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CHM684A

PROJECT-3A

SET3A

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NORMAL MODE ANALYSIS OF A MOLECULE

In this project, you will be writing a program to perform normal mode analysis of a molecule. A normal mode is a vector, along which the motion of the atoms of a molecule is uncoupled to the motion along other normal modes. The vibrational/rotational/translational motion of the atoms in a molecule can be always represented using linear combination of all the normal modes. Motion along a particular normal mode will change only a part to the potential, and the sum of all such contributions will then give the total potential.

How to obtain normal modes of molecular motion (vibrational/translational/rotational)?

Let us first define a force-constant matrix $\mathbf{K} = \mathbf{M}^{-1/2}\mathbf{H}\mathbf{M}^{-1/2}$ where $\mathbf{H}$ is the Hessian matrix (i.e. the matrix of $\partial^2 E/\partial q_i \partial q_j$, where q_i is a degree of freedom) computed for the molecule in its minimum energy structure. The size of the Hessian matrix is $3N \times 3N$ where N is the number of atoms. In the above, $\mathbf{M}$ is $3N \times 3N$ diagonal

matrix with mass of each degree of freedom as elements:
$\mathbf{M} = \mathrm{diag}(M_1, M_1, M_1, M_2, M_2, M_2, M_3, \cdots, M_N)$.

The eigenvectors of the matrix $\mathbf{K}$ are the normal modes. Each column of $\mathbf{K}$ will be of size $3N \times 1$. The eigenvalues $\{\lambda_i\}$ are related to frequencies of motion along the corresponding normal mode as $\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}$ (in s^{-1}). Note the units of λ_i is Jm^{-2}.

For additional information, you may watch some my video lectures here (from 5 min onwards) and here.

Your specific task is to write program to perform vibrational analysis for the **Lennard-Jones** cluster with 6 atoms. You can use the same force-field which you have used in Project 2 (for Lennard-Jones fluid).

1. First optimize the structure of the molecule by taking the initial structure from here. To optimize the initial structure of the molecule do the following:
   a) Download the BFGS based Quasi-Newton-Raphson code from here.
   b) Implement the energy and the force calculation for the molecule within the file energy.f90.
   c) Install BLAS and LAPACK mathematical libraries in your computer and compile the optimization code (see compile.sh)
   c) Run the code to optimize the structure until the the maximum gradient of the structure decreases below 5 x 10^{-5}. Note you may need to change some part of the code to do this.

2. After finding the minimum energy conformation of the molecule, compute the force-constant matrix $\mathbf{K}$ by a separate program. The program should contain the following ingredients:

   a. Using finite differences of gradients, compute the Hessian matrix:

$$(\mathbf{H})_{ij} \equiv \frac{\partial^2 E}{\partial q_i \partial q_j} = \frac{1}{\partial q_i}\left(\frac{\partial E}{\partial q_j}\right) = \frac{1}{\partial q_i} g_j \,,$$

   where g_j is the j-th component of the gradient vector $\mathbf{g}$.

Now, $\frac{1}{\partial q_i} g_j \approx \frac{1}{2\,\Delta q}\left(g_j^{+} - g_j^{-}\right)$, where g_j^{+} and g_j^{-} are the j-th component of $\mathbf{g}$ computed for the optimized coordinates of the system, but by changing q_i to $q_i + \Delta q$ and $q_i - \Delta q$, respectively. $\Delta q = 0.01\ \sigma$ would be an ideal parameter to take. Then Perform QR factorization of the the $\mathbf{K}$ matrix to identify eigenvalues and eigenvectors. Convert the eigenvalues to frequency in cm^{-1}. NOTE: due to numerical accuracy issues or poorly optimized geometry, some of the eigenvalues may go below "zero". You have to avoid taking square root of negative numbers. Thus forcefully change them to positive number (of same magnitude) and then put negative sign after taking the square root. In this manner, complex frequencies can be indicated as negative.

b. Use the subroutine given in this link to create "VIB1.log" file, which prints eigenvalues and eigenvectors in some specific format for the visualization of atomic motions along each of normal modes using the MOLDEN program. Use the subroutine given in this link to print a `.nmd` file, which can be opened within VMD (using the Normal Mode Wizard plugin) to visualize the normal modes for all the eigenvalues.

3. Create movie files of the animations of the vibrational motions from MOLDEN(See the online help pages on MOLDEN). Upload these files in GoogleDrive or Youtube and give the link in the report. Pictures of normal mode vectors can be exported from VMD as any image file and can be included in the report.

4. How many eigenvalues are nearly zero in your calculation? Explain why? What are these modes correspond to?

REPORT

The report should contain introduction to the problem and aim of the project. Subsequently, "Methods and Models" part should give details about the model, algorithm, program design, and other technical/theoretical details. The details given here should help someone else to reproduce your results. In the "Results" part, explain the results with figures (and tables if needed). All the tables and figures should have captions, with figure/table numbers. Indicate the units in the axis while making plots.

Final section of the report should be “Conclusion” where you conclude the results of your work. You can add the codes to the report as Appendix.