A Markov Model of Quantum Wires

A. P. Mullhaupt

1. An Idealized Model of a Quantum Wire

Consider a system which can occupy any of n states which we label 1 through n, which can be thought of as a linear lattice of locations where a particle may be found. We distinguish three types of states; state 1 is the 'donor' state, state n is the 'acceptor' state, and the other states are called 'bridge' states.

We define a transition matrix A_{ij} which represents the probability that if the system is in state j at a time t that the system will be in state i at time $t+1$. We have not fixed the units, so 1 is supposed to represent a short but finite time. We assume that the probabilities A_{ij} do not depend on the state of the system or the time. Let $p_j(t)$ be the probability that if the system is observed at time t that the system is in state j. Then we have the equation

$$p_i(t+1) = \sum_{j=1}^{n} A_{ij} p_j(t) \tag{1}$$

which is the same as

$$p(t+1) = Ap(t) \tag{2}$$

where $p(t)$ is the vector with j^{th} component $p_j(t)$.

In order for these probabilities to be sensible, we must have $0 \leq p_j(t) \leq 1$ for all j and t,we must also have $0 \leq A_{ij} \leq 1$. In order for the probability model to be complete we must have at any time t

$$\sum_{i} p_j(t) = 1. \tag{3}$$

It follows that the transition probabilities A_{ij} must preserve this property, which implies that for each j we have

$$\sum_{i=1}^{n} A_{ij} = 1, \tag{4}$$

which ensures that

$$\begin{aligned} \sum_{i=1}^{n} p_i(t+1) &= \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} p_j(t) && (5) \\ &= \sum_{j=1}^{n} \left(\sum_{i=1}^{n} A_{ij} \right) p_j(t) && (6) \end{aligned}$$

$$\begin{aligned} &= \sum_{j=1}^{n} p_j(t) && (7) \\ &= 1. && (8) \end{aligned}$$

A matrix A with these properties is called a *stochastic* matrix.

Lemma 1. *The product of two stochastic matrices A and B is also stochastic.*

Proof. Since the ij^{th} element of the product

$$(AB)_{ij} = \sum_{k=1}^{n} A_{ik} B_{kj} \tag{9}$$

is a sum of products of nonnegative numbers A_{ik} and B_{kj} then $(AB)_{ij}$ is also nonnegative. In addition the column sums are unity

$$\begin{aligned} \sum_{i=1}^{n} (AB)_{ij} &= \sum_{i=1}^{n} \sum_{k=1}^{n} A_{ik} B_{kj} && (10) \\ &= \sum_{k=1}^{n} \left(\sum_{i=1}^{n} A_{ik} \right) B_{kj} && (11) \\ &= \sum_{k=1}^{n} B_{kj} && (12) \\ &= 1 && (13) \end{aligned}$$

from which it follows that all the individual elements are bounded by 1, and the product is a nonnegative stochastic matrix. ■

This can be interpreted as a 'conservation of probability' result. In particular it shows that any number of applications of stochastic transition matrices to a probability vector will result in a legitimate probability vector.

This particular situation is called a Markov chain and arises in many applications. There is an extensive theory which has been developed to deal with Markov chains, and we will use only a little bit of it.

In our model, we will assume that the system starts off in the 'pure' donor state

$$p(0) = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \tag{14}$$

and that the transition matrix is of the form

$$A = \begin{pmatrix} A_{11} & A_{12} & 0 & & & & 0 \\ A_{21} & A_{22} & A_{23} & 0 & & & \\ 0 & A_{32} & \ddots & \ddots & 0 & & \\ \vdots & 0 & \ddots & \ddots & A_{n-3,n-2} & 0 & \\ \vdots & & \ddots & \ddots & A_{n-2,n-2} & A_{n-2,n-1} & 0 \\ 0 & & & 0 & A_{n-1,n-2} & A_{n-1,n-1} & 0 \\ A_{n1} & 0 & \cdots & 0 & 0 & A_{n,n-1} & A_{nn} \end{pmatrix} \tag{15}$$

in other words we are neglecting the chance of state transitions between nonadjacent states except for the possibility of transition from state 1 directly to state n. Then at time $t = 1$ the probability vector of the system is

$$p(1) = \begin{pmatrix} A_{11} \\ A_{21} \\ 0 \\ \vdots \\ 0 \\ A_{n1} \end{pmatrix} \tag{16}$$

with the interpretation that A_{21} is the probability of entering the bridge, A_{n1} is the probability of tunnelling, and A_{11} is the probability of no state change. First we decide that A_{n1} is of the form $e^{-\gamma n}$ where γ is some complicated constant to be named later. Then we decide that A_{21} is an increasing function of n, say $\phi(n)$. In this business, we figure out A_{21} and A_{n1} and set $A_{11} = 1 - (A_{21} + A_{n1})$. This is the pattern for assigning all the columns. The n^{th} column is easy. We have decided that the n^{th} state is completely absorbing, so $A_{nn} = 1$.

