Chemistry with computers

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> Preparation (circa 2 hours): Read this manual and general background information about delocalization and conjugation in organic molecules (Chapter 7, Organic Chemistry 2nd ed. Claydon, Greeves, Warren and Wothers, pages 151-171).

Introduction

One of the central problems in (physical) chemistry is the study of properties of molecules and materials. These properties can for instance be electrostatic, such as the dipole moment of a molecule, or optical, for instance the color of light absorbed by a molecule. In many cases it is possible to study the properties of molecules and materials experimentally but sometimes this can be very expensive and time consuming. In addition, there are several properties of molecules that are virtually impossible to determine by experimental techniques. Examples of this are the distribution of electrons in a molecule and the length of specific bonds in a molecule.

A very powerful alternative way to study properties of molecules is to use techniques from modern computational chemistry. Using these techniques it is possible to study the properties of molecules in a very detailed way with an accuracy that is sometimes better than in experiments, even for molecules that do not exist (yet). This last point is quite interesting since it becomes possible to design molecules with specific properties using computer simulations, before they are actually synthesized.
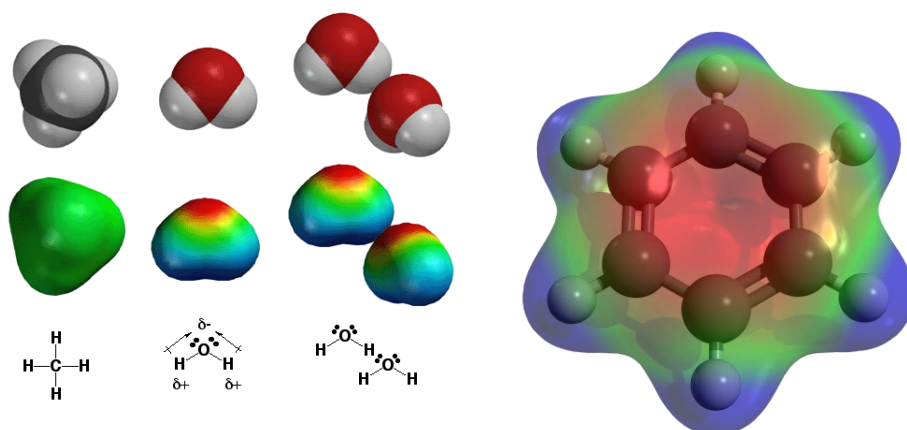
Figure 1: Visualization of charge distribution in methane, water and benzene. Red colors indicate net negative charge while blue indicates a net positive charge.

When we consider the properties of molecules, it is important to realize that all there is to know about molecules is completely determined by the electron cloud is distributed over the different atoms. The electron cloud is what keeps the nuclei together, or in other words, the electrons are involved in the formation of bonds between atoms. Around 1900 it was found that the movement of electrons in molecules cannot be described by the classical laws of mechanics as established by

Newton. Instead, a new theory was derived, called quantum mechanics, which is able to describe the motion of electrons in a very detailed way. In principle, this theory can be used to calculate the properties of any molecule or material exactly. However, in practice the time it takes to do such a calculation can be infinite. Therefore, in computational chemistry, people use approximate solutions of the equations of quantum mechanics. In this lab experiment we will use such an approximate theory, so-called Density Functional Theory (DFT), to study the properties of organic molecules. Using this theory it is possible to calculate virtually any property of a molecules. In this lab course we will use DFT methods to:
- study the geometry of organic molecules
- investigate the charge distribution and molecular orbitals
- calculate the UV/VIS absorption spectrum of a series of conjugated molecules

This requires that we perform two basic types of calculations, (1) single point energy calculations and (2) geometry optimizations

Single point energy calculations
The purpose of a single point calculation is to calculate the electron distribution for a certain molecule that is defined by the positions of the nuclei in space. This means that the only input for the calculation is a set of xyz coordinates for each nucleus. Using DFT we can then derive the optimal (lowest energy) distribution of the electron cloud around these nuclei. This is an iterative calculation and it gives us the electronic structure (electron density, molecular orbitals) of the ground state of the molecule. Once we know the ground state electron density, we can in principle derive all properties of the molecule from that. One of the standard things that are calculated in a DFT single point calculation is the dipole moment of the molecule. It is also possible to derive partial charges on each atom from the electron distribution by a so-called Mulliken population analysis. This give a good intuitive picture of the charge distribution and the charges can be seen as δ+ and δ- charges as they are commonly used in organic chemistry, see also Figure 1.

