ALGORITHMIC PERSPECTIVE ON STRONGLY CORRELATED SYSTEMS

Last Time: Your first QMC code.

But… we made assumptions that everything was positive.

Q: What do we do when these assumptions are not correct.

Guess a wave-function, compute it's properties.

Once we have a wave-function, we need to 'simply' compute the following integrals.

$$E = \frac{\int |\Psi(r_1, r_2, .. r_n)|^2 \frac{[H\Psi](R)}{\Psi(R)} dR}{\int |\Psi(r_1, r_2, .. r_n)|^2 dR}$$

$$O = \frac{\int |\Psi(r_1, r_2, .. r_n)|^2 O(R)}{\int |\Psi(r_1, r_2, .. r_n)|^2 dR}$$
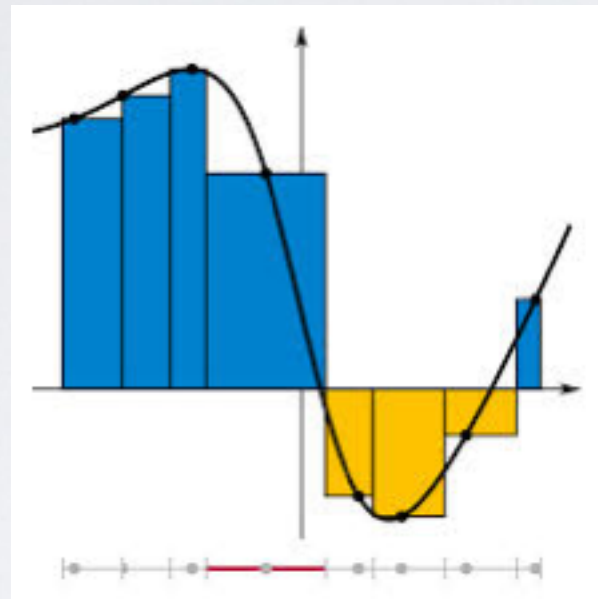
Note: These are integrals in thousands of dimensions!

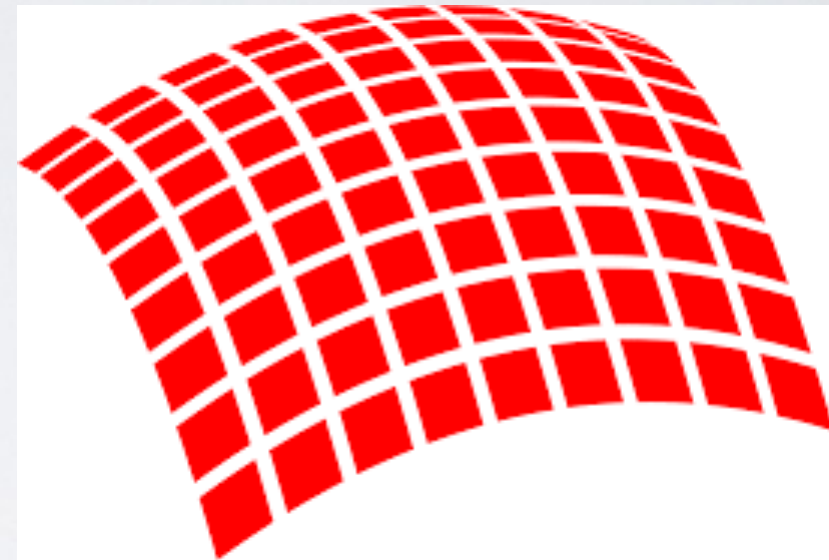We want to compute some property and we have the vector or function.

$$\langle O \rangle = \int \frac{|\Psi(R)|^2 O(R) dR}{|\Psi(R)|^2 dR}$$

How do we do it?

Integrate by grid

8 bars

91 bars

L points per dimension - grid cube size $h = 1/L$

error: h^2 **for trapezoid rule**

time: L^D

time for fixed error: $\epsilon^{-D/2}$

Even if we have the function (vector) this is not helpful.

(Improved) Integration by Grid

Trapezoid Rule: $\epsilon \sim f^{(2)}(x)h^2$

Simpson's Rule: $\epsilon \sim f^{(4)}(x)h^4$

... Rule: $\epsilon \sim f^{(\alpha)}(x)h^\alpha$

Total Time: $T \sim \epsilon^{-D/\alpha}$

Instead of doing integration exactly, we should use Monte Carlo!

