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

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

for arbitrary Δt. In particular,

$$\frac{\partial P(n, t)}{\partial t} = \lim_{\Delta t \to 0} \frac{P(n, t+\Delta t) - P(n, t)}{\Delta t}$$

$$= \lim_{\Delta t \to 0} \frac{1}{\Delta t} \sum_{m=1}^{M} P(m, t) \left[P_{1|1}(m, t \mid n, t+\Delta t) - \delta_{mn} \right] \tag{5.51}$$

where

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

Let

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

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

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

and

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

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

= probability of remaining in state m during $(t, t+\Delta t)$

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

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

For $m = n$,

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

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

Combining both cases gives

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

(5.51) thus becomes

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

$$= -\sum_{k=1}^{M} P(n, t)\, w_{nk}(t) + \sum_{m=1}^{M} P(m, t)\, w_{mn}(t)$$

$$= -\sum_{m=1}^{M} P(n, t)\, w_{nm}(t) + \sum_{m=1}^{M} P(m, t)\, w_{mn}(t)$$

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

which is known as the master equation.

Similarly, the Chapman-Kolmogorov equation (5.21) becomes

$$P_{1|1}(n_0, 0 \mid n, t+\Delta t) = \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t)\, P_{1|1}(m, t \mid n, t+\Delta t)$$

$$= \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t) \left\{ \delta_{mn} \left[1 - \Delta t \sum_{k=1}^{M} w_{mk}(t) \right] + w_{mn}(t)\,\Delta t \right\} + O(\Delta t)^2$$

$$= P_{1|1}(n_0, 0 \mid n, t) - P_{1|1}(n_0, 0 \mid n, t)\,\Delta t \sum_{k=1}^{M} w_{nk}(t)$$

$$+ \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t)\, w_{mn}(t)\,\Delta t + O(\Delta t)^2$$

$$\to \qquad \frac{\partial P_{1|1}(n_0, 0 \mid n, t)}{\partial t} = \lim_{\Delta t \to 0} \frac{P_{1|1}(n_0, 0 \mid n, t+\Delta t) - P_{1|1}(n_0, 0 \mid n, t)}{\Delta t}$$

$$= -P_{1|1}(n_0, 0 \mid n, t) \sum_{k=1}^{M} w_{nk}(t) + \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t)\, w_{mn}(t)$$

$$= -P_{1|1}(n_0, 0 \mid n, t) \sum_{m=1}^{M} w_{nm}(t) + \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t)\, w_{mn}(t)$$

$$= \sum_{m=1}^{M} \left[P_{1|1}(n_0, 0 \mid m, t)\, w_{mn}(t) - P_{1|1}(n_0, 0 \mid n, t)\, w_{nm}(t) \right] \tag{5.54}$$

From (5.51a), we see that $P_{1|1}(n_0, 0 \mid n, t)$ obeys the initial condition

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

Using

$$\sum_{m=1}^{M} P(n, t)\, w_{nm}(t) = \sum_{m,k=1}^{M} \delta_{kn}\, P(k, t)\, w_{km}(t)$$

$$= \sum_{m,k=1}^{M} \delta_{mn}\, P(m, t)\, w_{mk}(t)$$

the master equation (5.53) can be written as

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

$$= \sum_{m=1}^{M} P(m, t)\, W_{mn}(t) \tag{5.56}$$

where

$$W_{mn}(t) = w_{mn}(t) - \delta_{mn} \sum_{k=1}^{M} w_{mk}(t) \tag{5.55}$$

$$\equiv \langle m \mid \boldsymbol{W}(t) \mid n \rangle$$

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

For $m \neq n$, (5.55) gives

$$W_{mn}(t) = w_{mn}(t) \geq 0 \tag{5.57a}$$

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

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

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

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

(5.57) then implies

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

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

Using

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

(5.56) becomes

$$\frac{\partial \langle p(t) \mid n \rangle}{\partial t} = \sum_{m=1}^{M} \langle p(t) \mid m \rangle \langle m \mid \boldsymbol{W}(t) \mid n \rangle$$

$$= \langle p(t) \mid \boldsymbol{W}(t) \mid n \rangle \qquad \forall\ n$$

$$\rightarrow \qquad \frac{\partial \langle p(t) \mid}{\partial t} = \langle p(t) \mid \boldsymbol{W}(t) \tag{5.58}$$

Similarly, using

$$\sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid n, t)\, w_{nm}(t) = \sum_{m,k=1}^{M} \delta_{kn}\, P_{1|1}(n_0, 0 \mid k, t)\, w_{km}(t)$$

$$= \sum_{m,k=1}^{M} \delta_{mn}\, P_{1|1}(n_0, 0 \mid m, t)\, w_{mk}(t)$$

(5.54) can be written as

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

$$= \sum_{m=1}^{M} P_{1|1}(n_0, 0 \mid m, t)\, W_{mn}(t)$$

Using

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

we have

$$\frac{\partial \langle n_0 \mid \boldsymbol{P}(0 \mid t) \mid n \rangle}{\partial t} = \sum_{m=1}^{M} \langle n_0 \mid \boldsymbol{P}(0 \mid t) \mid m \rangle \langle m \mid \boldsymbol{W}(t) \mid n \rangle$$

$$= \langle n_0 \mid \boldsymbol{P}(0 \mid t)\, \boldsymbol{W}(t) \mid n \rangle \qquad \forall\ n_0, n$$

$$\rightarrow \qquad \frac{\partial \boldsymbol{P}(0 \mid t)}{\partial t} = \boldsymbol{P}(0 \mid t)\, \boldsymbol{W}(t) \tag{5.59}$$

Since $\boldsymbol{W}(t)$ 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 $\boldsymbol{W}(t)$ so that the completeness relation is not satisfied. Spectral decomposition of $\boldsymbol{W}(t)$ 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

$$\langle p(t) \mid = \langle p(0) \mid e^{\boldsymbol{W} t} \qquad \text{(a)}$$

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

$$\boldsymbol{W} = \sum_{i=0}^{M-1} \lambda_i \mid \psi_i \rangle \langle \chi_i \mid \qquad \text{(b)}$$

to write (a) as

$$\langle p(t) \mid = \sum_{i=0}^{M-1} \langle p(0) \mid \psi_i \rangle\, e^{\lambda_i t} \langle \chi_i \mid \qquad \text{(c)}$$

→ $$\langle p(t) \mid n \rangle = \sum_{i=0}^{M-1} \sum_{m=1}^{M} \langle p(0) \mid m \rangle \langle m \mid \psi_i \rangle e^{\lambda_i t} \langle \chi_i \mid n \rangle$$

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

where

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

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

Reminder: Since $\boldsymbol{W}$ is real,

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

$\boldsymbol{W} \mid \psi_i \rangle = \lambda_i \mid \psi_i \rangle$ $\qquad$ $\boldsymbol{W}^T \mid \chi_i \rangle = \lambda_i \mid \chi_i \rangle$

In order for $P(n, t)$ to remain finite as $t \to \infty$, we must have $\text{Re}\,\lambda_i \le 0$ 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

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