

Computational Organic Electronics Laboratory

Richard G. Hennig

Cornell University, Materials Science & Engineering

rhennig@cornell.edu

1. Introduction to Molecular Mechanics

In this lab, we will use several tools to generate molecular structures, convert the file formats for different tools, relax the structure with empirical force fields, modify the structures and perform some structural searches for different molecular conformations and defects.

For these labs, we will use the following four tools

- 1) Generation of molecular structures using Avogadro.

<http://avogadro.openmolecules.net/>

- 2) Conversion between chemical file formats using OpenBabel.

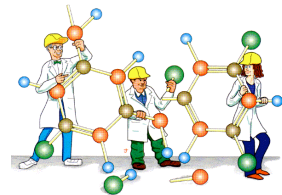
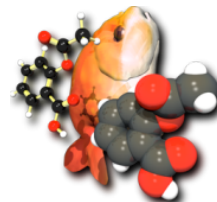
<http://openbabel.org/>

- 3) Molecular mechanics (MM) calculations using Tinker and the MM2 force field.

<http://dasher.wustl.edu/tinker/>

- 4) Quantum mechanical calculations using the PCGameSS/Firefly program.

<http://classic.chem.msu.su/gran/gamess/index.html>



The specific system we will study is a buckyball interacting with a naphthalene molecule first and later molecules of the acene series. Some questions to consider:

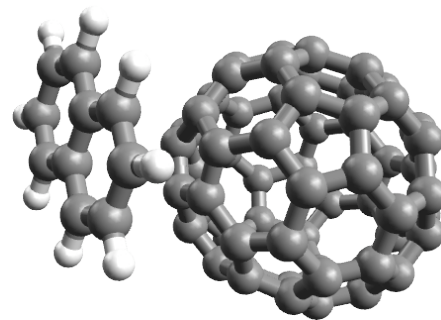
- What is the type of interaction between the naphthalene molecule and buckyball and what is the interaction within each of the molecules?
- What do you expect for the interaction strength within each molecule and between the molecules?
- How should the HOMO/LUMO gap change with increasing size of the molecules in the acene series?

2. Buckyball - Naphthalene Demonstration


We will use the molecular editor Avogadro to first construct our molecular structure and perform some simple and quick structure optimizations. Then we will export this structure and convert it into the Tinker format. In Tinker we will perform structural optimizations using the more accurate MM3 force field and perform a search for saddle points.

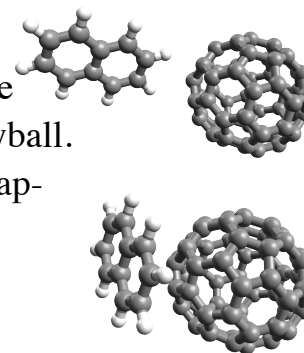
1) Generate structure with Avogadro.

- Start Avogadro.
- Click on “Fragment Library.”
- Click on “Buckminsterfullerene.cml.”
- Click on “Insert Fragment.”
- Click in the region called “View 1” to place the buckyball.
- Click on “Stop Inserting.”
- Find the naphthalene molecule, click on it and insert it the same way next to the buckyball. If the naphthalene molecule overlaps with the buckyball, you need to undo your last step (Control-Z or Menu Edit/Undo) and place it the naphthalene molecule a bit further away from the buckyball next time.



2) Relax the structure using simple empirical force fields in Avogadro

- Click on the symbol for the optimization tool 
- Select the MMFF94 force field and the conjugate gradient method.
- Start the relaxation and watch.
- You can move the molecules by hand around by just clicking on an atom with the mouse and dragging it around.
- Generate two structure:
 - ▶ The first one, let’s call it “perpendicular,” where the naphthalene molecule stands on its end on the buckyball.
 - ▶ The second one, let’s call it “parallel,” where the naphthalene molecules lies flat on the buckyball.
- Save both structures in the cml file format.
- What is the energy difference between the structures?
- Why is the energy different?



3) Conversion of molecular structure files to Tinker xyz format

- To convert the files from the cml to the Tinker xyz format, we use the OpenBabel tool. Under Windows and Mac, we can use the graphical interface. On Linux we need to use the command line interface.
- Convert the files from cml to the txyz format.


4) Structure relaxation in Tinker using the MM3 empirical force field.

Tinker provides a large number of molecular mechanics tools. We will only use a small number of them in this lab. For more information on the methods and how to use them, please read the documentation on the Tinker website:

<http://dasher.wustl.edu/tinker/>

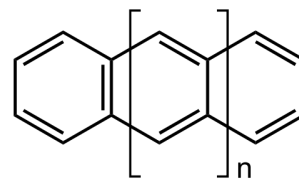
In the following we will explore some of Tinkers capabilities in calculating the energy of structures using empirical force fields, optimize the geometry, perform molecular dynamics simulations and search for minimum energy structures.

