Homework 6. Due April 1.

1. **(8 pts)** Consider an irreducible continuous-time Markov chain with N states, and generator matrix L which is in the detailed balance with the equilibrium distribution π, i.e., $\pi_i L_{ij} = \pi_j L_{ji}$. Prove the following statements:

   (a) The detailed balance condition can be rewritten as $PL = L^T P$, where P is the diagonal matrix with the equilibrium distribution $[\pi_1, \dots, \pi_N]$ along the main diagonal.

   (b) L can be decomposed as $L = P^{-1}Q$ where P is defined in (a) and Q is a symmetric matrix.

   (c) All eigenvalues of L are real and nonpositive (you need to show this without referring to the Perron-Frobenius theorem).

   (d) The left and right eigenvectors of L relate as follows. If λ is an eigenvalue and v is the corresponding right eigenvector, then the corresponding left eigenvector is $u = Pv$. Conclude that the eigendecomposition of L is

   $$L = V\Lambda V^\top P.$$

   Hint: find the relationship between the eigenvectors of $L_{sym} := P^{1/2}LP^{-1/2}$ and L and use it to prove this statement.

   (e) Let p_0 be an $1 \times N$ row vector representing the initial probability distribution. Let $V = [v^0, \dots, v^{N-1}]$ where $v_0 = [1, \dots, 1]^\top$ be the matrix of right eigenvectors of L, the row vectors $u^k = [\pi_1 v_1^k, \dots, \pi_N v_N^k]$, $k = 0, \dots, N-1$, be the rows of the matrix $V^\top P$, and $0 = \lambda_0 > -\lambda_1 > \dots > -\lambda_{N-1}$ be the eigenvalues of L. Show that the probability distribution at time t is given by

   $$p(t) = \pi + \sum_{k=1}^{N-1} (p_0 v^k) e^{-\lambda_k t} u^k.$$

   Now assume that $\lambda_1 \ll \lambda_2$ and $t \approx \lambda_1^{-1}$. Give a simple expression approximating the probability distribution and explain the significance of the left eigenvector u^1.

   (f) The forward and backward committor are related via

   $$q_i^- = 1 - q_i^+, \quad i \in S.$$

   Hence we can simplify the notations: denote the forward commuter by $q = (q_i)_{i \in S}$. Then the backward commuter is merely $1 - q$.

(g) The reactive current $F_{ij} := f_{ij} - f_{ji}$ is given by

$$F_{ij} = \pi_i L_{ij}(q_j - q_i).$$

(h) The transition rate from A to B can be rewritten as

$$\nu_R = \frac{1}{2}\sum_{i,j\in S} \pi_i L_{ij}(q_j - q_i)^2. \tag{1}$$

2. **(10 pts)** In this problem, we will apply the spectral analysis and the tools of the transition path theory to the system of 7 atoms interacting according to the Lennard-Jones potential (the LJ_7 cluster). At low temperatures (e.g. $T = 0.05$), the dynamics of LJ_7 can be modeled by a continuous-time Markov chain shown in Figure 1. The states correspond to local energy minima (there are 4 of them in total). The edges correspond to Morse index one saddle points, i.e., those with exactly one negative eigenvalue of the Hessian matrix of the potential energy function. The transition rate from minimum i to minimum j is equal to the sum of transition rates along all edges connecting i and j. In turn, the transition rate along a given edge from i to j is calculated by the formula in the Figure.

   Download `LJ7.zip`. The program `MakeGenerator.m` computes the generator matrix for temperature $T = 0.05$.

   (a) Compute the invariant probability distribution π.

   (b) Compute eigenvalues of $(-L)$ (so that they are nonnegative) and the corresponding left and right eigenvectors. For each eigenvalue λ_k, $k = 1, 2, 3$:

      i. Compute the corresponding eigencurrent F^k_{ij}.

      ii. Identify the edge along which the eigencurrent is maximal in absolute value. If necessary, multiply ϕ_k by (-1) so that the maximal in absolute value component of F^k_{ij} is directed to minimum with a larger value of π.

      iii. Note that the amount of eigencurrent emitted or absorbed at a state i is proportional to $\pi_i\phi^k_i$ where ϕ^k is the corresponding right eigenvector. Identify the states where F^k is mostly emitted and mostly absorbed.

      iv. Conclude, to which transition process (i.e., primarily between which pair of states) the pair (λ_k, ϕ_k) corresponds to.

   (c) Let A and B be minima 2 and 1 respectively. Compute the forward committor, the reactive current, and the escape rate

   $$k_{A,B} = \frac{\nu_R}{\rho_A}, \quad \rho_A = \sum_{i\in S} \pi_i(1 - q_i)$$

   (ρ_A is the proportion of time such that the trajectory last hit A). Compare the transition rate with the eigenvalue corresponding to the transition process between minima 1 and 2. You should get nearly a coincidence between these two numbers.

(d) Repeat the previous task for A and B being minima 4 and 1 respectively. Along which edges the reactive current is focused? To which eigenvalue the transition rate $k_{A,B}$ is closest to?

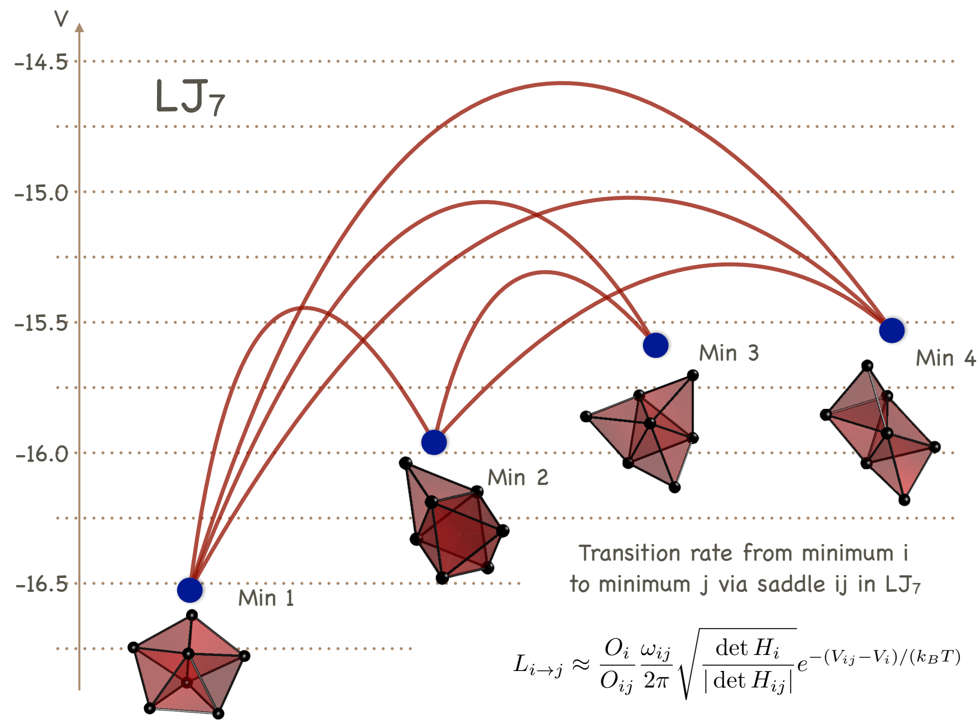

Figure 1: A depiction of the LJ_7 network modeling the low-temperature dynamics of the cluster of 7 atoms interaction according to the Lennard-Jones pair potential ($V(r) = 4(r^{-12} - r^{-6})$ where r is the interatomic distance) (e.g. Ar, Kr, Xe, Rn).