

5.D.2. Detailed Balance

(5.53) implies that $P(n, t)$ is time-independent, i.e., $\frac{\partial}{\partial t} P(n, t) = 0$, if

$$P(m, t) w_{mn}(t) = P(n, t) w_{nm}(t) \quad \forall m \quad (5.60a)$$

For processes with time-independent w_{mn} (and hence \mathbf{W}), the stationary state $\langle p^s |$ is given by [see (5.58)]

$$\langle p^s | \mathbf{W} = 0$$

i.e., it is a left eigenvector of the transition matrix \mathbf{W} .

Setting

$$P^s(n) = \langle p^s | n \rangle \equiv \lim_{t \rightarrow \infty} P(n, t)$$

turns (5.60a) into

$$P^s(m) w_{mn} = P^s(n) w_{nm} \quad \forall m \quad (5.60)$$

which is called **detailed balance** since it means during any Δt ,

average number of transitions from m into n

= average number of transitions out of n back to m .

Note that $P^s(n)$ can be obtained by iteration using (5.60). For example, expressing all $P^s(n)$'s in terms of $P^s(1)$, we have

$$P^s(2) = P^s(1) \frac{w_{1,2}}{w_{2,1}}$$

$$P^s(3) = P^s(2) \frac{w_{2,3}}{w_{3,2}} = P^s(1) \frac{w_{1,2}}{w_{2,1}} \frac{w_{2,3}}{w_{3,2}}$$

and so on. The normalization

$$\sum_{n=1}^M P^s(n) = 1$$

then becomes a linear equation for $P^s(1)$ and be solved trivially.

(5.60) can be written in a symmetric form by dividing it with $\sqrt{P^s(m) P^s(n)}$ so that

$$\sqrt{\frac{P^s(m)}{P^s(n)}} w_{mn} = \sqrt{\frac{P^s(n)}{P^s(m)}} w_{nm} \quad (5.60b)$$

Note that (5.60b) is just an identity, $w_{mm} = w_{mm}$, for $n = m$.

Let

$$V_{mn} = \sqrt{\frac{P^s(m)}{P^s(n)}} w_{mn} \quad \forall m \neq n \quad (5.61a)$$

Setting $m \leftrightarrow n$ gives

$$V_{nm} = \sqrt{\frac{P^s(n)}{P^s(m)}} w_{nm} \quad \forall m \neq n$$

so that (5.61) becomes

$$V_{mn} = V_{nm} \quad \forall m \neq n \quad (5.61b)$$

From (5.55), we see that for $m \neq n$, $w_{mn} = W_{mn}$ so that by setting

$$V_{mn} = \sqrt{\frac{P^s(m)}{P^s(n)}} W_{mn} \quad \forall m, n$$

$$= \sqrt{\frac{P^s(m)}{P^s(n)}} \left(W_{mn} - \delta_{mn} \sum_{k=1}^M W_{mk} \right) \quad (5.61)$$

(5.61b) is still valid. What's new is that we now have

$$V_{mm} = W_{mm} = W_{mm} - \sum_{k=1}^M W_{mk}$$

(5.56) then becomes

$$\begin{aligned} \frac{\partial P(n, t)}{\partial t} &= \sum_{m=1}^M P(m, t) \sqrt{\frac{P^s(n)}{P^s(m)}} V_{mn} \\ \rightarrow \frac{\partial \tilde{P}(n, t)}{\partial t} &= \sum_{m=1}^M \tilde{P}(m, t) V_{mn} \end{aligned} \quad (5.62)$$

where

$$\tilde{P}(n, t) = \frac{P(n, t)}{\sqrt{P^s(n)}}$$

In terms of the Dirac notations, (5.62) becomes

$$\begin{aligned} \frac{\partial \langle \tilde{p}(t) | n \rangle}{\partial t} &= \sum_{m=1}^M \langle \tilde{p}(t) | m \rangle \langle m | \mathbf{V} | n \rangle \\ &= \langle \tilde{p}(t) | \mathbf{V} | n \rangle \end{aligned} \quad (5.62a)$$

where

$$\langle \tilde{p}(t) | n \rangle = \tilde{P}(n, t) \quad \langle m | \mathbf{V} | n \rangle = V_{mn}$$