Geometry optimization
Using a geometry optimization we can calculate the equilibrium structure of a molecule. This can be most easily be visualized by considering the total energy of a di-atomic molecule when the bond length is varied. The total energy of the molecule depends both of the interaction between the nuclei and the attractive force between the nuclei and the electron cloud. When the total energy of the di-atomic molecule is plotted as a function of the bond length a typical picture as shown in Figure 2 is obtained.

The minimum in such a potential energy curve corresponds to the equilibrium bend length of the molecule. The depth of the minimum defines how much energy is gained by making a bond, or in other words, the depth indicates the energy required to break the bond. For a molecule consisting of two atoms it is easy to draw a curve as shown in Figure 2 and find the minimum, however, when there are three or more atoms this is not so easy to do manually. In the software that we use for these experiments the optimum, equilibrium geometry can be calculated automatically bye the computer using the electron density from a DFT calculation. In general, the geometry that is obtained corresponds very well with the observed experimental geometries. One of the main advantages of computer simulations is that is very easy to change the

molecular structure and check how the geometry changes. This is something that we will explore in the computer experiments below.
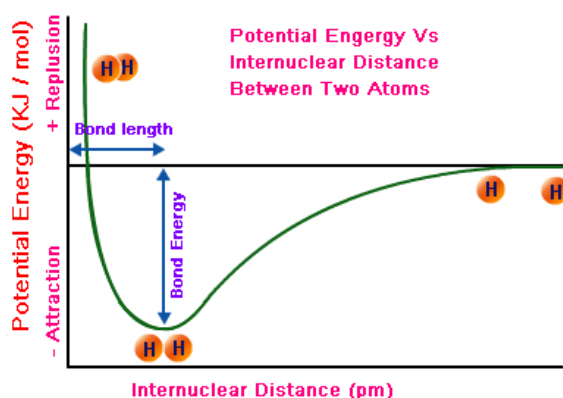

Figure 2: Total energy as a function of bond length for H_2.

UV/VIS absorption spectra
Once the ground state geometry and the ground state electron distribution is known, it is in principle possible to calculate all properties of a molecule, even those that relate to electronically excited states. It is for instance possible to calculate the optical absorption spectrum. This is very useful since it is also possible to do such calculations if no experimental data is available yet. In the last part of this lab experiment we will study how the wavelength of light that is absorbed by an organic molecule depends on the size of that molecule.

Average molecular structures
In organic chemistry it is common to draw bonds between atoms in a molecules as single, double and triple lines to indicate the bond order. Each line is assumed to indicate an electron pair that is responsible for the bonding. While this is a very powerful way of drawing molecular structures, especially when considering chemical reactions, it may also be somewhat confusing when thinking about the geometry of molecules. This is very clear in the case of a benzene molecule that is often drawn as a cyclo-hexatriene, see Figure 3, while it is well-known that all six C-C bonds in benzene have equal length. A solution is to consider all possible resonance structures. In the case of benzene there are two with the double bonds at different positions. The true equilibrium geometry of the molecule is then some average of the different possible resonance structures.
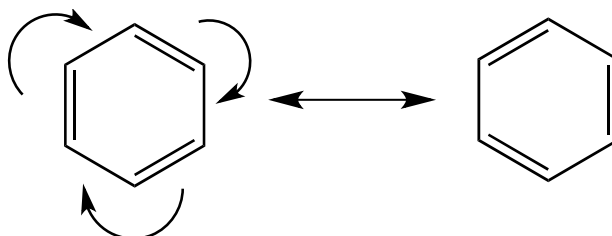

Figure 3: The two resonance (Kekule) structures for a benzene molecule can be turned into each other by 'flipping' the bonds around.

In a DFT calculation the software in principle knows nothing about positions of single and double bonds, it only is concerned with the electron cloud as a whole. Therefore,

if a geometry optimization is performed, for instance for a benzene molecule, the calculation will automatically give as a result the average structure, implicitly containing all resonance structures. It should be realized that this average structure is the actual 'real structure' of the molecule. The different resonance forms only serve as model by which to still represent molecules in terms of discrete single and double (and triple) bonds. A more detailed description of delocalization and resonance can be found in any introductory organic chemistry textbook (e.g. Organic Chemistry, 2nd edition by J.Clayden, N Greeves and S.Warren).

