is conserved, the fluctuation theorem further simplifies. For example, for the SET we have conservation of the total particle number $n_L + n_R + n_d = \text{const.}$, where $n_d \in \{0, 1\}$ denotes the number of electrons on the dot. In the long-time limit, many particles will have been exchanged with the central dot of the SET and its terminals, and we will have in an approximate sense the conservation law $n_L = -n_R$. Furthermore, transferred energy and particles are tightly coupled in the master equation description, such that $\Delta E_\alpha = \Delta N_\alpha \varepsilon$ with dot level ε . Therefore, one can quantify the long-term entropy production simply by counting the number of particles transferring the SET, e.g., from left to right. Denoting the corresponding distribution by $P_n(t)$, the fluctuation theorem for equal temperatures simply becomes

$$\lim_{t \rightarrow \infty} \frac{P_{+n}}{P_{-n}} = e^{n\beta(\mu_L - \mu_R)}. \quad (4.91)$$

Exercise 4.9 (Fluctuation theorem) Find the fluctuation theorem, i.e., a symmetry in the cumulant-generating function, for the SET

$$\mathcal{L}(\chi) = \begin{pmatrix} -\Gamma_L f_L - \Gamma_R f_R & +\Gamma_L(1 - f_L) + \Gamma_R(1 - f_R)e^{+i\chi} \\ +\Gamma_L f_L + \Gamma_R f_R e^{-i\chi} & -\Gamma_L(1 - f_L) - \Gamma_R(1 - f_R) \end{pmatrix}.$$

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