CHEM 0019: Computational Experiment: Huckel Theory and Molecular Orbitals

Question 1(ethene).

- The output of the Huckel calculation for ethene:

  Eigenvalue: (1, -1)

  Eigenvector: $\begin{pmatrix} 0.70710678 & -0.70710678 \\ 0.70710678 & 0.70710678 \end{pmatrix}$

  Hence the orbital energies are:

  $$\epsilon_1 = \alpha - \beta$$
  $$\epsilon_2 = \alpha + \beta$$

- The Hückel method involves solving the secular determinant for the π-electron system of ethene:

  $$\begin{vmatrix} \propto -E & \beta \\ \beta & \propto -E \end{vmatrix} = 0$$

  Hence the MO wavefunctions are:

  $$\varphi_1 = \frac{1}{\sqrt{2}}pA + \frac{1}{\sqrt{2}}pB \quad \text{(Bonding MO)}$$

  $$\varphi_2 = \frac{1}{\sqrt{2}}pA - \frac{1}{\sqrt{2}}B \quad \text{(Antibonding MO)}$$

- The table of the data

π MO label	DFT MO label	Huckel MO energy	DFT MO Energy(Ha)
1	8	α+β	-0.267
2	9	α-β	0.019

Fig 1.1 the π system energy of the ethene

Question 2(propene):

- The output of the Huckel calculation for propene:

  Eigenvalue : $(-\sqrt{2}, 0, \sqrt{2})$

  Eigenvector: $\begin{pmatrix} \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ -\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & -\frac{1}{\sqrt{2}} & \frac{1}{2} \end{pmatrix}$

- Hückel energies in terms of α and β by using the standard Hückel approximation

  $$E_i = \propto + \lambda_i \beta$$

$$\lambda_i \text{ repersent the eigenvalues}$$

$$E_1 = \alpha - \sqrt{2}\,\beta \quad E_2 = \alpha \quad E_3 = \alpha + \sqrt{2}\beta$$
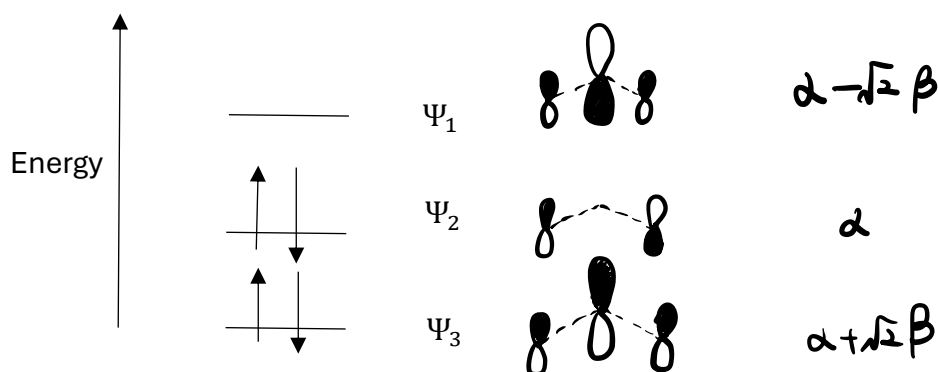
The DFT value is

- Molecular Orbital Diagram for propene

$$\Psi_1 = \frac{1}{2}p_{z,1} - \frac{1}{\sqrt{2}}p_{z,2} + \frac{1}{2}p_{z,3}\,(Antibond\ orbital)$$

$$\Psi_2 = \frac{1}{\sqrt{2}}(p_{z,1} - p_{z,3}),\,(medium\ one)$$

$$\Psi_3 = \frac{1}{2}p_{z,1} + \frac{1}{\sqrt{2}}p_{z,2} + \frac{1}{2}p_{z,3}\,(Bonding\ oribtal)$$

π MO label	DFT MO label	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)
1	13	$\alpha-\sqrt{2}\beta$	0.078	0.021
2	12	α	-0.124	-0.248
3	9	$\alpha+\sqrt{2}\beta$	-0.326	-0.408

Fig1.2 the energy of π system for propene by using Huckel theory and B3LYP/6-31G

- Prove the three Mos are normalised
  The equation we used to check the normalization is

$$\int |\Psi_i|^2 dV = 1$$

For each eigenvector, the normalization equation means

$$\sum_j v_{z,j}{}^2 = 1$$

For Ψ_1:

$$(\frac{1}{2})^2 + (-\frac{1}{\sqrt{2}})^2 + (\frac{1}{2})^2 = 1$$

So Ψ_1 approved the condition of normalization.

