

### 5.D.1. Derivation of the Master Equation

The **master equation** governs the evolution of the probability densities for processes in which  $Y$  is discrete but  $t$  is continuous.

(5.12) thus becomes

$$P(n, t + \Delta t) = \sum_{m=1}^M P(m, t) P_{1|1}(m, t | n, t + \Delta t) \quad (5.50)$$

for arbitrary  $\Delta t$ . In particular,

$$\begin{aligned} \frac{\partial P(n, t)}{\partial t} &= \lim_{\Delta t \rightarrow 0} \frac{P(n, t + \Delta t) - P(n, t)}{\Delta t} \\ &= \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \sum_{m=1}^M P(m, t) \left[ P_{1|1}(m, t | n, t + \Delta t) - \delta_{mn} \right] \end{aligned} \quad (5.51)$$

where, for obvious reasons,

$$P_{1|1}(m, t | n, t) = \delta_{mn} \quad (5.51a)$$

Let

$w_{mn}(t)$  = transition probability rate

so that for  $\Delta t \rightarrow 0$ ,

$w_{mn}(t) \Delta t$  = probability of transition  $m \rightarrow n$  during interval  $(t, t + \Delta t)$

and

$\Delta t \sum_{k=1}^M w_{mk}(t)$  = probability of at least 1 transition out of state  $m$  during interval  $(t, t + \Delta t)$

$1 - \Delta t \sum_{k=1}^M w_{mk}(t)$  = probability of no transition for state  $m$  during interval  $(t, t + \Delta t)$

$$\begin{aligned} \left[ 1 - \Delta t \sum_{k=1}^M w_{mk}(t) \right] + \Delta t w_{mm}(t) &= 1 - \Delta t \sum_{k \neq m} w_{mk}(t) \\ &= \text{probability of either no transition or transition } m \rightarrow m \text{ during interval } (t, t + \Delta t) \\ &= \text{probability of system staying in state } m \text{ during interval } (t, t + \Delta t) \end{aligned}$$

Thus, for  $m \neq n$ , we have

$$P_{1|1}(m, t | n, t + \Delta t) = w_{mn}(t) \Delta t + O(\Delta t)^2$$

and

$$P_{1|1}(m, t | m, t + \Delta t) = 1 - \Delta t \sum_{k=1}^M w_{mk}(t) + w_{mm}(t) \Delta t + O(\Delta t)^2$$

Combining both cases gives

$$P_{1|1}(m, t | n, t + \Delta t) = \delta_{mn} \left[ 1 - \Delta t \sum_{k=1}^M w_{mk}(t) \right] + w_{mn}(t) \Delta t + O(\Delta t)^2 \quad (5.52)$$

(5.51) thus becomes

$$\begin{aligned} \frac{\partial P(n, t)}{\partial t} &= \sum_{m=1}^M P(m, t) \left[ -\delta_{mn} \sum_{k=1}^M w_{mk}(t) + w_{mn}(t) \right] \\ &= - \sum_{k=1}^M P(n, t) w_{nk}(t) + \sum_{m=1}^M P(m, t) w_{mn}(t) \end{aligned}$$

$$\begin{aligned}
 &= - \sum_{m=1}^M P(n, t) w_{nm}(t) + \sum_{m=1}^M P(m, t) w_{mn}(t) \\
 &= \sum_{m=1}^M \left[ P(m, t) w_{mn}(t) - P(n, t) w_{nm}(t) \right]
 \end{aligned} \tag{5.53}$$

which is known as the **master equation**.