Running DFT calculations
In this course we will perform some density functional theory calculations to learn about the geometry and electronic structure of organic molecules. For these calculations we will use the Amsterdam Density Functional (ADF) theory program package. ADF is a very extensive professional piece of software that is used by academic and industrial researchers to perform a wide variety of calculation on all sorts of materials. While there is an almost infinite number of calculation types and option in the software we will restrict ourselves to only the most basic options.

Molecules can be built and calculations can be set up in the graphical user interface ADFinput, while a lot of data analysis and visualization can be done in ADFview. Both of these graphical interfaces are relatively intuitive to use, but some things require some time to get familiar with. On the blackboard site an extensive manual that shows most of the basic operations that are used in the computer experiments in this course. There is also a link to a short movie that illustrates building molecules and running calculations.

File locations: The files that you make during the experiments will be stored locally on the hard disk of the computer by default. Please use the same computer on the second day, you files will still be there. After all experiments are done: remove them from the disk (you may copy them to you network location before doing so). Before logging out and leaving: ask one of the teaching assistants to check whether you removed the files correctly.

The measurement report
In this lab experiment we will not work in groups. Each student has to do all calculations and hand in an individual measurement report. The measurement report should contain all data that is required from the calculations and answers to the question about these data that are in the text. On blackboard there is a word-template of the measurement report. It is required to use this format. The report should be handed in two days after the practicum, usually friday, before midnight, preferably by email.

Important (required !!):
- **When arriving, report with one of the teaching assistant so they can register your presence.**
- **Ask one of the TAs to check the date you get from the calculations and sign off if correct (if you do not have the results checked and found ok you will not pass!!)**
- **Ask one of the teaching assistants to check whether you removed the files correctly and sign off on this.**

Part 1: Geometry, dipole moment and charge distribution of small molecules

In this first computer experiment we will study the geometry and electric properties of a series of small molecules, methane, ammonia, water and hydrogenfluoride (see Figure 2). We will use the Amsterdam Density Functional (ADF) theory package to build a molecule and subsequently perform a density functional theory calculation to obtain the optimized geometry and the electron distribution in the molecule.
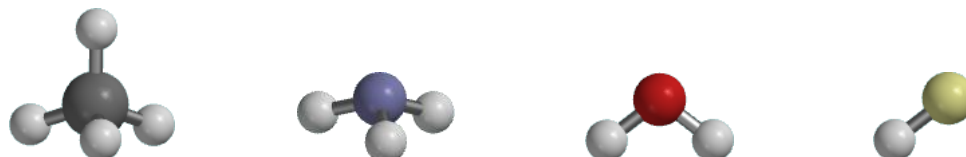

Figure 4: Molecular structure of methane, ammonia, water and hydrogenfluoride

For each molecule:
- Build the molecule in the ADF graphical user interface and pre-optimize them by pressing the cogwheel in the menu bar. **Note:** this is not a DFT geometry optimization, it only serves to give a reasonable starting geometry !!
- Run a geometry optimization calculation using the basis set 'DZP'
  This requires that you modify two fields in the ADF input screen: "Preset" and "Basis set"
- Analyze the results by visualizing them in ADFview and assemble the bond length, bond angle and the Mulliken charge of the hydrogen and the C, N, O and F.
- Find the experimental bond lengths and add them to the table

	CH4	NH3	H2O	HF
Bond length				
Exp.				
Bond angle				
Exp.		106.7	104.5	
Charge H				
Charge C,N,O,F				

Questions:
1.1 How do the calculated bond lengths and angles compare to the experimental values? Do you feel that the calculations can give a good prediction of the molecular structure?
1.2 Can you explain the trend in the series of compounds taking the atomic radius of the different atoms into consideration?
1.3 Discuss the partial charges for the different compounds and explain the trends observed in terms of the electronegativity of the different atoms.

