Problem set 4: Computational Molecular Physics and Methods of Molecular Simulations

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Please hand in by: 27th May, 2014 (4pm)

1. Eigenvalues and Eigenvectors

(15 points) Given are the same transition matrices as from last week:

$$P_1 = \begin{pmatrix} 1/2 & 2/5 & 1/10 \\ 8/25 & 2/5 & 7/25 \\ 2/19 & 7/19 & 10/19 \end{pmatrix}, P_2 = \begin{pmatrix} 1/2 & 1/4 & 1/4 \\ 1/3 & 0 & 2/3 \\ 0 & 5/9 & 4/9 \end{pmatrix} \quad (1)$$

(a) Calculate the eigenvalues of both matrices as well as their left and right eigenvectors.
(b) Show that one eigenvector of each matrix corresponds to the stationary vector of the process.
(c) What do you notice about the eigenvalues?

2. Monte Carlo vs. Markov Chain Monte Carlo

(30 points) In this question you will implement in your favourite programming language a Markov Chain Monte Carlo algorithm as well as a "standard" Monte Carlo algorithm. Suppose you have a probability distribution function given by the following 3-D normal distribution:

$$P(x, y, z) = \exp\Big(- \Big(\frac{x^2}{2} + \frac{y^2}{2} + \frac{z^2}{2} \Big) \Big)$$

A random point on the distribution is given by: $q = (x, y, z)$
(a) (Monte Carlo) Pick two random points (q and $\tilde{q}$) according to the distribution $P(x, y, z)$ and measure their euclidean distance $|q - \tilde{q}|$. Repeat this 10000 times, in order to get a good estimate of the mean distance of the two points. Indicate the distribution of distances and their mean in a histogram plot.

(b) (Markov Chain Monte Carlo) Choose a random initial point q from the distribution, propose a new point $\tilde{q}$ by choosing it uniform randomly from an interval [-0.5,0.5] in all 3 dimensions **around that point** q. Accept/Reject the newly proposed position $\tilde{q}$ according to the Metropolis acceptance criterion: $\min\{1, P(\tilde{q}) - P(q)\}$.

(i) Compute your mean acceptance of proposed steps over $N = 100, 1000, 10000$ trials.
(ii) Again, compute the mean euclidean distance of the two points and indicate the distribution in a histogram.
(iii) Choose a uniform interval around your initial point, such that the acceptance rate is larger than 75%. What do you observe for the mean of the distances of $|q - \tilde{q}|$? Give a reason for your observation.

3. Cyclohexane (Compulsory for anyone taking Thursdays lectures)

(15 points) Figure 1 shows the energy profile of the transition between two different conformational states of cyclohexane calculated with two different methods.

Method 1: A scan is carried out along a dihedral angle, i.e. the dihedral angle is constrained to a given value and the remaining coordinates are minimized at each step.
Method 2: Conjugate peak refinement

(a) Compare the energy change as a function of the dihedral angle in the two transitions and describe the major differences.
(b) Describe the differences between conjugate peak refinement and Method 1.
(c) Which of the two curves in Figure 1 corresponds to conjugate peak refinement?

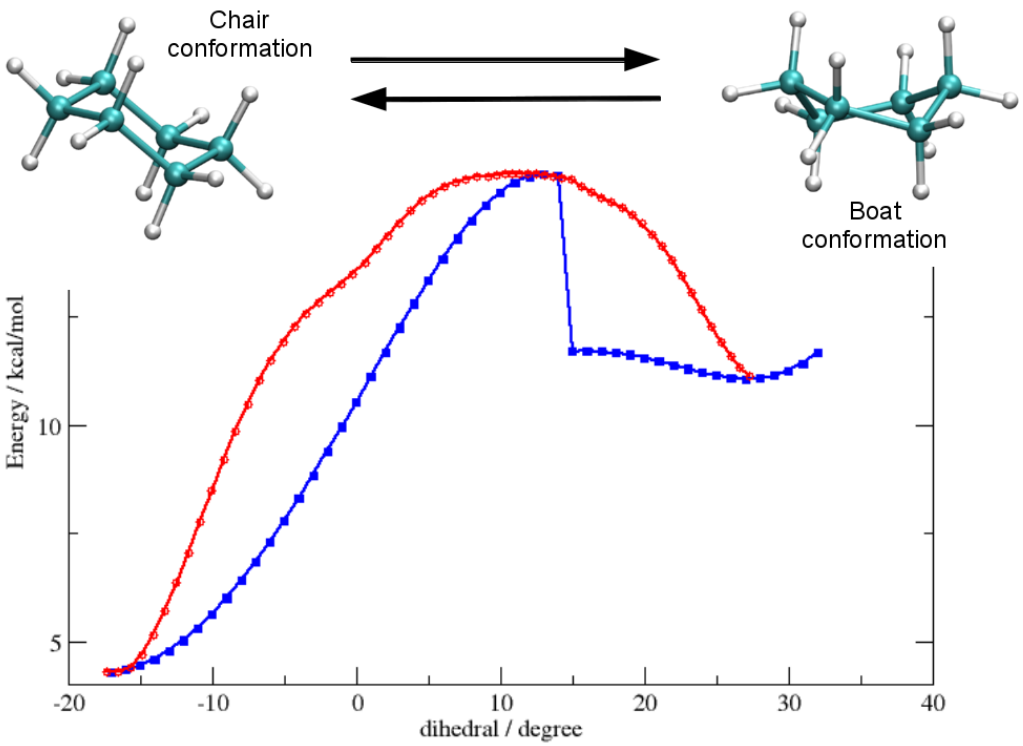

Figure 1: Transition between two conformations ("chair" and "boat") in cyclohexane calculated with two different methods