For Ψ_2:

$$(\frac{1}{\sqrt{2}})^2 + 0^2 + (-\frac{1}{\sqrt{2}})^2 = 1$$

So Ψ_2 approved the condition of normalization

For Ψ_3:

$$(\frac{1}{2})^2 + (\frac{1}{\sqrt{2}})^2 + (\frac{1}{2})^2 = 1$$

So Ψ_3 approved the condition of normalization

Therefore, all the normalization of Mos are proved.

Question3:

- The output of the Huckel calculation for butadiene and cyclobutadiene
  the result for butadiene:
  Eigenvalue:(-1.61803399, -0.61803399, 1.61803399, 0.61803399)
  Eigenvector=[
  [0.37174803 0.60150096 -0.37174803 -0.60150096]
  [-0.60150096 -0.37174803 -0.60150096 -0.37174803]
  [0.60150096 -0.37174803 -0.60150096 0.37174803]
  [-0.37174803 0.60150096 -0.37174803 0.60150096]
  ]
  The result for cyclobutadiene:
  Eigenvalue:(-2, 2, 0, 0)
  Eigenvectors = [
  [0.5, -0.5, 0.0, 0.0],
  [-0.5, -0.5, -0.7071, -0.7071],
  [0.5, -0.5, 0.0, 0.0],
  [-0.5, -0.5, 0.7071, 0.7071]
  ]
- The energy of Mos of two compounds;
  Hückel energies in terms of α and β by using the standard Hückel approximation

$$E_i = \propto + \lambda_i \beta$$

$$\lambda_i \; repersent \; the \; eigenvalues$$

For the butadiene molecule:

$$E_1 = \alpha - 1.618\beta \quad E_2 = \alpha - 0.618\beta \quad E_3 = \alpha + 1.618\beta \quad E_4 = \alpha + 0.618\beta$$

For the cyclobutadiene:

$$E_1 = \alpha - 2\beta \quad E_2 = \alpha + 2\beta \quad E_3 = \alpha \quad E_4 = \alpha$$

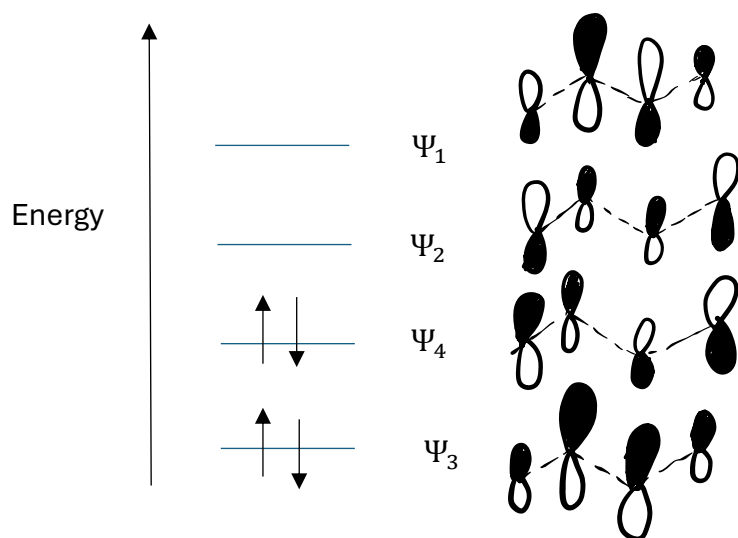- Molecular Orbital Diagram for two molecules