Part 2: Charge distribution and resonance structures in carboxylic acids
In this experiment you will see how the different <u>resonance structures</u> that you can draw for organic carboxylic acids together represent the molecular structure of a molecule.
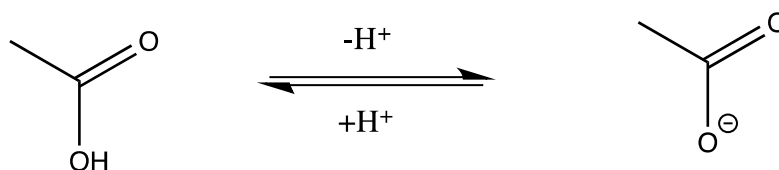

Figure 5: Deprotonation of acetic acid

Perform the following calculations:
- Build the acetic acid molecule in the ADF graphical user interface and pre-optimize it by pressing the cogwheel in the menu bar
- Run a geometry optimization calculation using a DZP basis set.
- Remove the H on the acid group and optimize the geometry again. (**Note**: the total charge of the molecule has changed, this should be modified in the ADF input screen).
- Analyze the results by visualizing them in ADFview and assemble the C-O bond lengths and the Mulliken charge of the two O atoms for both forms of the molecule.

	r, CO-1	r, CO2	q, O1	q, O2
CH_3COOH				
CH_3COO^-				

Questions:
2.1 Draw the two resonance structures for the deprotonated form of the acetic acid.
2.2 Explain how the observed charge distribution and bond lenths correspond to the resonance structures drawn above.
2.3 Check whether the negative charge in the acetate is fully localized in the COO^- group.

Part 3: Charge distribution, resonance structures and molecular orbitals in dimethyl-amino-benzonitrile
Dimethyl-amino-benzonitrile is a so-called push-pull system. In such a molecule a central aromatic moiety (a benzene ring) has two substituents: one that is strongly electron donating (dimethylamino) and one that is strongly electron withdrawing (cyano). This typically results in very large dipole moments but also has interesting implications for the geometry and distribution of electrons in the molecule.
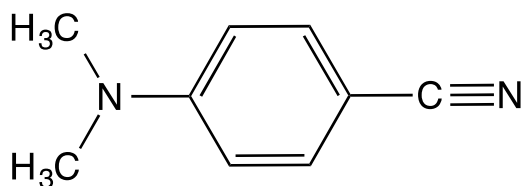

Figure 6: Molecular structure of dimethyl-amino-benzonitrile, DMABN.

In this part you will check how electron donation and electron withdrawing groups change the electronic structure and geometry of aromatic rings. As a start we will first perform some calculations on small model systems, ethane, ethylene and benzene, in order to obtain bond lengths for 'typical' C-C single, double and aromatic bonds.

Perform the following calculations:
- Build the ethane, ethylene and benzene molecules in the ADF graphical user interface and pre-optimize them by pressing the cogwheel in the menu bar
- Run a geometry optimization calculation keeping all other setting to their default values.
- Collect the 'typical' bond lengths for a C-C single, double and aromatic bond in the table
- Build the DMABN molecule and optimize its geometry (first a pre-optimization and subsequently a DFT geometry optimization).
- Analyze the bond length, charge distribution and dipole moment of the DMABN molecule
- Use ADFview to make pictures of the HOMO and LUMO orbitals of the DMABN molecule.

Typical bond lengths:

	C-C bond length
Ethane	
Ethylene	
Benzene	

Bond lengths DMABN:
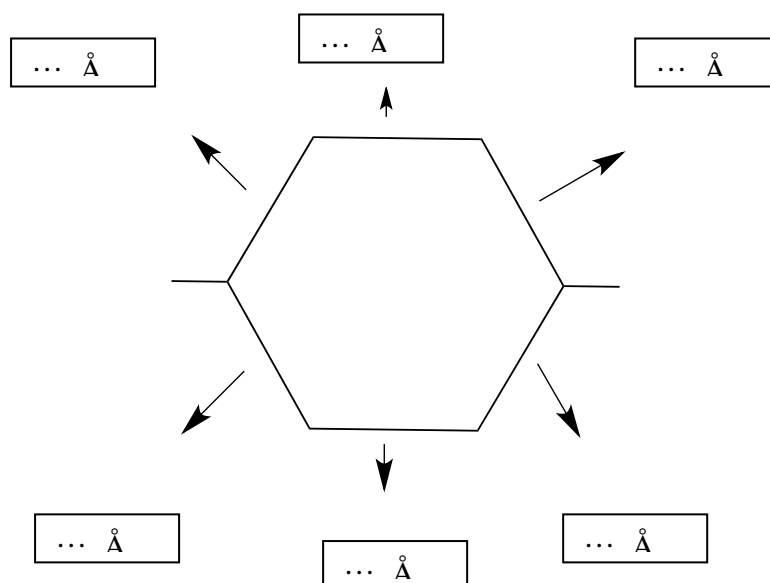
Questions:

3.1 Consider the bond lengths obtained for typical C-C single double and aromatic bonds. Do the values for benzene correspond to what you expected based on resonance structures?