Since (5.62a) is true for all n , we have

$$\frac{\partial \langle \tilde{p}(t) |}{\partial t} = \langle \tilde{p}(t) | \mathbf{V} \quad (5.62b)$$

Since \mathbf{V} is time-independent, the solution to (5.62b) is simply

$$\langle \tilde{p}(t) | = \langle \tilde{p}(0) | e^{\mathbf{V}t} \quad (5.63)$$

Since \mathbf{V} is a real symmetric matrix, the left and right eigenvectors of the same non-degenerate eigenvalue are related by a transpose operation, i.e.,

$$\mathbf{V} | \psi_i \rangle = \lambda_i | \psi_i \rangle \quad \langle \psi_i | \mathbf{V} = \langle \psi_i | \lambda_i$$

For degenerate eigenvalues, they can be chosen as transpose pairs.

Furthermore, it always has a complete orthonormal set of eigenvectors so that

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \sum_{i=0}^{M-1} | \psi_i \rangle \langle \psi_i | = 1$$

[See (5.67) for the reason of the choice of the range of i .]

Thus,

$$\begin{aligned} \mathbf{V} &= \sum_{i=0}^{M-1} \lambda_i | \psi_i \rangle \langle \psi_i | \\ \rightarrow e^{\mathbf{V}t} &= \sum_{i=0}^{M-1} e^{\lambda_i t} | \psi_i \rangle \langle \psi_i | \end{aligned}$$

and (5.63) becomes

$$\langle \tilde{p}(t) | = \sum_{i=0}^{M-1} \langle \tilde{p}(0) | \psi_i \rangle e^{\lambda_i t} \langle \psi_i | \quad (5.64)$$

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

$$\text{or } \tilde{P}(n, t) = \sum_{i=0}^{M-1} \sum_{m=1}^M \tilde{P}(m, 0) \psi_i(m) e^{\lambda_i t} \psi_i(n) \quad (5.65a)$$

where $\psi_i(m) = \langle m | \psi_i \rangle$ is the m^{th} component of the (column) eigenvector $|\psi_i\rangle$. In terms of the probability, we have

$$P(n, t) = \sum_{i=0}^{M-1} \sum_{m=1}^M \sqrt{\frac{P^s(n)}{P^s(m)}} P(m, 0) \psi_i(m) e^{\lambda_i t} \psi_i(n) \quad (5.65)$$

In order for $P(n, t)$ to remain finite as $t \rightarrow \infty$, we must have $\lambda_i \leq 0$ for all i . In which case, property (5.57) guarantees an eigenvalue $\lambda_0 = 0$ so that (5.65) gives

$$P^s(n) = \sum_{m=1}^M \sqrt{\frac{P^s(n)}{P^s(m)}} P(m, 0) \psi_0(m) \psi_0(n) \quad (5.65b)$$

$$\rightarrow \frac{\sqrt{P^s(n)}}{\psi_0(n)} = \sum_{m=1}^M \frac{P(m, 0)}{\sqrt{P^s(m)}} \psi_0(m) = \text{const} \quad \forall n \quad (5.65c)$$

Exercise 5.2.

Consider an asymmetric random walk on an open-ended lattice with 4 lattice sites. The transition rates are

$$w_{1,2} = w_{4,3} = 1 \quad w_{2,3} = w_{3,4} = \frac{3}{4} \quad w_{2,1} = w_{3,2} = \frac{1}{4}$$

and $w_{ij} = 0$ otherwise.

- Write the transition matrix \mathbf{W} and show that it obeys detailed balance.
- Compute \mathbf{V} and find its eigenvalues & eigenvectors.
- Write $P(n, t)$ for the case $P(n, 0) = \delta_{n1}$. What is $P(2, t)$?