Monte Carlo!!

Location of the electrons

Configuration Space: $\{R\}$

Probability: $|\Psi(R)|^2$

Stochastic Integration

Sample x with probability $p(x)$ to compute $\dfrac{\int p(x)f(x)dx}{\int p(x)dx}$

$p(x)$ need not be normalized

time for fixed error: ϵ^{-2}

10 times the error bar (one decimal point) => 100 times the work

But still wins for D>4 (trapezoid rule)

$D > 2\alpha$ **(generally)**

(We're hiding a variance)

The Best of the 20th Century: Editors Name Top 10 Algorithms

1946: John von Neumann, Stan Ulam, and Nick Metropolis, all at the Los Alamos Scientific Laboratory, cook up the Metropolis algorithm, also known as the **Monte Carlo method.**

Equation of State Calculations by Fast Computing Machines

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(Received March 6, 1953)

A general method, suitable for fast computing machines, for investigating such properties as equations of state for substances consisting of interacting individual molecules is described. The method consists of a modified Monte Carlo integration over configuration space. Results for the two-dimensional rigid-sphere system have been obtained on the Los Alamos MANIAC and are presented here. These results are compared to the free volume equation of state and to a four-term virial coefficient expansion.

I. INTRODUCTION

THE purpose of this paper is to describe a general method, suitable for fast electronic computing machines, of calculating the properties of any substance which may be considered as composed of interacting individual molecules. Classical statistics is assumed, only two-body forces are considered, and the potential field of a molecule is assumed spherically symmetric. These are the usual assumptions made in theories of liquids. Subject to the above assumptions, the method is not restricted to any range of temperature or density. This paper will also present results of a preliminary two-dimensional calculation for the rigid-sphere system. Work on the two-dimensional case with a Lennard-Jones potential is in progress and will be reported in a later paper. Also, the problem in three dimensions is being investigated.

* Now at the Radiation Laboratory of the University of California, Livermore, California.
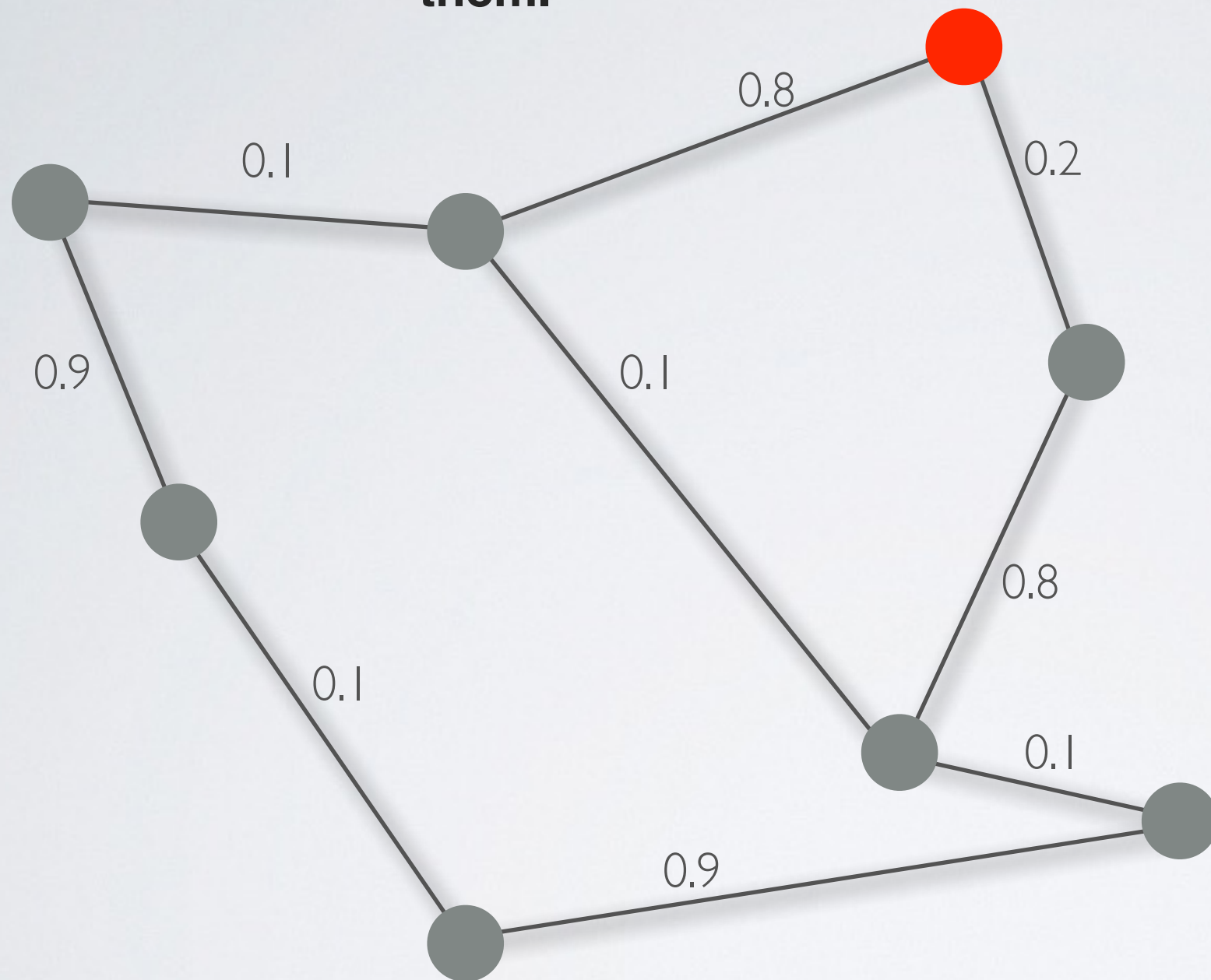
II. THE GENERAL METHOD FOR AN ARBITRARY POTENTIAL BETWEEN THE PARTICLES

