Lab3, Electrostatics, molecular bonding and reaction energy

A. Revisit \( N_2 \)

In Lab2 you calculated the molecular orbitals of \( N_2 \) molecule and when you set up the molecule in GaussView you chose a triple bond between the two atoms. But, how does the choice of bonding affect the calculation? The Hartree-Fock method does not require any previous knowledge of the bonding between the atoms, it is an example of an \textit{ab initio} method.

For comparison, create a \( N_2 \) molecule bonded by a single bond and carry out again Hartree-Fock calculations using the 3-21G\(^*\) basis set. GaussView does not allow you to work with a singly bonded N-atom so a roundabout method needs to be used. First, create a \( N_2 \) molecule with a triple bond and then select \textbf{Modify Bond} and change to a single bond. Then run the calculation.

\textit{Q1: How does the bond length and final energy compare with the results form Lab2 (where a triple bond was specified)? After the calculation has converged, does the graphical representation in GaussView display a triple bond, or does it still show a single bond?}

This simple calculation illustrates an important point. The choice of single, double and triple bonds, as well as other bond connectivity issues when a molecule is created in GaussView only affect the initial location of the atoms in the molecule. After an ab initio calculation has been carried out and the atom coordinates changed to find the lowest energy configuration, the initial bonding configuration does not matter (unless there are multiple stable configurations, then minimization of the energy may result in the local minimum that is closest to the initial structure). Also, it illustrates that the simple graphics rendering of the molecule in GaussView does not use information about the result of the quantum chemistry calculation (here, does not realize that the calculation ends up giving a triple bond, while the initial guess had just a single bond). So, don’t take the bonding in a graphics window too seriously.

In order to calculate the bond energy, the energy of two isolated N-atoms needs to be subtracted from the energy of the \( N_2 \) molecule. Carry out the calculation of an isolated N-atom using exactly the same level of theory (level of approximation, basis set, etc.). It is an essential rule in calculations of this sort to only add and subtract numbers that are calculated at the same level of theory. This way errors in the two calculations that are compared tend to cancel out.

\textit{Q2: What estimate of the bond energy do you obtain? This is one of the strongest bonds between two atoms. Compare with the bond energy of the \( H_2 \) molecule.}
B. Nitronium cation and benzene

The nitronium ion, NO$_2^+$, is the active reagent in the nitration of benzene and other aromatics. Build this ion (it doesn’t matter whether you start with a N-atom with two 1.5 fold bonds, or one double and one single bond). Do an energy minimization using Hartree-Fock and the 3-21G* basis set.

Q3: What is the lowest energy geometry of the NO$_2^+$ ion (linear or bent)? What are the N-O bond lengths (the same or different)? Compare with a common, isoelectronic molecule that is much in the news these days. Record the energy of the ion.

Create a picture of the electrostatic potential mapped onto the total electron density in the following way. Go to 'Results > Surfaces and Contours' and 'Cube actions' to select 'Total density'. Click on OK. In 'Surface Actions', select 'New Mapped Surfaces'. Select 'Generate values only at surface points' and for 'Type' choose 'ESP' (electrostatic potential). You may need to adjust the scale at the top of the window to use the full spectrum of colours.

Q4: Where in the molecule is the positive charge mostly located? Based on your calculation, draw the Lewis dot structure that best represents the nitronium cation. Include the picture showing the electrostatic potential in your report.

Now build a benzene molecule. Go to 'Ring Fragment' and select a benzene ring. Optimise using 3-21G* basis set. As for the nitronium ion, get a map of the electrostatic potential. Also, record the energy of the benzene molecule.

Q5: Judging from the electrostatics, how do you expect the nitronium ion reacts with the benzene molecule (which part of the nitronium ion will most likely collide with what part of the benzene molecule?). Draw a Lewis structure of the nitronium cation-benzene adduct.

The adduct is metastable and its structure and energy can be calculated with Hartree-Fock. Build the NO$_2$-benzene adduct by first placing a benzene ring in the window, then add a nitrogen atom to the window to the side of the ring and bind it to two oxygen atoms. Finally, select 'Modify Bond' and select the N-atom and one of the C-atoms and select a single bond from the 'Bond type'. Then, click on the icon that looks like a brush and has the name 'Clean'. It minimizes the structure using a rough, empirical potential function. Save and set up a Hartree-Fock minimization using the 3-21G* basis set. Click on 'ignore symmetry'. The calculation will take a few minutes.

Q6: Place a picture of the adduct in your report. How do you describe the bonding (get the C-C bond lengths in the ring)? What is the binding energy of the adduct (energy of the adduct compared with the isolated nitronium ion and benzene molecule). Open the log file with GaussView (not the NotePad editor) and look at the picture of the molecule. There the bonding arrangement is deduced from the final configuration rather than the initial structure.

Now create a picture of the electrostatic potential mapped onto the total electron density isosurface for the adduct. Play with the color scheme.