Ans. (a)

$$\mathbf{W} = \begin{pmatrix} -1 & 1 & 0 & 0 \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ 0 & 0 & 1 & -1 \end{pmatrix}$$

From the *Mathematica* code below, we get, in order of decreasing magnitude,

$$\lambda_0 = 0 \quad \lambda_1 = -\frac{1}{4}(4 - \sqrt{3}) \quad \lambda_2 = -2 \quad \lambda_3 = -\frac{1}{4}(4 + \sqrt{3})$$

The corresponding (unnormalized) right eigenvectors are

$$\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad \begin{pmatrix} -3\sqrt{3} \\ -\frac{9}{4} \\ \frac{\sqrt{3}}{4} \\ 1 \end{pmatrix} \quad \begin{pmatrix} -1 \\ 1 \\ -1 \\ 1 \end{pmatrix} \quad \begin{pmatrix} 3\sqrt{3} \\ -\frac{9}{4} \\ -\frac{\sqrt{3}}{4} \\ 1 \end{pmatrix}$$

The corresponding (unnormalized) left eigenvectors are

$$\left(\frac{1}{9} \frac{4}{9} \frac{4}{3} 1\right), \left(-\frac{1}{\sqrt{3}} -1 \frac{1}{\sqrt{3}} 1\right), \left(-\frac{1}{9} \frac{4}{9} -\frac{4}{3} 1\right), \left(\frac{1}{\sqrt{3}} -1 -\frac{1}{\sqrt{3}} 1\right)$$

The stationary state $\langle p^s |$ is just the left eigenvector for λ_0 normalized to $\sum_{n=1}^M \langle p^s | n \rangle = 1$.

$$\langle p^s | = \langle \chi_0 | = \frac{9}{26} \left(\frac{1}{9} \frac{4}{9} \frac{4}{3} 1\right) = \left(\frac{1}{26} \frac{2}{13} \frac{6}{13} \frac{9}{26}\right)$$

$$P^s(n) = \langle p^s | n \rangle = \langle \chi_0 | n \rangle$$

Interestingly, $\sum_{n=1}^M \langle \chi_j | n \rangle = 0$ for $j = 1, 2, 3$.

The detailed balance

$$P^s(n) w_{nm} = P^s(m) w_{mn}$$

is equivalent to saying that the matrix \mathbf{A} with elements

$$A_{nm} = P^s(n) w_{nm} \quad \rightarrow \quad A_{mn} = P^s(m) w_{mn}$$

is symmetric.

As shown in §Code (a),

$$\mathbf{A} = \begin{pmatrix} -\frac{1}{26} & \frac{1}{26} & 0 & 0 \\ \frac{1}{26} & -\frac{2}{13} & \frac{3}{26} & 0 \\ 0 & \frac{3}{26} & -\frac{6}{13} & \frac{9}{26} \\ 0 & 0 & \frac{9}{26} & -\frac{9}{26} \end{pmatrix}$$

is indeed symmetric.

Code (a)

$$\mathbf{W} = \begin{pmatrix} -1 & 1 & 0 & 0 \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ 0 & 0 & 1 & -1 \end{pmatrix};$$

(* eigenvalues & right eigenvectors $|\psi_i\rangle$ *)

`{λ, rv} = Eigensystem[W]`

$$\left\{ \{-2, \frac{1}{4}(-4 - \sqrt{3}), \frac{1}{4}(-4 + \sqrt{3}), 0\}, \right.$$

$$\left. \left\{ \{-1, 1, -1, 1\}, \{3\sqrt{3}, -\frac{9}{4}, -\frac{\sqrt{3}}{4}, 1\}, \{-3\sqrt{3}, -\frac{9}{4}, \frac{\sqrt{3}}{4}, 1\}, \{1, 1, 1, 1\} \right\} \right\}$$

(* rows of rv are right eigenvectors *)

`Table[W.rv[[i]] == λ[[i]] rv[[i]], {i, 4}]`

`{True, True, True, True}`

(* columns of rv^T are right eigenvectors *)

rv^T // MatrixForm

$$\begin{pmatrix} -1 & 3\sqrt{3} & -3\sqrt{3} & 1 \\ 1 & -\frac{9}{4} & -\frac{9}{4} & 1 \\ -1 & -\frac{\sqrt{3}}{4} & \frac{\sqrt{3}}{4} & 1 \\ 1 & 1 & 1 & 1 \end{pmatrix}$$

(* eigenvalues & left eigenvectors $\langle \chi_i |$ *)

$\{\lambda, lv\} = \text{Eigensystem}[W^T]$

$$\left\{ \left\{ -2, \frac{1}{4}(-4 - \sqrt{3}), \frac{1}{4}(-4 + \sqrt{3}), 0 \right\}, \left\{ \left\{ -\frac{1}{9}, \frac{4}{9}, -\frac{4}{3}, 1 \right\}, \left\{ \frac{1}{\sqrt{3}}, -1, -\frac{1}{\sqrt{3}}, 1 \right\}, \left\{ -\frac{1}{\sqrt{3}}, -1, \frac{1}{\sqrt{3}}, 1 \right\}, \left\{ \frac{1}{9}, \frac{4}{9}, \frac{4}{3}, 1 \right\} \right\} \right\}$$