In order to reduce the problem to a feasible size for numerical work, we can, of course, consider only a finite number of particles. This number N may be as high as several hundred. Our system consists of a square† containing N particles. In order to minimize the surface effects we suppose the complete substance to be periodic, consisting of many such squares, each square containing N particles in the same configuration. Thus we define d_{AB}, the minimum distance between particles A and B, as the shortest distance between A and any of the particles B, of which there is one in each of the squares which comprise the complete substance. If we have a potential which falls off rapidly with distance, there will be at most one of the distances AB which can make a substantial contribution; hence we need consider only the minimum distance d_{AB}.

† We will use the two-dimensional nomenclature here since it is easier to visualize. The extension to three dimensions is obvious.

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A simple goal: sample a probability distribution $\pi(R)$

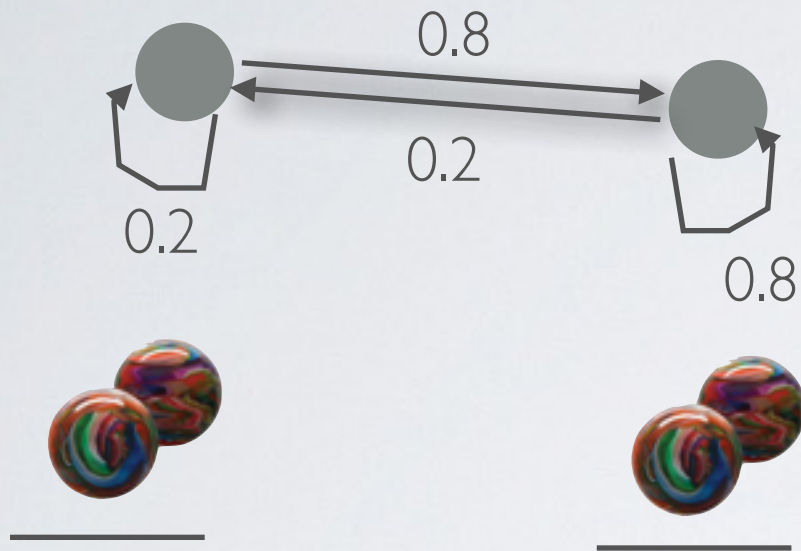**Markov Chain**   **A graph with (directed) edges and probability to move between them.**

Q: Suppose I walk around this graph.

After 1000 steps, what is the probability I am on a red node?

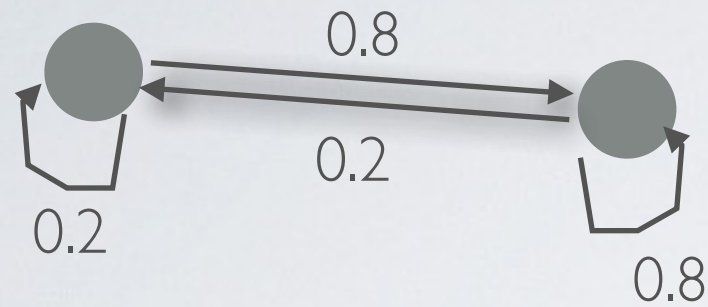After 5000 steps, what is the probability I am on a red node?

