CHEM 361B – Activity 16

Visualising Molecular Orbitals

Examination of Mo_2

In this first part, we will calculate the molecular orbitals of a diatomic molecule using IQMol and QChem.

1) Open IQMol and follow slides 2 – 8 in the IQMol tutorial to create an Mo_2 molecule
    a. Select Mo from the Build Element menu
    b. Hold Alt and click in the viewer to add an Mo atom
    c. Click on one of the Mo atoms and drag to the other to make a bond
    d. Click on the minimize energy button to make a good initial guess for the geometry of the molecule

2) Follow slides 13 – 20 in the IQMol tutorial and do a geometry relaxation of Mo_2 using QChem Servers:
    a. Select Calculation -> QChem Setup
    b. Have only 1 job. Select 'Job 1' and input the following options:
        i. Calculate: Geometry
        ii. Method: B3LYP
        iii. Basis: LANL2DZ
        iv. Multiplicity: 1
        v. ECP: LANL2DZ
    c. Under "Wavefunction Analysis" make sure the "Generate Checkpoint File" box is checked
    d. Make sure that Server says QChem and click 'Submit'. You will be prompted to give a name to your job.
3) While the calculation is running read the Wikipedia entry on delta bonding (https://en.wikipedia.org/wiki/Delta_bond).
4) Once the QChem calculation ends you will be prompted. Save the output in a new directory. It should then open the output file.
    a. Click on the arrow beside your completed job to open a drop down menu.
    b. Click the arrow beside "Surfaces" to present a submenu called "Canonical Orbitals". Double click on that to be presented a new menu. It will show you the molecular orbital diagram for the frontier orbitals. Lines with green dots refer to filled orbitals. Lines without green dots are unfilled orbitals. The find the highest line with a green dot and record the energy. This is called the Highest Occupied Molecular Orbital (HOMO). Find the lowest line without a green dot and record the energy. This is called the Lowest Unoccupied

Molecular Orbital (LUMO). What is the frequency of the photo required to excite Mo_2 in the ground state to the first excited state?

c. Make the following settings (leave the rest as defaults):
   i. Type: "Alpha Orbital"
   ii. Orbitals: 1 to 14 (HOMO)
   iii. Isovalue: 0.1
d. Click "Calculate". When it is finished, under "Canonical Orbitals" there should now appear 14 checkboxes. When one is checked you will see the molecular orbitals associated with it.
e. View all of the occupied molecular orbitals and for each, identify the dominant atomic orbitals involved (s,p,d), whether the molecular orbital is predominately σ, π, or δ, and whether the molecular orbital is bonding or anti-bonding.
f. Determine the bond order of Mo_2.

Using Frontier Orbitals to Examine an S_N2 Reaction Mechanism

5) The reaction of CH_3I with CN^- is a textbook example of a S_N2 reaction. Read the introduction and reaction mechanism sections in the Wikipedia entry on S_N2 reactions (https://en.wikipedia.org/wiki/SN2_reaction) and then draw a sketch of the mechanism of this reaction.

6) Set up a new molecule in IQMol using File -> New Molecule. Set up a carbon and nitrogen atom to make CN^-.
   a. Start a new calculation using Calculation -> QChem Setup and set up the following options:
      i. Have only 1 job. Select 'Job 1' and input the following options:
      ii. Calculate: Geometry
      iii. Method: B3LYP
      iv. Basis: 6-31G**
      v. Charge: -1
      vi. Multiplicity: 1
      vii. ECP: None
   b. Under "Wavefunction Analysis" make sure the "Generate Checkpoint File" box is checked
   c. Click "Submit"
   d. When the file converges, save it locally. Under Surfaces you will find Canonical Orbitals. Double click it to open the menu. Make the following settings and leave the rest as defaults:
      i. Type: "Alpha Orbital"
      ii. Orbitals: 7 (HOMO) to 8 (LUMO)

iii. Isovalue: 0.05

e. Click “Calculate”. When it is finished, under “Canonical Orbitals” there should now appear 2 checkboxes. When one is checked you will see the molecular orbitals associated with it.

7) Set up a new molecule in IQMol using File -> New Molecule. Under the “Add Fragment” tool select “Molecules” and add a methane. Substitute one of the hydrogens with Iodine to form CH_3I.
   a. Start a new calculation using Calculation -> QChem Setup and set up the following options:
      i. Have only 1 job. Select ‘Job 1’ and input the following options:
      ii. Calculate: Geometry
      iii. Method: B3LYP
      iv. Basis: LANL2DZ
      v. Charge: 0
      vi. Multiplicity: 1
      vii. ECP: LANL2DZ
   b. Under “Wavefunction Analysis” make sure the “Generate Checkpoint File” box is checked
   c. Click “Submit”
   d. When the file converges, save it locally. Under Surfaces you will find Canonical Orbitals. Double click it to open the menu. Make the following settings and leave the rest as defaults:
      i. Type: “Alpha Orbital”
      ii. Orbitals: 7 (HOMO) to 8 (LUMO)
      iii. Isovalue: 0.05
8) Click “Calculate”. When it is finished, under “Canonical Orbitals” there should now appear 2 checkboxes. When one is checked you will see the molecular orbitals associated with it.
9) While it is running read the OpenTextBC entry on Lewis Acids and Bases (https://opentextbc.ca/chemistry/chapter/15-2-lewis-acids-and-bases/)
   a. Does CN^- act as a Lewis acid or base in the S_N2 reaction? Does CH_3I act as a Lewis acid or base?
10) **View the HOMO and LUMO molecular orbitals for both molecules. Identify for both molecules whether the HOMO or LUMO is relevant to the S_N2 reaction? How does the shape of the relevant frontier molecular orbital help to explain the mechanism of the S_N2 reaction?**