Let j be such that $1 < j < n$. We decide that

$$\frac{A_{j+1,j}}{A_{j-1,j}} = 1 + \mu \tag{17}$$

where $\mu > 0$ so that there is a greater probability that the system will transition from state j to $j+1$ than from j back to $j-1$. It follows that

$$\begin{aligned} A_{jj} &= 1 - (A_{j-1,j} + A_{j+1,j}) && (18) \\ &= 1 - A_{j-1,j}(2+\mu) && (19) \end{aligned}$$

and that we must require

$$A_{j-1,j} < \frac{1}{(2+\mu)}. \tag{20}$$

We can for simplicity assign $A_{j-1,j}$to any positive value subject to this constraint. We will pick this value to be the same for all j and call it α. If follows that $A_{jj} = 1 - \alpha(2+\mu)$. The transition matrix is then of the form

$$A = \begin{pmatrix} 1-\phi(n)-e^{-\gamma n} & \alpha & 0 & & & & 0 \\ \phi(n) & 1-\alpha(2+\mu) & \alpha & 0 & & & \\ 0 & (1+\mu)\alpha & \ddots & \ddots & 0 & & \\ \vdots & 0 & \ddots & \ddots & \alpha & 0 & \\ \vdots & & \ddots & \ddots & 1-\alpha(2+\mu) & \alpha & 0 \\ 0 & & & 0 & (1+\mu)\alpha & 1-\alpha(2+\mu) & 0 \\ e^{-\gamma n} & 0 & \cdots & 0 & 0 & (1+\mu)\alpha & 1 \end{pmatrix} \tag{21}$$

Fine. Now what.

2. Running the Model

There are some important observations to make regarding the model. The absorbing state corresponds to the fact that A has an eigenvalue 1 with corresponding eigenvector

$$v^{(1)} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}. \tag{22}$$

Remark 1. *Suppose the entry to the bridge has very low probability $\phi(n) \approx 0$, and we use the approximate transition probability $A_{21} = 0$. Then for the given initial condition we have $A_{11} = 1 - e^{-\gamma n}$, $0 < 1 - e^{-\gamma n} < 1$ and*

$$p(t) = \begin{pmatrix} \left(1-e^{-\gamma n}\right)^t \\ 0 \\ \vdots \\ 0 \\ 1-\left(1-e^{-\gamma n}\right)^t \end{pmatrix} \tag{23}$$

so that as $t \to \infty$

$$p(t) \to \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \end{pmatrix}. \tag{24}$$

That is, if you wait long enough, the probability of observing the system in the absorbing state is unity. This is called 'tunneling', since the probability of observing the system in any of the bridge states was zero at all times.

Remark 2. *As n grows, $e^{-\gamma n}$ decreases to 0 and $\phi(n)$ increases so that at some n, $\phi(n)$ is many times greater than $e^{-\gamma n}$. Then an approximate model for the transition matrix is $A_{11} = 1 - \phi(n)$ and $A_{12} = \phi(n)$. We then have the tridiagonal transition matrix*

$$A = \begin{pmatrix} 1-\phi(n) & \alpha & 0 & & & & 0 \\ \phi(n) & 1-\alpha(2+\mu) & \alpha & 0 & & & \\ 0 & (1+\mu)\alpha & \ddots & \ddots & 0 & & \\ \vdots & 0 & \ddots & \ddots & \alpha & 0 & \\ \vdots & & \ddots & \ddots & 1-\alpha(2+\mu) & \alpha & 0 \\ 0 & & & 0 & (1+\mu)\alpha & 1-\alpha(2+\mu) & 0 \\ 0 & 0 & \cdots & 0 & 0 & (1+\mu)\alpha & 1 \end{pmatrix} \quad (25)$$

which provides only for transitions between adjacent states. Even so, if $\phi(n)$, α, and μ are positive, then the system will eventually be trapped in the absorbing state n with probability 1. This can be proven, but this requires techniques which are unnecessarily complicated. But there are three 'phenomena' in this model. The first is the particle injection with probability $\phi(n)$, the second is diffusion with probability α and the third is the drift superimposed on the diffusion determined by the bias μ. As it happens, as long as α and is positive then the system will be trapped in the absorbing state, although the amount of time it takes is greatly affected by the presence of bias.