A simple goal: sample a probability distribution $\pi(R)$

Markov Chain   **A graph with (directed) edges and probability to move between them.**

0.8

0.2

0.2

0.8

After 1000 steps, what is the probability I am on a red node?

After 5000 steps, what is the probability I am on a red node?

A simple goal: sample a probability distribution $\pi(R)$

Markov Chain **A graph with (directed) edges and probability to move between them.**

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0.2

0.2

0.8

10

4

4

10

16

16

After 1000 steps, what is the probability I am on a red node?

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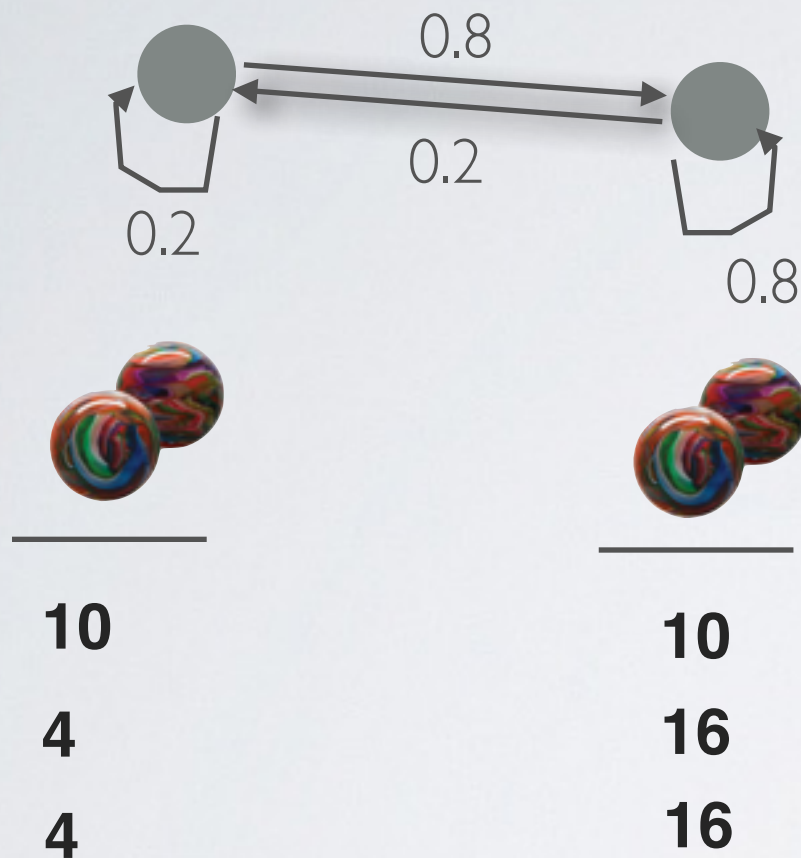After 5000 steps, what is the probability I am on a red node?

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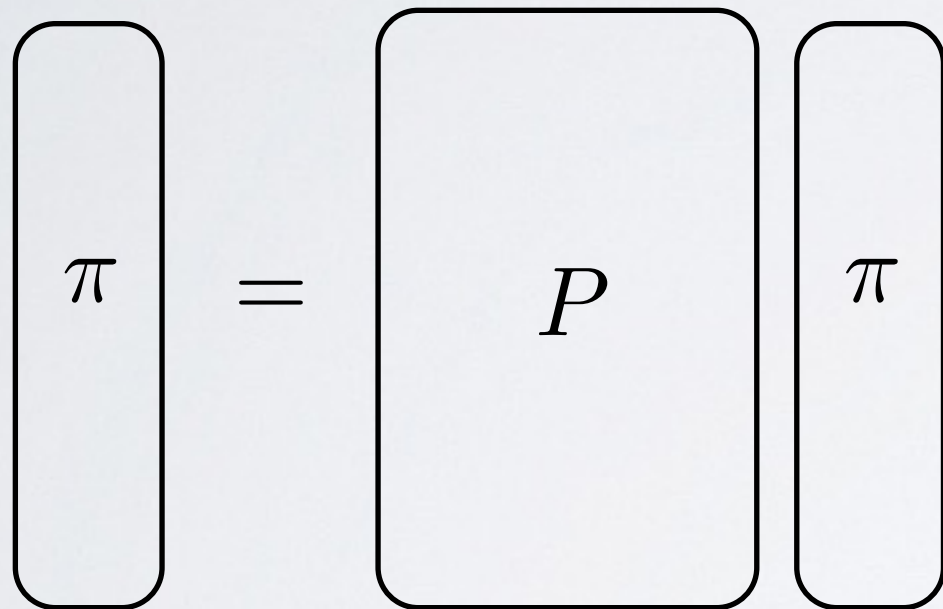$$\pi(2) = \pi(1)P[1 \to 2] + \pi(2)P[2 \to 2]$$