Similarly, the Chapman-Kolmogorov equation (5.21) becomes

$$\begin{aligned}
 P_{1|1}(n_0, 0 | n, t + \Delta t) &= \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) P_{1|1}(m, t | n, t + \Delta t) \\
 &= \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) \left\{ \delta_{mn} \left[ 1 - \Delta t \sum_{k=1}^M w_{mk}(t) \right] + w_{mn}(t) \Delta t \right\} + O(\Delta t)^2 \\
 &= P_{1|1}(n_0, 0 | n, t) - P_{1|1}(n_0, 0 | n, t) \Delta t \sum_{k=1}^M w_{nk}(t) \\
 &\quad + \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) w_{mn}(t) \Delta t + O(\Delta t)^2 \\
 \rightarrow \frac{\partial P_{1|1}(n_0, 0 | n, t)}{\partial t} &= \lim_{\Delta t \rightarrow 0} \frac{P_{1|1}(n_0, 0 | n, t + \Delta t) - P_{1|1}(n_0, 0 | n, t)}{\Delta t} \\
 &= -P_{1|1}(n_0, 0 | n, t) \sum_{k=1}^M w_{nk}(t) + \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) w_{mn}(t) \\
 &= -P_{1|1}(n_0, 0 | n, t) \sum_{m=1}^M w_{nm}(t) + \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) w_{mn}(t) \\
 &= \sum_{m=1}^M \left[ P_{1|1}(n_0, 0 | m, t) w_{mn}(t) - P_{1|1}(n_0, 0 | n, t) w_{nm}(t) \right]
 \end{aligned} \tag{5.54}$$

with the initial condition [ see (5.51a) or (5.52) ]

$$P_{1|1}(n_0, 0 | n, 0) = \delta_{n_0 n}$$

Using

$$\begin{aligned}
 \sum_{m=1}^M P(n, t) w_{nm}(t) &= \sum_{m,k=1}^M \delta_{kn} P(k, t) w_{km}(t) \\
 &= \sum_{m,k=1}^M \delta_{mn} P(m, t) w_{mk}(t) \quad [ m \leftrightarrow k ]
 \end{aligned}$$

the master equation (5.53) can be written as

$$\begin{aligned}
 \frac{\partial P(n, t)}{\partial t} &= \sum_{m=1}^M P(m, t) \left[ w_{mn}(t) - \delta_{mn} \sum_{k=1}^M w_{mk}(t) \right] \\
 &= \sum_{m=1}^M P(m, t) W_{mn}(t)
 \end{aligned} \tag{5.56}$$

where

$$\begin{aligned}
 W_{mn}(t) &= w_{mn}(t) - \delta_{mn} \sum_{k=1}^M w_{mk}(t) \\
 &= \begin{cases} - \sum_{k \neq m} w_{mk}(t) & \text{for } m = n \\ w_{mn}(t) & \text{for } m \neq n \end{cases}
 \end{aligned} \tag{5.55}$$

$$= \langle m | \mathbf{W}(t) | n \rangle$$

and  $\mathbf{W}(t)$  is called the **transition matrix**.

$\sum_{n=1}^M$  (5.55) gives

$$\sum_{n=1}^M W_{mn}(t) = \sum_{n=1}^M w_{mn}(t) - \sum_{k=1}^M w_{mk}(t) = 0 \quad \forall m \quad (5.57)$$

Consider now the eigen-equation for  $\mathbf{W}$ ,

$$\sum_{n=1}^M W_{mn} \psi(n) = \lambda \psi(m)$$

(5.57) then implies

$$\psi(n) = c \quad \forall n$$

is always an eigenvector of  $\mathbf{W}$  with eigenvalue  $\lambda = 0$ .

Using

$$P(n, t) = \langle p(t) | n \rangle$$

(5.56) becomes

$$\begin{aligned} \frac{\partial \langle p(t) | n \rangle}{\partial t} &= \sum_{m=1}^M \langle p(t) | m \rangle \langle m | \mathbf{W}(t) | n \rangle \\ &= \langle p(t) | \mathbf{W}(t) | n \rangle \quad \forall n \\ \rightarrow \frac{\partial \langle p(t) |}{\partial t} &= \langle p(t) | \mathbf{W}(t) \end{aligned} \quad (5.58)$$

Similarly, using

$$\begin{aligned} \sum_{m=1}^M P_{1|1}(n_0, 0 | n, t) w_{nm}(t) &= \sum_{m,k=1}^M \delta_{kn} P_{1|1}(n_0, 0 | k, t) w_{km}(t) \\ &= \sum_{m,k=1}^M \delta_{mn} P_{1|1}(n_0, 0 | m, t) w_{mk}(t) \end{aligned}$$

