Chem 275A/B Refresher, PS I

Abdul Aldossary

July 17, 2021

Problem 1. *The goal of this assignment is to get your started again working with Python and C++. We will rely on a very simple chemistry concept, which is Huckel theory. The main linear algebra concept we are using is to solve for the eigenvectors and eigenvalues.*

Here's some links you can look at as refreshers, although you don't really need to understand it fully to do this week's HW:

1. https://chem.libretexts.org/@go/page/33248
2. https://ocw.mit.edu/courses/chemistry/5-61-physical-chemistry-fall-2007/lecture-notes/lecture31.pdf
3. https://en.wikipedia.org/wiki/H%C3%BCckel_method

What you will have to do for this week:

1. Make a simple Python program to construct the hamiltonian from the connectivity graph for C_3H_5 (allyl radical), where the connectivity is given (in the adjacency directory) and the hamiltonian should look like:

$$\begin{bmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{bmatrix}$$

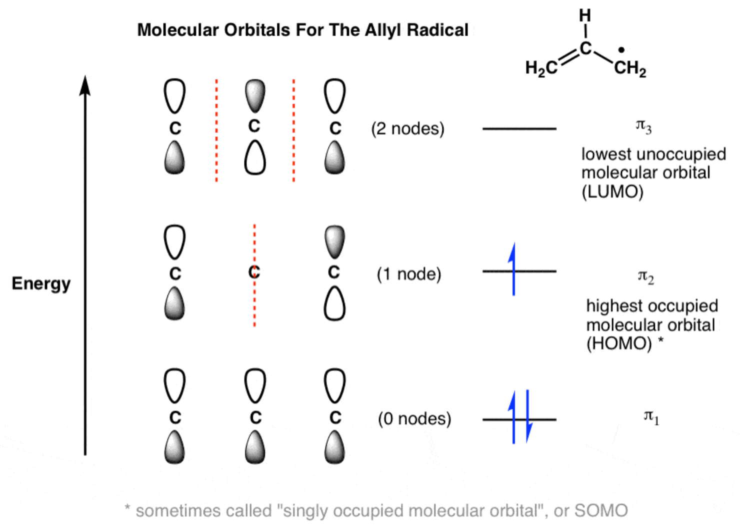
Molecular Orbitals For The Allyl Radical
Energy
C
(2 nodes)
π_3
lowest unoccupied molecular orbital (LUMO)
(1 node)
π_2
highest occupied molecular orbital (HOMO) *
(0 nodes)
π_1
H
H_2C
CH_2
* sometimes called "singly occupied molecular orbital", or SOMO

Figure 1: Allyl chemistry. Source: https://www.masterorganicchemistry.com/2017/02/16/molecular-orbitals-of-the-allyl-cation-allyl-radical-and-allyl-anion/

2. Diagonalize the Huckel hamiltonian and plot the eigenvalues, and make sure they agree with your chemistry knowledge.

3. Use the program above to construct the MO diagram for the simple benzene (C_6H_6) and cyclopentadienyl ($C_5H_5^-$) by making a csv file (by hand....) with the appropriate connectivity. The Huckel Hamiltonian for the latter system should look like:

$$\begin{bmatrix} \alpha & \beta & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & \beta & \alpha \end{bmatrix}$$

4. Make a Python program to make the connectivity of the above molecules, given the coordinates of the atoms. The coordinates are given in an ".xyz" file. More details are in the project specs.
Hint:

5. Use what you have to make it for C60 (aka, bucky ball), where XYZ file is given.

Bonus problems:

1. To make our graph closer to what we think of as "MO diagram", make your x values reflect the degeneracy such that a doubly degenerate will be ± 1, and triply degenerate are $\pm 2, 0$, and so forth. You will need to make it examine the degeneracy of your eigenvalues, and produce the appropriate x values (where the y values are the energies).

2. Think about how you can make your code run faster. One way you can improve involves the symmetry of the problem.

3. Repeat what you have on some continuous function that exponentially decays from α at 0, β at 1.2, and to zero at 4. How does that affect your result?

Project Specs

In this section we will get into some detail about some of the specs for this assignment.

0.1 XYZ format

xyz format tells you where your atoms are located. From the coordinates of each atom, you can know a lot about the chemistry. The first line tells you the number of atoms, second line is a comment line where you can have any details about your system, and the rest are coordinates for each atom. More details here: https://en.wikipedia.org/wiki/XYZ_file_format

This file format is pretty standard in computational chemistry. It can be opened by a number of open-source free software, such as Avogadro, VMD, or IQmol. You might wanna open some of these xyz files and look at them.

0.2 Connectivity files, csv

To find the connectivity of your atoms, you can make a matrix of M, where $M_{ij} = |\vec{R}_i - \vec{R}_j|$, the distance between your atoms, i and j. Only keep elements less than $2\mathring{A}$, since an average bond length is between 1.2-1.5, and it is unlikely to find the next neighbor around a $2\mathring{A}$ cutoff. Then use the plotting function given to build a graph! Those are also known as adjacency matrices in graph theory.

0.3 Make more XYZ files

XYZ files are commonly found in the literature. One way to make your own is to construct a molecule using any of the software mentioned above, and export XYZ. Some of them also can take SMILES as input, where 1,3-butadiene is simply "C=C-C=C". The bond lengths won't be exact to experimental accuracy, but they are good starting point for any computational chemistry application, such as this one!