$$\pi(1) = \pi(1)P[1 \to 1] + \pi(2)P[2 \to 1]$$

Stationary State: Marbles in = Marbles out

$$\pi(2) = \pi(1)P[1 \to 2] + \pi(2)P[2 \to 2]$$

$$\pi(1) = \pi(1)P[1 \to 1] + \pi(2)P[2 \to 1]$$

$$\pi_j = \sum_i P_{ji}\pi_i$$

This is matrix multiplication

$$\pi = P \, \pi$$

$$\pi(2) = \pi(1)P[1 \to 2] + \pi(2)P[2 \to 2]$$

$$\pi(1) = \pi(1)P[1 \to 1] + \pi(2)P[2 \to 1]$$

$$\boxed{\pi_j = \sum_i P_{ji}\pi_i}$$

This is matrix multiplication

Consider the eigenvectors of P

$$vP = \epsilon vP$$

Suppose you are in an eigenvector of P with $|\epsilon| < 1$

Suppose instead you are in an eigenvector of P with $|\epsilon| = 1$

How many of those can there be?

Suppose you start somewhere else?

$$\pi(2) = \pi(1)P[1 \to 2] + \pi(2)P[2 \to 2]$$

$$\pi(1) = \pi(1)P[1 \to 1] + \pi(2)P[2 \to 1]$$

$$\pi_j = \sum_i P_{ji}\pi_i$$

This is matrix multiplication

$$\pi = P \pi$$

Q: Is their a fixed point?

yes

Q: How many fixed points?

1 (usually)

Q: Do you approach a fixed point?

yes

Q: What's going on with molecular dynamics?

Q: What about if I only walk right?

Eigenvalues

$$P^n v = P^n [\alpha_0 v_0 + \alpha_1 v_1 + \alpha_2 v_2 + ...]$$

$$= [\epsilon_0^n \alpha_0 v_0 + \epsilon_1^n \alpha_1 v_1 + \epsilon_2^n \alpha_2 v_2 + ...]$$

(WLOG, order by size of eigenvalues)

If v is a probability distribution:

No term can go negative.

The state has to stay normalized

If v0 has negative terms in it, eventually that term will dominate and go negative.

If it has all positive terms and $|\epsilon_0| > 1$ eventually it will not be normalized

Eigenvalues

$$P^n v = P^n [\alpha_0 v_0 + \alpha_1 v_1 + \alpha_2 v_2 + ...]$$

$$= [\epsilon_0^n \alpha_0 v_0 + \epsilon_1^n \alpha_1 v_1 + \epsilon_2^n \alpha_2 v_2 + ...]$$

(WLOG, order by size of eigenvalues)

If v is a probability distribution:

No term can go negative.

The state has to stay normalized

If $|\epsilon_0| < 1$ eventually the state will be 0 and not normalized

Eigenvalues

$$P^n v = P^n [\alpha_0 v_0 + \alpha_1 v_1 + \alpha_2 v_2 + ...]$$

$$= [\epsilon_0^n \alpha_0 v_0 + \epsilon_1^n \alpha_1 v_1 + \epsilon_2^n \alpha_2 v_2 + ...]$$

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If v is a probability distribution:

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If $\epsilon_0 \neq 1$ you have a limit cycle. Choose uniform superposition over cycle.

Eigenvalues

$$P^n v = P^n [\alpha_0 v_0 + \alpha_1 v_1 + \alpha_2 v_2 + ...]$$

$$= [\epsilon_0^n \alpha_0 v_0 + \epsilon_1^n \alpha_1 v_1 + \epsilon_2^n \alpha_2 v_2 + ...]$$

(WLOG, order by size of eigenvalues)

If v is a probability distribution:

No term can go negative.