(* Stationary state $\langle p^s |$ *)

$lvnC = \text{Plus}@@lv[[4]]$

$ps = lv[[4]]/lvnC$

$\frac{26}{9}$

9

$$\left\{ \frac{1}{26}, \frac{2}{13}, \frac{6}{13}, \frac{9}{26} \right\}$$

(* $A_{nm} = P^s(n)w_{nm}$ *)

$(A = \text{Table}[ps[[n]]W[[n, m]], \{n, 4\}, \{m, 4\}])$ // MatrixForm

$$\begin{pmatrix} -\frac{1}{26} & \frac{1}{26} & 0 & 0 \\ \frac{1}{26} & -\frac{2}{13} & \frac{3}{26} & 0 \\ 0 & \frac{3}{26} & -\frac{6}{13} & \frac{9}{26} \\ 0 & 0 & \frac{9}{26} & -\frac{9}{26} \end{pmatrix}$$

(* rows of lv are left eigenvectors *)

$\text{Table}[lv[[i]].W == \lambda[[i]]lv[[i]], \{i, 4\}]$

{True, True, True, True}

lv // MatrixForm

$$\begin{pmatrix} -\frac{1}{9} & \frac{4}{9} & -\frac{4}{3} & 1 \\ \frac{1}{\sqrt{3}} & -1 & -\frac{1}{\sqrt{3}} & 1 \\ -\frac{1}{\sqrt{3}} & -1 & \frac{1}{\sqrt{3}} & 1 \\ \frac{1}{9} & \frac{4}{9} & \frac{4}{3} & 1 \end{pmatrix}$$

```

(* orthogonality  $\langle \chi_i | \psi_j \rangle \propto \delta_{ij}$  *)
(* left eigenvector in row form, right eigenvector in column form *)
(nC = lv.rv^T) // MatrixForm

$$\begin{pmatrix} \frac{26}{9} & 0 & 0 & 0 \\ 0 & \frac{13}{2} & 0 & 0 \\ 0 & 0 & \frac{13}{2} & 0 \\ 0 & 0 & 0 & \frac{26}{9} \end{pmatrix}$$


(* normalized left eigenvectors  $\langle \chi_i | \rightarrow \frac{\langle \chi_i |}{\langle \chi_i | \psi_i \rangle}$  *)
lvn = Table[lv[[i]]/nC[[i, i]], {i, 4}]

$$\left\{ \left\{ -\frac{1}{26}, \frac{2}{13}, -\frac{6}{13}, \frac{9}{26} \right\}, \left\{ \frac{2}{13\sqrt{3}}, -\frac{2}{13}, -\frac{2}{13\sqrt{3}}, \frac{2}{13} \right\}, \right.$$


$$\left. \left\{ -\frac{2}{13\sqrt{3}}, -\frac{2}{13}, \frac{2}{13\sqrt{3}}, \frac{2}{13} \right\}, \left\{ \frac{1}{26}, \frac{2}{13}, \frac{6}{13}, \frac{9}{26} \right\} \right\}$$


(* orthonormality  $\langle \chi_i | \psi_j \rangle = \delta_{ij}$  *)
(* left eigenvector in row form, right eigenvector in column form *)
(nC = lvn.rv^T) // MatrixForm

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$


(* completeness  $\sum_i |\psi_i\rangle\langle\chi_i| = I$  *)
(* right eigenvector in row form, left eigenvector in column form *)
rv.lvn^T // MatrixForm

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$


```

Ans. (b)

From §Code (b), we have

$$V = \begin{pmatrix} -1 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & -1 & \frac{\sqrt{3}}{4} & 0 \\ 0 & \frac{\sqrt{3}}{4} & -1 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -1 \end{pmatrix}$$

Also, in order of decreasing magnitude,

$$\lambda_0 = 0 \quad \lambda_1 = -\frac{1}{4}(4 - \sqrt{3}) \quad \lambda_2 = -2 \quad \lambda_3 = -\frac{1}{4}(4 + \sqrt{3})$$