3.2 Draw a resonance structure for the DMABN molecule in which there is a negative charge on the cyano group and a positive charge on the dimethylamino.

3.3 Consider the C-C bond lengths in the central benzene ring. Is the contribution of the 'charged' resonance structure reflected in these bondlengths ?

3.4 How does the dipole moment of DMABN compare to that for the water molecule?

3.5 Add the plots of the HOMO and LUMO orbitals to the measurement report. If you remove and electron from this molecule, where would the positive charge be localized mostly? Does this agree with what you know about the electron withdrawing character of the cyano and dimethylamino groups ?

Part 4: UV/VIS spectra of conjugated molecules

Generally, the wavelengths of light that are absorbed by a molecule are determined by the energies of the different occupied and virtual orbitals. These energies depend to a large extent on the degree of delocalization of these orbitals. In the series of molecules shown in Figure 7 the conjugation of the double bonds leads to delocalization of the orbitals along the whole molecule. This has interesting implication for the UV/VIS spectrum. In this part we will optimize the geometry, investigated the shape of the molecular orbitals and calculate the UV/VIS spectra.

butadiene   hexatriene   octatetraene
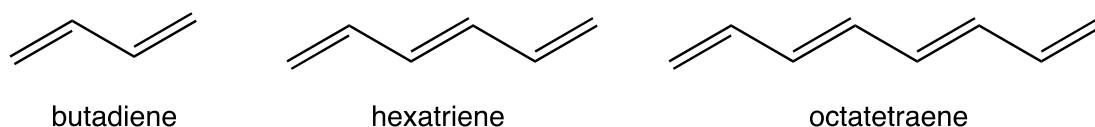
Figure 7: Molecular structures of oligoenes.

For each molecule:
-   Build the molecule in the ADF graphical user interface and pre-optimize them by pressing the cogwheel in the menu bar
-   Run a geometry optimization calculation keeping all other setting to their default values.
-   Calculate the UV/VIS absorption spectrum and assemble the transition energies in a table (in eV).

For butadiene:
-   Make plots of the HOMO and LUMO orbitals

	Transition energy (eV)
butadiene	
hexatriene	
octatetraene	

Questions:
4.1   Show the plots of the HOMO and LUMO orbitals and confirm that they are delocalized over the whole molecule
4.2   Do the orbitals look as you expected ? (Compare: Organic Chemistry, Claydon et al.)
4.3   Plot the excitation energies against $1/N$, where N is the number of carbon atoms. Does the excitation energy depend linearly on $1/N$?
4.4   What transition energy do you expect for an infinitely long conjugated carbon chains ?

Part 5 Hydrogen bonds in small molecules and DNA base pairs

In this part we will study hydrogen bonding in small molecules and DNA base pairs. Using computer simulations it is possible to optimize the geometry of a dimer of water, ammonia or hydrogen fluoride molecules, or even of very large systems such as DNA bases that are bound together by two or three hydrogen bonds. Apart from the geometry we can also calculate the bonding energy of the two interacting molecules by comparing the energy of the dimer with that of the individual molecules.

As a first step we will study the hydrogen bonding in dimers of H_2O, NH_3 and HF:

   -    Make the dimers of the molecules in ADFinput is such a way that they reflect roughly the geometry that you expect. The molecules have to be close enough together. A convenient way to do this is sometimes to build the molecules as if there is a bond between them. You can remove bonds afterwards, or change a nitrogen into another atom for instance.
   -    **Do not** do a pre-optimization, this will destroy the structure in most cases !!! If you do a preoptimization you may get you original structure back by clicking undo (edit menu).
   -    Optimize the geometry using the DZP basis set. In some cases the calculation will not converge, as indicated in red in ADFjobs. In this case, read the last coordinates and just run the calculation again. Save pictures of the geometry of the H2O and NH3 dimers.
   -    Measure the length of the hydrogen bond for all three dimers
   -    Write down the charges for the two heavy atoms (C, N, F) and the hydrogen involved in the hydrogen bond.
   -    Calculate the interaction energy between the two molecules. In order to do this you need the total energy of the dimer and subtract the total energy of two separate molecules (optimize a single molecule also !!). The total energy can

be found in the output file (ADFoutput, Properties -> Bonding energy decomposition, under Total Bonding Energy). Write down the numbers in kJ/mol

