

# Homework #2

## Electronic Structure and Molecular Properties

- At the beginning of development of quantum chemistry, the speed of computers is still very low. Therefore, various theories were developed to enable the prediction of molecular electronic structure by introducing different levels of approximations. The German chemical physicist, Erich Hückel, proposed the famous Hückel method to calculate the molecular orbitals for  $\pi$ -electrons in  $\pi$ -delocalized molecules. This question is request you to learn the theory and use it to predict the  $\pi$  orbitals of benzene, and compare it with your results of xtb benzene computation.

(a) Please learn the Hückel theory from Wiki page and ChemLibretexts ([https://chem.libretexts.org/Courses/Knox\\_College/Chem\\_322%3A\\_Physical\\_Chemistry\\_II/14%3A\\_Bonding\\_in\\_Polyatomic\\_Molecules/14.06%3A\\_Butadiene\\_is\\_Stabilized\\_by\\_a\\_Delocalization\\_Energy](https://chem.libretexts.org/Courses/Knox_College/Chem_322%3A_Physical_Chemistry_II/14%3A_Bonding_in_Polyatomic_Molecules/14.06%3A_Butadiene_is_Stabilized_by_a_Delocalization_Energy)).

(b) The wavefunction of the  $\pi$  MOs ( $\Psi_\pi$ ) of 1,3-butadiene is written as:

$$\Psi_\pi = c_1\phi_{p_z,1} + c_2\phi_{p_z,2} + c_3\phi_{p_z,3} + c_4\phi_{p_z,4}$$

where  $\phi_{p_z,n}$  is the  $p_z$  atomic orbital of atom  $n$  and  $c_n$  is the associated coefficients. Please write down the  $\Psi_\pi$  for benzene.

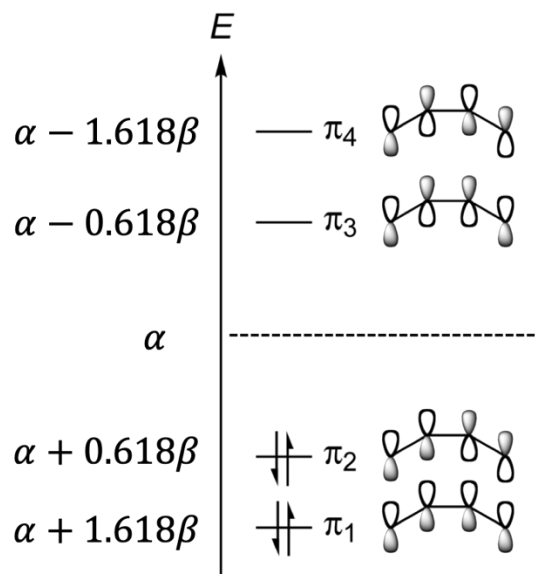
(c) The Hamiltonian matrix for 1,3-butadiene is:

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

where  $\alpha$  is  $\int \phi_{p_z,n}^* \hat{H} \phi_{p_z,n} dr_1 dr_2$  and  $\beta$  is  $\int \phi_{p_z,m}^* \hat{H} \phi_{p_z,n} dr_1 dr_2$  where  $m \neq n$ . Following the similar manner, write down the Hamiltonian matrix for benzene.

(d) Solve the secular equation for benzene. You should get 6 solutions ( $\Psi_{\pi 1}, \Psi_{\pi 2}, \dots \Psi_{\pi 6}$ ) and their associated MO energies ( $E_{\pi 1}, E_{\pi 2}, \dots E_{\pi 6}$ ).

(e) Plot the energy diagrams for benzene like the figure (for 1,3-butadiene) shown below. The shaded and bright area represent the opposite phase (like + and -).



- (f) Finally, compare the six  $\Psi_\pi$  and  $E_\pi$  you obtain from Hückel method with that from the xTB. Explain your findings.
2. Similar to the ionization energy defined for the energy difference between cationic and neutral state, the electron affinity (EA) is defined for the energy difference between anionic and neutral state. There are different sign conventions of EA in chemistry and physics:

$$\text{Physics: } EA_{\text{adiabatic}} = E_{aA} - E_{nN} < 0 \text{ (usually)}$$

$$\text{Chemistry: } EA_{\text{adiabatic}} = E_{nN} - E_{aA} > 0 \text{ (usually)}$$

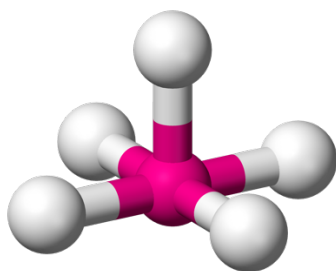
where aA is the anionic state (a) at anionic ground state geometry (A). In this question, we adopt the chemistry convention. Calculate the adiabatic and vertical electron affinity and the LUMO energy for naphthalene using xTB and compare it with exp. value (you can find it from NIST). How large are the differences between these calculated values and exp. one?

3. Calculate the HOMO, LUMO and their difference ( $\text{GAP}_{\text{HOMO-LUMO}}$ ) for oligothiophene from  $n=1\sim 5$ .
- (a) Make a figure set with figure (a) HOMO, (b) LUMO and (c)  $\text{GAP}_{\text{HOMO-LUMO}}$  in the y-axis and the x-axis is the number of unit  $n$ . Explain your observation.
- (b) Plot the HOMO and LUMO for all oligomers from  $n=1\sim 5$ . Explain your findings on the HOMO/LUMO distribution.
4. This question requests you to calculate the MOs for  $\text{VF}_5$  metal complex

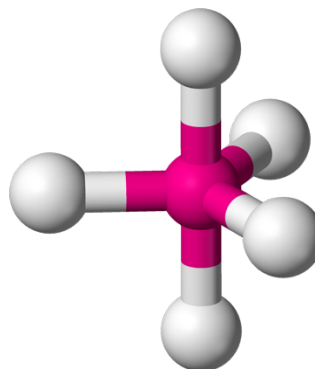
(charge: 0, unpaired electron: 0). The procedure is almost the same as what we did in class.

- (a) According to crystal field theory, the metal complex with 5 identical ligands could be either square pyramidal or trigonal bipyramidal, as shown below:

square pyramidal



trigonal bipyramidal



Please generate two  $\text{VF}_5$  structures (square pyramidal and trigonal bipyramidal) and perform geometry optimization for both of them. Do both structures retain their shapes after optimization? Identify the bond lengths and angles for both of them.

- (b) Following the results you obtain in (a), which one is more stable?
- (c) Following the similar steps of our hands-on session, please plot the MO of the stable structure you obtain in question (b). You just need to plot the 5 MOs that are mainly contributed by the d orbitals of the metal (like p29 and p30 in the course slide). And specify what d orbitals are they ( $d_{xy}$ ,  $d_{xz}$ , ...) for each of them.
- (d) Construct the MO energy diagram using the d orbitals you plot in (c) and compare it with the prediction of CFT. Do the ordering of the energy levels of the d orbitals agree with each other? What are the energy splitting you get according to your xTB results?