For butadiene molecule:

$$\Psi_1 = 0.3717p_{z,1} - 0.6015p_{z,2} + 0.6015p_{z,3} - 0.3717p_{z,4}$$
$$\Psi_2 = 0.6015p_{z,1} - 0.3717p_{z,2} - 0.3717p_{z,3} - 0.6015p_{z,4}$$
$$\Psi_3 = -0.3717p_{z,1} - 0.6015p_{z,2} - 0.6015p_{z,3} - 0.3717p_{z,4}$$
$$\Psi_4 = -0.6015p_{z,1} - 0.3717p_{z,2} + 0.3717p_{z,3} + 0.6015p_{z,4}$$

The MO diagram for butadiene molecule:

π MO label	DFT MO label	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)
1	17	α-1.618β	0.107	0.085
2	16	α-0.618β	-0.0356	-0.023
4	15	α+0.618β	-0.212	-0.229
3	14	α+1.618β	-0.355	-0.32

Fig 1.4 the energy of ϖ system for butadiene by using Hückel theory and B3LYP/6-31G

For cyclobutadiene molecule:

$$\Psi_1 = 0.5p_{z,1} - 0.5p_{z,2} + 0.5p_{z,3} - 0.5p_{z,4}$$
$$\Psi_2 = -0.5p_{z,1} - 0.5p_{z,2} - 0.5p_{z,3} - 0.5p_{z,4}$$
$$\Psi_3 = -0.7071p_{z,2} + 0.7071p_{z,4}$$
$$\Psi_3 = -0.7071p_{z,2} + 0.7071p_{z,4}$$

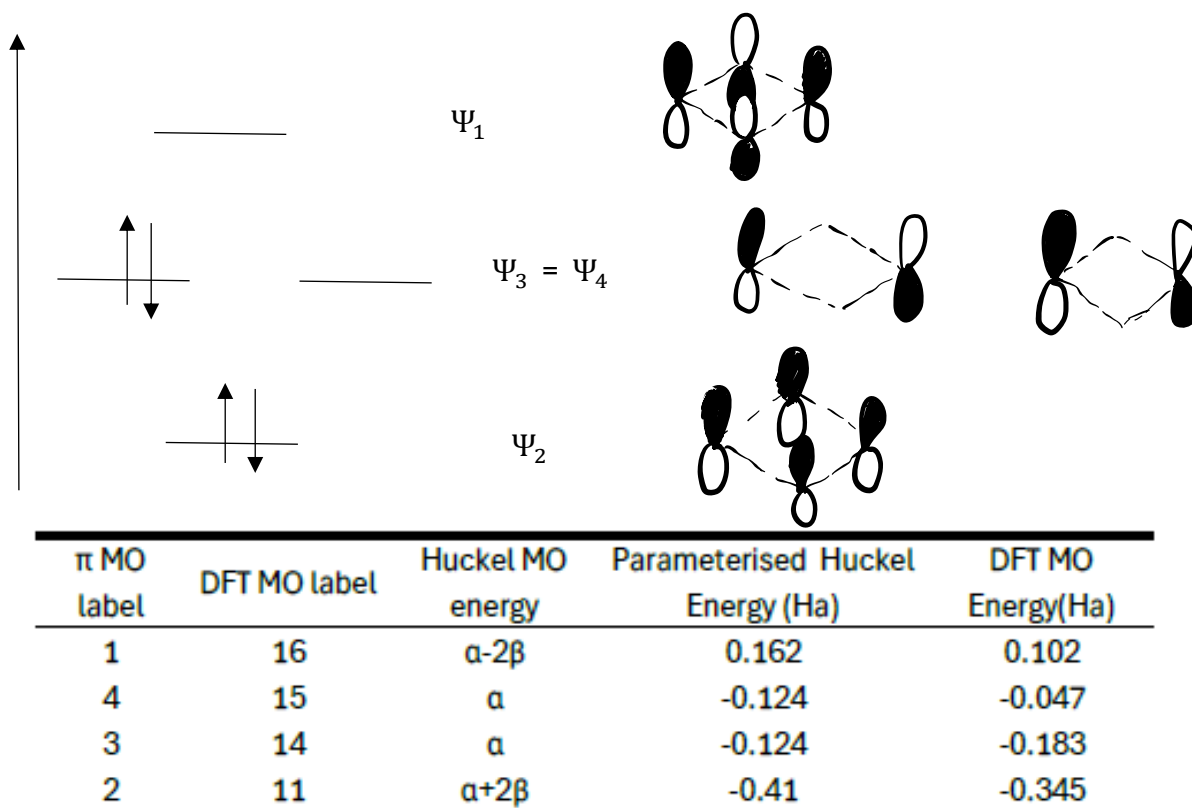| π MO label	DFT MO label	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)
1	16	α-2β	0.162	0.102
4	15	α	-0.124	-0.047
3	14	α	-0.124	-0.183
2	11	α+2β	-0.41	-0.345