2.1. How to Run the Model. It's quite simple in practice to apply this model once the parameters have been determined; one simply computes $p(t) = A^t p(0)$ for successive t until $p(t)$ has converged to equilibrium (as we will see below Perron's theorem always guarantees this). Then you can extract whatever information you want from the probabilities.

Remark 3 [The doubling method]**.** *One simple way of finding the equilibrium distribution without computing all the intervening distributions is by computing the sequence*

$$A^{2^{k+1}} = \left(A^{2^k}\right)\left(A^{2^k}\right) \quad (26)$$

until $\left(A^{2^{k+1}} - A^{2^k}\right)$ is small in whatever sense you want, and then you can compute $p\left(2^{k+1}\right) = A^{2^{k+1}} p(0)$ having done only k matrix multiplications and one matrix-vector multiplication, which is typically much less than the alternative of 2^{k+1} matrix-vector multiplications.

3. Perron-Frobenius Theory

As it happens, we have simplified our transition matrix, but to an extent where we have ceded a significant mathematical advantage. In reality, we can assume that all the elements of the transition matrix are positive, although perhaps extremely small. A matrix A which has all positive elements is called a positive matrix, and we write this as $A > 0$, and a vector x which has all positive components is called positive, written $x > 0$. Recall that $\rho(A)$ is the spectral radius of A, that is the modulus of the largest eigenvalue of A:

$$\rho(A) = \max_i |\lambda_i(A)| \tag{27}$$

For positive matrices we have Perron's theorem:

Theorem 2. *Suppose $A > 0$. Then:*

1. $\rho(A) > 0$
2. $\rho(A)$ is an eigenvalue of A
3. There is an x with $x > 0$ and $\sum_{i=1}^{n} x_i = 1$ such that $Ax = \rho(A)x$ and a $y > 0$ such that $y^T A = \rho(A) y^T$ and $x^T y = 1$. x is called the Perron vector.
4. All other eigenvalues of A are strictly smaller in modulus than $\rho(A)$
5. $\left[\rho(A)^{-1} A\right]^t \to xy^T$ as $t \to \infty$
6. $\rho(A) = \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} x_j$

■

We omit the rather involved proof of this extremely useful theorem. There is a version for nonnegative matrices, but there are more technical details.

3.1. Application of Perron's Theorem to Positive Stochastic Matrices.

For a positive stochastic matrix, the property $\sum_{i=1}^{n} A_{ij} = 1$ results in

$$\begin{aligned}
\rho(A) &= \sum_{i=1}^{n} \sum_{j=1}^{n} A_{ij} x_j &(28)\\
&= \sum_{j=1}^{n} x_j \left(\sum_{i=1}^{n} A_{ij} \right) &(29)\\
&= \sum_{j=1}^{n} x_j &(30)\\
&= 1 &(31)
\end{aligned}$$

so that the unique eigenvalue of largest modulus of a positive stochastic matrix is 1, and the Perron vector x is the corresponding eigenvalue:

$$x = Ax. \tag{32}$$

Furthermore,

$$\lim_{t\to\infty} A^t = xy^T \tag{33}$$

but by 'conservation of probability' it follows that xy^T is a stochastic matrix, so that for any probability vector q we have

$$\begin{aligned} \lim_{t\to\infty} A^t q &= xy^T q & (34)\\ &= x\left(y^T q\right) & (35) \end{aligned}$$

and since this is a probability vector, (the components must sum to unity) and the Perron vector x is a probability vector, then $y^T q = 1$. It follows that

$$y^T = \begin{pmatrix} \frac{1}{n} & \cdots & \frac{1}{n} \end{pmatrix} \tag{36}$$

and more importantly, that for any probability vector q that

$$\lim_{t\to\infty} A^t q = x. \tag{37}$$

In other words, there is a unique limiting probability distribution given by the Perron vector x regardless of any starting probability distribution for a Markov chain with a positive transition matrix. You can find the Perron vector x easily because it is the unique solution of

$$Ax = x. \tag{38}$$

4. What's Left?

The model we have should easily produce qualitative agreement with experiment - for small n the $e^{-\gamma n}$ tunneling term can dominate the $\phi(n)$ probability of transition to the first bridge state, but as n increases, the drift-diffusion across the bridge will be the dominant mode of transport. There will be the obligatory spooky quantum effect region where these two effects compete, but you might have to find molecules which have the right parameters.

It remains to actually compute the transition probabilities from quantum mechanics; these are simply the overlap integrals between the different *molecular* wave functions for the different states. There is no real need for the states to be concentrated geometrically, as we tacitly presumed in our model transition matrix. Extended wave functions can lead to large transition matrix elements far from the main diagonal, although Perron's theorem guarantees that there is always a unique limiting distribution, which determines the quantum statistics.