The corresponding (unnormalized) eigenvectors are

$$\begin{pmatrix} \frac{1}{3} \\ \frac{2}{3} \\ \frac{2}{\sqrt{3}} \\ 1 \end{pmatrix} \quad \begin{pmatrix} -\sqrt{3} \\ -\frac{3}{2} \\ \frac{1}{2} \\ 1 \end{pmatrix} \quad \begin{pmatrix} -\frac{1}{3} \\ \frac{2}{3} \\ -\frac{2}{\sqrt{3}} \\ 1 \end{pmatrix} \quad \begin{pmatrix} \sqrt{3} \\ -\frac{3}{2} \\ -\frac{1}{2} \\ 1 \end{pmatrix}$$

With the normalization

$$|\psi_i\rangle \rightarrow \frac{|\psi_i\rangle}{\sqrt{\langle \psi_i | \psi_i \rangle}}$$

the normalized eigenvectors are

$$|\psi_0\rangle = \begin{pmatrix} \frac{1}{\sqrt{26}} \\ \sqrt{\frac{2}{13}} \\ \sqrt{\frac{6}{13}} \\ \frac{3}{\sqrt{26}} \end{pmatrix} \quad |\psi_1\rangle = \begin{pmatrix} -\sqrt{\frac{6}{13}} \\ -\frac{3}{\sqrt{26}} \\ \frac{1}{\sqrt{26}} \\ \sqrt{\frac{2}{13}} \end{pmatrix} \quad |\psi_2\rangle = \begin{pmatrix} -\frac{1}{\sqrt{26}} \\ \sqrt{\frac{2}{13}} \\ -\sqrt{\frac{6}{13}} \\ \frac{3}{\sqrt{26}} \end{pmatrix} \quad |\psi_3\rangle = \begin{pmatrix} \sqrt{\frac{6}{13}} \\ -\frac{3}{\sqrt{26}} \\ -\frac{1}{\sqrt{26}} \\ \sqrt{\frac{2}{13}} \end{pmatrix}$$

Code (b)

```
V = Table[ $\sqrt{\frac{\text{ps}[[n]]}{\text{ps}[[m]}}$  W[[n, m]], {n, 4}, {m, 4}];
```

```
V // MatrixForm
```

$$\begin{pmatrix} -1 & \frac{1}{2} & 0 & 0 \\ \frac{1}{2} & -1 & \frac{\sqrt{3}}{4} & 0 \\ 0 & \frac{\sqrt{3}}{4} & -1 & \frac{\sqrt{3}}{2} \\ 0 & 0 & \frac{\sqrt{3}}{2} & -1 \end{pmatrix}$$

```
(* eigenvalues & eigenvectors  $|\psi_i\rangle$  *)
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```
{λp, ev} = Eigensystem[V]
```

$$\left\{ \left\{ -2, \frac{1}{4}(-4 - \sqrt{3}) \right\}, \left\{ \frac{1}{4}(-4 + \sqrt{3}), 0 \right\}, \right.$$

$$\left. \left\{ \left\{ -\frac{1}{3}, \frac{2}{3}, -\frac{2}{\sqrt{3}}, 1 \right\}, \left\{ \sqrt{3}, -\frac{3}{2}, -\frac{1}{2}, 1 \right\}, \left\{ -\sqrt{3}, -\frac{3}{2}, \frac{1}{2}, 1 \right\}, \left\{ \frac{1}{3}, \frac{2}{3}, \frac{2}{\sqrt{3}}, 1 \right\} \right\} \right\}$$

```
(* orthogonality  $\langle \psi_i | \psi_j \rangle \propto \delta_{ij}$  *)
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```
(nCp = ev.ev^T) // MatrixForm
```

$$\begin{pmatrix} \frac{26}{9} & 0 & 0 & 0 \\ 0 & \frac{13}{2} & 0 & 0 \\ 0 & 0 & \frac{13}{2} & 0 \\ 0 & 0 & 0 & \frac{26}{9} \end{pmatrix}$$