(5.54) can be written as

$$\begin{aligned} \frac{\partial P_{1|1}(n_0, 0 | n, t)}{\partial t} &= \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) \left[ w_{mn}(t) - \delta_{mn} \sum_{k=1}^M w_{mk}(t) \right] \\ &= \sum_{m=1}^M P_{1|1}(n_0, 0 | m, t) W_{mn}(t) \end{aligned}$$

Using

$$P_{1|1}(n_0, 0 | n, t) = \langle n_0 | \mathbf{P}(0 | t) | n \rangle$$

we have

$$\begin{aligned} \frac{\partial \langle n_0 | \mathbf{P}(0 | t) | n \rangle}{\partial t} &= \sum_{m=1}^M \langle n_0 | \mathbf{P}(0 | t) | m \rangle \langle m | \mathbf{W}(t) | n \rangle \\ &= \langle n_0 | \mathbf{P}(0 | t) \mathbf{W}(t) | n \rangle \quad \forall n_0, n \\ \rightarrow \frac{\partial \mathbf{P}(0 | t)}{\partial t} &= \mathbf{P}(0 | t) \mathbf{W}(t) \end{aligned} \quad (5.59)$$

Since  $\mathbf{W}(t)$  is not a symmetric matrix, its Jordan form may contain sub-blocks of dimensions greater than 1. In which case, the number of independent eigenvectors is less than the dimension of  $\mathbf{W}(t)$  so that the completeness relation is not satisfied. Spectral decomposition of  $\mathbf{W}(t)$  is then not

possible.

Fortunately, processes with transition rates  $w_{mn}(t)$  satisfying **detailed balance** can be transformed to a symmetric matrix form possessing a complete set of eigenvectors. This will be proved in the next section.

For time independent transition rates, the solution to (5.58) is simply

$$\langle \rho(t) | = \langle \rho(0) | e^{\mathbf{W}t} \quad (\text{a})$$

Assuming there is no deficit in the number of independent eigenvectors, we can use the spectral decomposition

$$\mathbf{W} = \sum_{i=0}^{M-1} \lambda_i | \psi_i \rangle \langle \chi_i | \quad \lambda_0 = 0 \quad (\text{b})$$

to write (a) as

$$\langle \rho(t) | = \sum_{i=0}^{M-1} \langle \rho(0) | \psi_i \rangle e^{\lambda_i t} \langle \chi_i | \quad (\text{c})$$

$$\rightarrow \langle \rho(t) | n \rangle = \sum_{i=0}^{M-1} \sum_{m=1}^M \langle \rho(0) | m \rangle \langle m | \psi_i \rangle e^{\lambda_i t} \langle \chi_i | n \rangle$$

$$\text{or } P(n, t) = \sum_{i=0}^{M-1} \sum_{m=1}^M P(m, 0) \psi_i(m) e^{\lambda_i t} \chi_i(n) \quad (\text{d})$$

where

$$\psi_i(m) = \langle m | \psi_i \rangle = m^{\text{th}} \text{ component of the right (column) eigenvector } | \psi_i \rangle$$

$$\chi_i(n) = \langle \chi_i | n \rangle = n^{\text{th}} \text{ component of the left (row) eigenvector } \langle \chi_i |$$

Reminder:

$$\langle \chi_i | = | \chi_i \rangle^T$$

$$\mathbf{W} | \psi_i \rangle = \lambda_i | \psi_i \rangle$$

$$\mathbf{W}^T | \chi_i \rangle = \lambda_i | \chi_i \rangle$$

In order for  $P(n, t)$  to remain finite as  $t \rightarrow \infty$ , we must have  $\text{Re } \lambda_i \leq 0$  for all  $i$ . In which case, property (5.57) guarantees an eigenvalue  $\lambda_0 = 0$  so that (d) gives the long time stationary state as

$$P^s(n) = \sum_{m=1}^M P(m, 0) \psi_0(m) \chi_0(n) \quad (\text{e})$$