Fig 1.5 the energy of ϖ system for cyclobutadiene by using Hückel theory and B3LYP/6-31G

- The total π energy of each system

  The energy for butadiene:

  $$E = -0.32 \times 2 - 0.229 \times 2 = -1.098 Har$$

  The energy for cyclobutadiene:

  $$E = -0.345 \times 2 - 0.183 \times 2 = -1.056 Har$$

  The energy of cyclobutadiene is more negative than butadiene, the π system of cyclobutadiene is lower, so cyclobutadiene is more stable.

Question 4:

- The output of the Hückel calculation for the cyclopentadienyl radical
  Eigenvalues:
  [-1.61803399 0.61803399 2.0   -1.61803399 0.61803399]
  Eigenvectors
  [[0.63245553 -0.63245553 -0.4472136 -0.22920749 0.07520313]
  [-0.51166727 -0.19543951 -0.4472136   0.53190907 0.62047262]
  [0.19543951 0.51166727 -0.4472136 -0.63143946 0.30827004]
  [0.19543951 0.51166727 -0.4472136   0.48978144 -0.42995126]
  [-0.51166727 -0.19543951 -0.4472136 -0.16104355 -0.57399453]]
- The Mos diagram
  Hückel energies in terms of α and β by using the standard Hückel approximation
  $$E_i = \propto + \lambda_i \beta$$

  $$\lambda_i \; repersent \; the \; eigenvalues$$

  $$E_1 = \alpha - 1.618\beta \quad E_2 = \alpha + 0.618\beta \quad E_3 = \alpha + 2\beta \quad E_4 = \alpha - 1.618\beta$$
  $$E_5 = \alpha + 0.618\beta$$

  $$\Psi_1 = 0.6325 p_{z,1} - 0.5117 p_{z,2} + 0.1954 p_{z,3} - 0.1954 p_{z,4} - 0.5117 p_{z,5}$$
  $$\Psi_2 = -0.6325 p_{z,1} - 0.1954 p_{z,2} + 0.5117 p_{z,3} + 0.5117 p_{z,4} - 0.1954 p_{z,5}$$
  $$\Psi_3 = -0.4472 p_{z,1} - 0.4472 p_{z,2} - 0.4472 p_{z,3} - 0.4472 p_{z,4} - 0.4472 p_{z,5}$$
  $$\Psi_4 = -0.2292 p_{z,1} - 0.5319 p_{z,2} - 0.6314 p_{z,3} + 0.4898 p_{z,4} - 0.1610 p_{z,5}$$
  $$\Psi_5 = 0.0752 p_{z,1} + 0.6204 p_{z,2} + 0.3083 p_{z,3} - 0.4300 p_{z,4} - 0.5740 p_{z,5}$$

The table for free radical:

π MO label	DFT MO label(α,β)	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)-α	DFT MO Energy(Ha)-β
1	20,105	α-1.618β	0.1073	0.065	0.092
4	19,104	α-1.618β	0.1073	0.064	0.092
5	18,103	α+0.618β	-0.2123	-0.214	-0.118
2	17,102	α+0.618β	-0.2123	-0.224	-0.208
3	15,101	α+2β	-0.41	-0.371	-0.338

Fig 1.6 the energy of ϖ system for cyclopentadienyl radical by using Hückel theory and B3LYP/6-31G

The table for cation:

π MO label	DFT MO label(α,β)	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)-α	DFT MO Energy(Ha)-β
1	20,105	α-1.618β	0.1073	-0.199	-0.138
4	19,104	α-1.618β	0.1073	-0.2	-0.138
5	18,103	α+0.618β	-0.2123	-0.472	-0.36
2	17,102	α+0.618β	-0.2123	-0.498	-0.388
3	13,101	α+2β	-0.41	-0.641	-0.572