(* normalized eigenvectors $|\psi_i\rangle \rightarrow \frac{|\psi_i\rangle}{\sqrt{\langle \psi_i | \psi_i \rangle}}$ *)

evn = Table[ev[[i]] / $\sqrt{\text{ncp}[[i, i]]}$, {i, 4}]

$$\left\{ \left\{ -\frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}}, -\sqrt{\frac{6}{13}}, \frac{3}{\sqrt{26}} \right\}, \left\{ \sqrt{\frac{6}{13}}, -\frac{3}{\sqrt{26}}, -\frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}} \right\}, \right. \\ \left. \left\{ -\sqrt{\frac{6}{13}}, -\frac{3}{\sqrt{26}}, \frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}} \right\}, \left\{ \frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}}, \sqrt{\frac{6}{13}}, \frac{3}{\sqrt{26}} \right\} \right\}$$

Ans. (c)

For the initial condition $P(n, 0) = \delta_{n1}$, (5.65) becomes

$$P(n, t) = P^s(n) + \sum_{i=1}^3 \sqrt{\frac{P^s(n)}{P^s(1)}} \psi_i(1) e^{\lambda_i t} \psi_i^*(n)$$

Hence,

$$\begin{aligned} P(2, t) &= P^s(2) + \sum_{i=1}^3 \sqrt{\frac{P^s(2)}{P^s(1)}} \psi_i(1) e^{\lambda_i t} \psi_i^*(2) \\ &= \frac{2}{13} - \frac{2e^{-2t}}{13} - \frac{6}{13} \sqrt{3} e^{\frac{1}{4}(-4-\sqrt{3})t} + \frac{6}{13} \sqrt{3} e^{\frac{1}{4}(-4+\sqrt{3})t} \\ &= 0.153846 - 0.153846 e^{-2.t} - 0.799408 e^{-1.43301 t} + 0.799408 e^{-0.566987 t} \end{aligned}$$

Code (c)

ps

$$\left\{ \frac{1}{26}, \frac{2}{13}, \frac{6}{13}, \frac{9}{26} \right\}$$

λp

$$\left\{ -2, \frac{1}{4}(-4-\sqrt{3}), \frac{1}{4}(-4+\sqrt{3}), 0 \right\}$$

evn

$$\left\{ \left\{ -\frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}}, -\sqrt{\frac{6}{13}}, \frac{3}{\sqrt{26}} \right\}, \left\{ \sqrt{\frac{6}{13}}, -\frac{3}{\sqrt{26}}, -\frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}} \right\}, \right. \\ \left. \left\{ -\sqrt{\frac{6}{13}}, -\frac{3}{\sqrt{26}}, \frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}} \right\}, \left\{ \frac{1}{\sqrt{26}}, \sqrt{\frac{2}{13}}, \sqrt{\frac{6}{13}}, \frac{3}{\sqrt{26}} \right\} \right\}$$

$$\text{ps}[[2]] + \sum_{i=1}^3 \sqrt{\frac{\text{ps}[[2]]}{\text{ps}[[1]]}} \text{evn}[[i, 1]] e^{\lambda p[[i]] t} \text{evn}[[i, 2]]$$

$$\frac{2}{13} - \frac{2e^{-2t}}{13} - \frac{6}{13} \sqrt{3} e^{\frac{1}{4}(-4-\sqrt{3})t} + \frac{6}{13} \sqrt{3} e^{\frac{1}{4}(-4+\sqrt{3})t}$$

% // N

$$0.153846 - 0.153846 e^{-2 \cdot t} - 0.799408 e^{-1.43301 t} + 0.799408 e^{-0.566987 t}$$

Exercise 5.3.

Consider an asymmetric random walk on a periodic lattice with 4 lattice sites. The transition rates are

$$w_{12} = w_{23} = w_{34} = w_{41} = \frac{3}{4} \qquad w_{21} = w_{32} = w_{43} = w_{14} = \frac{1}{4}$$

and $w_{ij} = 0$ otherwise.

Write the transition matrix \mathbf{W} and show that this system does not obey detailed balance.