Geometry and charges in hydrogen bonded dimers:

|	H-bond length	Charge (N,O,F)	Charge H	Charge (N,O,F)
NH_3				
H_2O				
HF				

Interaction energies for hydrogen bonded dimers (kJ/mol):

|	Energy dimer	Energy monomer	Interaction
NH_3			
H_2O			
HF			

Questions:

5.1 Insert the pictures of the geometry of the water and ammonia dimers. Do they look like what you expect on basis of the location of the lone pairs on these molecules?

5.2 Is there a trend in the length of the hydrogen bonds? Can you explain this trend (see also Part 1)?

5.3 Describe how the charge distribution in the molecules changes as a result of the interaction (compare to monomers in part 1) and explain this in terms of polarization effects.

5.4 Consider the interaction energies. How do they compare to what is know experimentally about the bonding strength of hydrogen bonds? Explain the trend in the hydrogen bond energy in the different dimers.

In the structure of DNA there are two different types of base pairs that are held together by two or three hydrogen bonds, G-C and A-T; these are depicted below. We will now investigate the interaction between the bases in DNA and also look at the electronic structure of the base pairs. Since the molecules considered here are quite large, the calculation will take quite a bit more time.
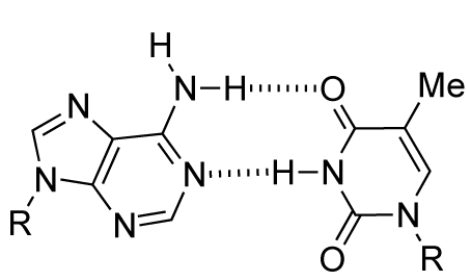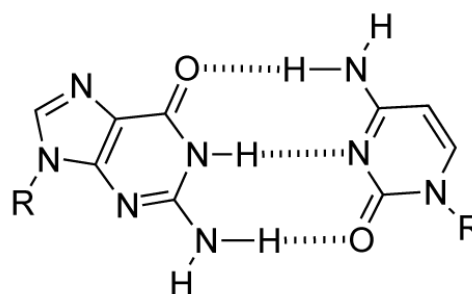
A·T base pair   G·C base pair

Figure 8: Molecular structures of DNA base pairs. The place where the bases are connected to the sugar-phosphate backbone is indicated by R.
For both base pairs:

- Build the structure of the base pair in ADFinput. Replace the 'R' in the structure by a hydrogen atom. Using the standard pre-optimization is not a good idea but you may use a somewhat more sophisticated pre-optimization by right-clicking on the cog-wheel and selecting 'Mopac'. Make sure the starting structure still looks as you expect for the base pair.
- Optimize the geometry of the DNA base pair using the DZ basis set.
- Write down the hydrogen bond lengths in the two base pairs.
- Save pictures of the HOMO and LUMO orbitals of both base pairs.
- Take the total energy of the base pairs from the output file and also calculate the total energy for all four individual bases. Use these numbers to calculate the interaction energy for the two base pairs

Hydrogen bond lengths:

	GC	AT
H-bond 1		
H-bond 2		
H-bond 3		-

Interaction energies (kJ/mol):

	E_{dimer}	E_{base1}	E_{base2}	Interaction
GC				
AT				

Questions:

5.5 Are all the hydrogen bonds drawn in Figure 8 'real' hydrogen bonds? How do the hydrogen bond lengths compare to those for the dimers of small molecules considered above?

5.6 Calculate the total interaction energy in the two base pairs (see table). Which base pair has a stronger bonding energy? Does it scale with the number of hydrogen bonds?

5.7 From the interaction energies you can calculate the average bonding energy per hydrogen bond. If you compare them to the bonding energies for the small molecules, are the hydrogen bonds in DNA strong or weak?

5.8 Insert the pictures of the HOMO and LUMO orbitals for the two base pairs. On basis of this picture: if a positive charge is put of the bases pairs on which base would it be localized? And where would a negative charge be localized?