Fig 1.7 the energy of ϖ system for cyclopentadienyl cation by using Hückel theory and B3LYP/6-31G

The table for anion:

π MO label	DFT MO label	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)
1	21	α-1.618β	0.1073	0.315
4	20	α-1.618β	0.1073	0.314
5	18	α+0.618β	-0.2123	0.054
2	17	α+0.618β	-0.2123	0.029
3	16	α+2β	-0.41	-0.109

Fig 1.8 the energy of ϖ system for cyclopentadienyl anion by using Hückel theory and B3LYP/6-31G

- The calculation:

Total Hucke π energy:

$$E_{radical} = 2 \times (-0.41) + 2 \times (-0.2123) + 1 \times (-0.2123) + 0 \times 0.1073 + 0 \times 0.1073$$
$$= -1.4569 Har$$

$$E_{cation} = 2 \times (-0.41) + 1 \times (-0.2123) + 1 \times (-0.2123) + 0 \times 0.1073 + 0 \times 0.1073$$
$$= -1.2446 Har$$

$$E_{anion} = 2 \times (-0.41) + 2 \times (-0.2123) + 2 \times (-0.2123) + 0 \times 0.1073 + 0 \times 0.1073$$
$$= -1.6692 Har$$

In this case, the total DFT energies are:

$$E_{radical} = -193.462 Har$$

$$E_{cation} = -193.163 Har$$

$$E_{anion} = -193.494 Har$$

The way to calculate the attachment energy and detachment energy is:

$$E_{attarch} = E_{anion} - E_{radical}$$

$$E_{detach} = E_{cation} - E_{radical}$$

Hence, by using the Hückel theory,

$$E_{attarch} = -1.6692 - (-1.4569) = 0.2123 Har$$

$$E_{detach} = -1.2446 - (-1.4569) = 0.2123 Har$$

By using the DFT energy,

$$E_{attarch} = -193.494 - (-193.462) = -0.032 Har$$

$$E_{detach} = -193.163 - (-193.462) = 0.299 Har$$

After comparing the values of the data we got from the different ways, we can find out that the absolute value of attachment energy and detachment energy are the same in Hückel's theory while different in DFT calculation. The reason why we have the difference is that Hückel's theory only considers π-electron interactions and ignores electron-electron repulsion and orbital relaxation. At the same time, DFT accounts for electron-electron repulsion and correlation effects which will be influenced by orbital relaxation and electron-electron repulsion effect when electrons are added or removed. In this case, Hückel theory only gives us simpler results but more accurate results are shown by DFT calculation.

The report of benzene

1. Introduction

The aim of the study is to discuss the effectiveness of Hückel theory and Density Functional Theory (DFT) in modelling the UV-Vis absorption spectrum of benzene. The Hückel theory is a simpler way to describe the electronic of conjugated π system in organic compound. However, DFT provides more precise description of all electron interaction by considering the electron density of the functional group. After the experiment, we can predict electronic transitions of benzene and get their reliability against experimental UV-Vis absorption data.

2. Computational details

The results are used both Hückel theory and DFT theory. For the Hückel theory, we used Python to construct the Hückel matrix for benzene, considering six π molecular orbitals. The value of α is -0.124Har and β is -0.143Har after the calculation For the other one, WebMO was used to get DFT calculations at the B3LYP/6-31G level of theory.

Here is the output from python

the eigenvalue of benzene:
$(-2,-1,2,-1,1,1)$
The eigenvector of benzene:

[[0.40824829 -0.57735027 0.40824829 -0.01992069 0.57735027 0.11404433]

[-0.40824829 0.28867513 0.40824829 -0.48974194 0.28867513 -0.4331262]

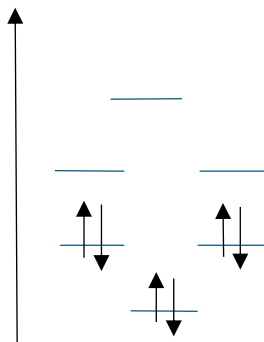[0.40824829 0.28867513 0.40824829 0.50966263 -0.28867513 -0.54717053]