Answer

$$\mathbf{W} = \begin{pmatrix} -1 & \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} & -1 \end{pmatrix}$$

The eigenvalues of \mathbf{W} are

$$\lambda_0 = 0 \qquad \lambda_1 = -1 + \frac{1}{2}i \qquad \lambda_2 = -1 - \frac{1}{2}i \qquad \lambda_3 = -2$$

with corresponding (unnormalized) right eigenvectors

$$\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \qquad \begin{pmatrix} i \\ -1 \\ -i \\ 1 \end{pmatrix} \qquad \begin{pmatrix} -i \\ -1 \\ i \\ 1 \end{pmatrix} \qquad \begin{pmatrix} -1 \\ 1 \\ -1 \\ 1 \end{pmatrix}$$

and left eigenvectors

$$(1 \ 1 \ 1 \ 1), \quad (-i \ -1 \ i \ 1), \quad (i \ -1 \ -i \ 1), \quad (-1 \ 1 \ -1 \ 1)$$

Since $\text{Re } \lambda_i \leq 0$ for all i , there is a long time stationary state given by the left eigenvector of $\lambda_0 = 0$.

Using the sum rule for probabilities, $\sum_{n=1}^M \langle p^s | n \rangle = 1$, we have

$$\langle p^s | = \langle \chi_0 | = \frac{1}{4} (1 \ 1 \ 1 \ 1) = \left(\frac{1}{4} \ \frac{1}{4} \ \frac{1}{4} \ \frac{1}{4} \right)$$

$$\rightarrow P^s(n) = \langle p^s | n \rangle = \langle \chi_0 | n \rangle = \frac{1}{4} \qquad \forall n$$

On the other hand, the normalization

$$\langle \chi_0 | \psi_0 \rangle = 1 \qquad \rightarrow \quad | \psi_0 \rangle = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}$$

Therefore, (e) in §5.D.1 also gives

$$P^s(n) = \frac{1}{4} \sum_{m=1}^M P(m, 0) = \frac{1}{4} \qquad \forall n$$

The detailed balance

$$P^S(n) w_{nm} = P^S(m) w_{mn}$$

is equivalent to saying that the matrix \mathbf{A} with elements

$$A_{nm} = P^S(n) w_{nm} \quad \rightarrow \quad A_{mn} = P^S(m) w_{mn}$$

is symmetric.

As shown in §Code,

$$\mathbf{A} = \begin{pmatrix} -\frac{1}{4} & \frac{3}{16} & 0 & \frac{1}{16} \\ \frac{1}{16} & -\frac{1}{4} & \frac{3}{16} & 0 \\ 0 & \frac{1}{16} & -\frac{1}{4} & \frac{3}{16} \\ \frac{3}{16} & 0 & \frac{1}{16} & -\frac{1}{4} \end{pmatrix}$$

is not symmetric so that detailed balance is not observed. Therefore,

$$\frac{\partial P(n, t)}{\partial t} \neq 0 \quad \forall t$$

and we have a probability current around the lattice permanently.

Code

```
In[1]:= W = 
$$\begin{pmatrix} -1 & \frac{3}{4} & 0 & \frac{1}{4} \\ \frac{1}{4} & -1 & \frac{3}{4} & 0 \\ 0 & \frac{1}{4} & -1 & \frac{3}{4} \\ \frac{3}{4} & 0 & \frac{1}{4} & -1 \end{pmatrix}$$

```

```
Out[1]= {{-1,  $\frac{3}{4}$ , 0,  $\frac{1}{4}$ }, { $\frac{1}{4}$ , -1,  $\frac{3}{4}$ , 0}, {0,  $\frac{1}{4}$ , -1,  $\frac{3}{4}$ }, { $\frac{3}{4}$ , 0,  $\frac{1}{4}$ , -1}}
```

```
In[2]:= (* eigenvalues  $\lambda_i = r\lambda[[i]]$  & right eigenvectors  $|\psi_i\rangle = rv[[i]$  *)
{rλ, rv} = Eigensystem[W]
```

```
Out[2]= {{-2, -1 +  $\frac{i}{2}$ , -1 -  $\frac{i}{2}$ , 0}, {{-1, 1, -1, 1}, {i, -1, -i, 1}, {-i, -1, i, 1}, {1, 1, 1, 1}}
```

```
In[3]:= (* eigenvalues  $\lambda_i = l\lambda[[i]]$  & left eigenvectors  $\langle\chi_i| = lv[[i]$  *)
{lλ, lv} = Eigensystem[WT]
```

```
Out[3]= {{-2, -1 +  $\frac{i}{2}$ , -1 -  $\frac{i}{2}$ , 0}, {{-1, 1, -1, 1}, {-i, -1, i, 1}, {i, -1, -i, 1}, {1, 1, 1, 1}}
```

```
In[4]:= (* Checking *)
```

```
Table[lv[[i]].W == lλ[[i]] lv[[i]], {i, 4}]
```

```
Out[4]= {True, True, True, True}
```

```
In[5]:= (* orthogonality *)
```

```
Table[lv[[i]].rv[[j]], {i, 4}, {j, 4}] // MatrixForm
```

```
Out[5]//MatrixForm=
```