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Suppose there are two stationary states...

Q: How do we set up a Markov chain with a particular distribution?

A: Metropolis

Q: Why does this work?

Metropolis

Starting at node i

Pick a node j with probability T(i,j)

Move to j with probability

$$\min \left(1, \frac{\pi(j)}{\pi(i)} \frac{T(j \to i)}{T(i \to j)} \right)$$

Q: How do we set up a Markov chain with a particular distribution?

A: Metropolis

Metropolis

Starting at node i

Pick a node j with probability T(i,j)

Move to j with probability

$$\min\left(1, \frac{\pi(j)}{\pi(i)} \frac{T(j \to i)}{T(i \to j)}\right)$$

Q: Why does this work?

$$P(i \to j) = T(i \to j)\min\left(1, \frac{\pi(j)}{\pi(i)} \frac{T(j \to i)}{T(i \to j)}\right)$$

$$P(j \to i) = T(j \to i)\min\left(1, \frac{\pi(i)}{\pi(j)} \frac{T(i \to j)}{T(j \to i)}\right)$$

Examples:

* Uniform hopping on a line

 * Uniform hopping on a hypercube

* Greater probability on one node

* Moving right more then left (how about always moving left?)

* Metropolis with a barrier (how to fix?)

Some intuition...

$\pi[1] = 0.25$ $\pi[2] = 0.25$

$T[2 \to 1] = 0.1$ $T[3 \to 2] = 0.1$ $T[4 \to 3] = 0.1$

$T[1 \to 2] = 0.9$ $T[2 \to 3] = 0.9$ $T[3 \to 4] = 0.9$
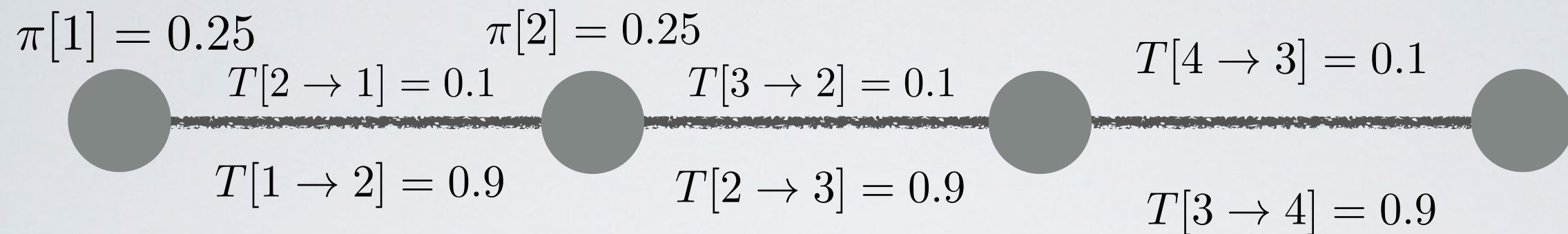
Q: Why doesn't it flow away?

Q: What's the probability to go right?

$$P(1 \to 2) = T(1 \to 2)\min\left(1, \frac{\pi(2)}{\pi(1)}\frac{T(2 \to 1)}{T(1 \to 2)}\right)$$

$$P(1 \to 2) = 0.9\min\left(1, 1\frac{0.1}{0.9}\right) = 0.1$$

$$P(2 \to 1) = T(2 \to 1)\min\left(1, \frac{\pi(1)}{\pi(2)}\frac{T(1 \to 2)}{T(2 \to 1)}\right)$$

$$P(2 \to 1) = 0.1\min\left(1, 1.0\frac{0.9}{0.1}\right) = 0.1$$

Build the graph...

A comment about mixing times...

The variational principle

$$E[\Psi(r_1, r_2, ...r_n)] \geq E_0$$
$$E[\Psi_0(r_1, r_2, ...r_n)] = E_0$$

Let's just guess the ground state.

More refined: Let's guess many states and assume the one with the lowest energy is the best guess.

Important steps:

1. How to compute energy?

2. What wave-functions?

3. How to optimize?

Variational Monte Carlo

Start in location R for the electrons

Choose a new location R'

If $|\Psi(R')|^2/|\Psi(R)|^2 > \text{rand}()$

    use R'

else:

    keep R

Measure:

$$\frac{H\Psi(R)}{\Psi(R)}$$