[-0.40824829 -0.57735027 0.40824829 -0.01992069 -0.57735027 -0.11404433]

[0.40824829 0.28867513 0.40824829 -0.48974194 -0.28867513 0.4331262]

[-0.40824829 0.28867513 0.40824829 0.50966263 0.28867513 0.54717053]]

3. Results and discussion

Ψ_6= 0.408$p_{z,1}$ -0.408 $p_{z,2}$ +0.408 $p_{z,3}$ - 0.408$p_{z,4}$ +0.408 $p_{z,5}$ -0.408 $p_{z,6}$

Ψ_5= - 0.577$p_{z,1}$ + 0.289$p_{z,2}$ + 0.289$p_{z,3}$ - 0.577$p_{z,4}$ + 0.289$p_{z,5}$ + 0.289$p_{z,6}$

Ψ_4= - 0.020$p_{z,1}$ - 0.490$p_{z,2}$ + 0.510$p_{z,3}$ - 0.020$p_{z,4}$ - 0.490$p_{z,5}$ + 0.510$p_{z,6}$

Ψ_3= 0.577$p_{z,1}$ + 0.289$p_{z,2}$ - 0.289$p_{z,3}$ − 0.577$p_{z,4}$ − 0.289$p_{z,5}$ + 0.289$p_{z,6}$

Ψ_2= 0.114$p_{z,1}$ - 0.433$p_{z,2}$ - 0.547$p_{z,3}$ - 0.114$p_{z,4}$ + 0.433$p_{z,5}$ + 0.547$p_{z,6}$

Ψ_1= 0.408$p_{z,1}$ +0.408 $p_{z,2}$ +0.408 $p_{z,3}$ +0.408$p_{z,4}$ +0.408 $p_{z,5}$ +0.408 $p_{z,6}$

Here is the table of the datas after analysing.

π MO label	DFT MO label	Huckel MO energy	Parameterised Huckel Energy (Ha)	DFT MO Energy(Ha)
1	17	α+2β	-0.41	-0.359
2	20	α+1β	-0.267	-0.246
3	21	α+1β	-0.267	-0.246
4	22	α-1β	0.019	0.004
5	23	α-1β	0.019	0.004
6	27	α-2β	0.162	0.164

Fig 1.9 the energy of ϖ system for benzene by using Hückel theory and B3LYP/6-31G

The absorption happens when one electron jump up to the LUMO from the HOMO. So the energy is calculated by the gap between the HOMO and LUMO in the benzene.

$$E_{\text{Hückel}} = 0.019 - (-0.267) = 0.286 Har$$

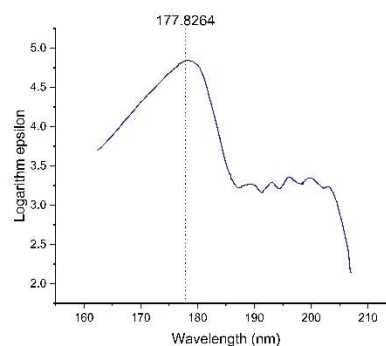$$E_{DFT} = 0.004 - (-0.246) = 0.250 Har$$

Fig2.0 graph shows the relationship between wavelength and logarithm epsilon by using UV-vis absorption data

The energy absorbed in the diagram is calculated by following ways:

$$E_{ab} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{177.8264 \times 10^{-9}} = 1.1178 \times 10^{-18} J = 0.256 Har$$

Comparing the percentage difference of experiment value and theoretic values which based on the experiment output:

$$\%_{\text{Hückel theory}} = \frac{0.286 - 0.256}{0.256} \times 100 = 11.7\%$$

$$\%_{DFT} = \frac{0.256 - 0.250}{0.256} \times 100 = 2.3\%$$

In this case, we can find that the value we got from DFT calculation is more accurate than the value from Hückel theory.

4.Conclusion

While Hückel theory is just the basic understanding of conjugation system by using α and β parameters. It is useful for quick and approximate calculations, while DFT is the more accurate method for predicting the electronic structure and absorption spectrum of benzene for the transition.