$$\begin{pmatrix} 4 & 0 & 0 & 0 \\ 0 & 4 & 0 & 0 \\ 0 & 0 & 4 & 0 \\ 0 & 0 & 0 & 4 \end{pmatrix}$$

In[6]:= (* normalized left eigenvectors *)

lvn = Table[lv[[i]] / (lv[[i]].rv[[i]]), {i, 4}]

Out[6]= $\left\{ \left\{ -\frac{1}{4}, \frac{1}{4}, -\frac{1}{4}, \frac{1}{4} \right\}, \left\{ -\frac{i}{4}, -\frac{1}{4}, \frac{i}{4}, \frac{1}{4} \right\}, \left\{ \frac{i}{4}, -\frac{1}{4}, -\frac{i}{4}, \frac{1}{4} \right\}, \left\{ \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right\} \right\}$

In[7]:= (* orthonormality *)

Table[lvn[[i]].rv[[j]], {i, 4}, {j, 4}] // MatrixForm

Out[7]//MatrixForm=

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

In[15]:= (* $|\psi_i\rangle\langle\chi_i|$ *)

r1Prod = Table[Outer[Times, rv[[i]], lvn[[i]], {i, 4}];

MatrixForm/@r1Prod

Out[16]= $\left\{ \begin{pmatrix} \frac{1}{4} & -\frac{1}{4} & \frac{1}{4} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{1}{4} & -\frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & -\frac{1}{4} & \frac{1}{4} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{1}{4} & -\frac{1}{4} & \frac{1}{4} \end{pmatrix}, \begin{pmatrix} \frac{1}{4} & -\frac{i}{4} & -\frac{1}{4} & \frac{i}{4} \\ \frac{i}{4} & \frac{1}{4} & -\frac{i}{4} & -\frac{1}{4} \\ -\frac{1}{4} & \frac{i}{4} & \frac{1}{4} & -\frac{i}{4} \\ -\frac{i}{4} & -\frac{1}{4} & \frac{i}{4} & \frac{1}{4} \end{pmatrix}, \begin{pmatrix} \frac{1}{4} & \frac{i}{4} & -\frac{1}{4} & -\frac{i}{4} \\ -\frac{i}{4} & \frac{1}{4} & \frac{i}{4} & -\frac{1}{4} \\ -\frac{1}{4} & -\frac{i}{4} & \frac{1}{4} & \frac{i}{4} \\ \frac{i}{4} & -\frac{1}{4} & -\frac{i}{4} & \frac{1}{4} \end{pmatrix}, \begin{pmatrix} \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \\ \frac{1}{4} & \frac{1}{4} & \frac{1}{4} & \frac{1}{4} \end{pmatrix} \right\}$

In[17]:= (* Completeness: $\sum_{i=1}^4 |\psi_i\rangle\langle\chi_i| = \mathbf{I}$ *)

$\sum_{i=1}^4$ r1Prod[[i]] // MatrixForm

Out[17]//MatrixForm=

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

In[13]:= (* Stationary state $\langle p^s |$ *)

ps = lvn[[4]]

Out[13]= $\left\{ \frac{1}{4}, \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right\}$

In[14]:= (* $A_{nm} = P^s(n)W_{nm}$ *)

(A = Table[ps[[n]] W[[n, m]], {n, 4}, {m, 4}]) // MatrixForm

Out[14]//MatrixForm=

$$\begin{pmatrix} -\frac{1}{4} & \frac{3}{16} & 0 & \frac{1}{16} \\ \frac{1}{16} & -\frac{1}{4} & \frac{3}{16} & 0 \\ 0 & \frac{1}{16} & -\frac{1}{4} & \frac{3}{16} \\ \frac{3}{16} & 0 & \frac{1}{16} & -\frac{1}{4} \end{pmatrix}$$