- Open the graphical interface to Tinker, the “Force Field Explorer” (FFE).
- Load the buckyball and perpendicular naphthalene molecule and choose the MM3 force field.
- Click on the panel “Graphics” to see the loaded molecule. You can change the way the molecules are displayed by selecting the different options under “Display.”
- In the panel “Keyword Editor” other important parameters can be set. For our simulation of the naphthalene and buckyball, we want to use periodic boundary conditions to make sure the two molecules do not simply fly apart at some point due to the weak binding between them. Select the keyword “Crystal Lattice and Periodic Boundary.” Set the lattice parameters a, b and c to 30Å and the space group to P1.
- In the panel “Modeling Commands” we select the various methods for modeling our molecular structure. Today we will use the following methods.
 - ▶ Analyze
 - ▶ Minimize
 - ▶ Dynamics

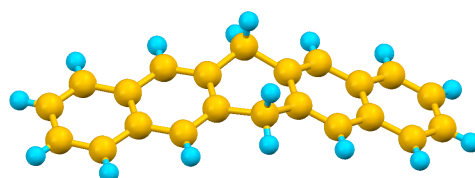
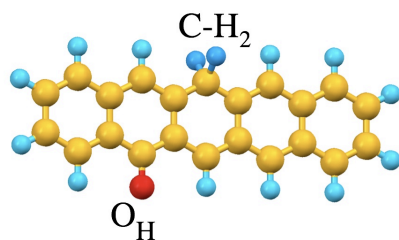
- For each of the methods we may want to change some of the parameters and options. After selecting a method, the parameters and options will be displayed together with a short description.
- Let's start with the "Analyze" tool.
 - ▶ This tool determines various static properties of the molecular structure, *e.g.* total energy and various contributions to the energy, dipole and quadrupole moments, moment of inertia and radius of gyration.
 - ▶ Select E, I and M to calculate the energy, dipole and quadrupole moments, moment of inertia and radius of gyration.
 - ▶ Click on the symbol  to start the calculation.
 - ▶ Afterwards click on the panel "Log" to view the results.
- Remember that the structure was not yet optimized with the MM3 force field. So let's do this now.
 - ▶ Select modeling command "Minimize" and start the optimization.
 - ▶ Go back to the panel "Graphic" to view the optimized structure.
 - ▶ You might want to decrease the tolerance of the residual forces to get a more accurately relaxed structure.
 - ▶ Is the perpendicular structure generated in Avogadro stable? It might not be!
 - ▶ What is the structure you obtain from the relaxation and what is its energy? Compare the results with your neighbors.
- Next we will perform a molecular dynamics simulation to see how the molecules will move at room temperature.
 - ▶ Select "Dynamic" for the method.
 - ▶ To simplify the visualization, go to the panel "Keyword Editor" and under the keyword "Output Control" select "Archive". This will create a single file containing the molecular dynamics trajectory for later analysis and visualization.
 - ▶ Run the molecular dynamics.
- Visualize the structures. What do you observe? What happens if you make the simulation box larger? How strong is the bonding between the naphthalene and buckyball at room temperature?

2. Chemical Defects in Acenes

When acene molecules and molecular crystals are exposed to air, the acenes can react with water and oxygen. We will study possible chemical defects in the acene molecules naphthalene, anthracene, tetracene and pentacene ($n = 0-3$) using the empirical force field MM3 in the Tinker code.



The addition of H, O or OH to acenes crystal and thin-films disrupts the π bonding and can lead to defect levels in the band. Here we will study are the C-H₂ and O_H defects:



What are the chemical reactions potentially leading to these types of defects.

Every group should look at one type of defect on a one of the acenes. Create the structure of the perfect acene and optimize the structure using the Avogadro tool and the MMFF94 force field. Save the structure in the cml format. Construct the structure of the defect and optimize the geometry again. Save the structure as well. What other molecules do you need to generate to calculate the energy of the chemical reaction? Create those molecules as well, relax them and save them.

Convert the molecular structures into the txyz format. Optimize the geometries in Tinker using the MM3 force field. What is the energy of the reaction? Is the defect energetically favorable?

$$\Delta E =$$

Compare the results with your class mates.

3. Quantum Chemistry calculations of HOMO/LUMO Gaps

We will use quantum mechanical methods to determine the HOMO/LUMO gap of the acenes. We will be using the PCGamess/Firefly code for our quantum mechanical calculations of molecular systems. PCGamess/Firefly is a quantum chemistry package implementing various density functional, Hartree-Fock and correlated electron methods. The code is freely available. Further information can be found at the PCGamess/Firefly website:

<http://classic.chem.msu.su/gran/gamess/index.html>

There are many other computational chemistry packages available that provide Hartree-Fock and a variety of higher-order correlated electron methods, including:

- **COLUMBUS** – <http://www.univie.ac.at/columbus/> (freely available)
- **GAMESS** – <http://www.msg.ameslab.gov/gamess/> (freely available)
- **Gaussian** – <http://www.gaussian.com> (moderate cost for academics ~\$3,000).

This tutorial describes how to optimize structures and calculate energies within different quantum chemistry methods using the PCGamess/Firefly code. To get familiar with the code we will start out with calculations for a water molecule before moving on to the more computationally demanding calculations for the acenes.

Problem 1. Hartree-Fock energy and HOMO/LUMO gap for water

Look at the first example

```
!      H2O      RHF calculation.
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE $END
$SYSTEM TIMLIM=2 MEMORY=100000 $END
$BASIS  GBASIS=N21 NGAUSS=3 $END
$GUESS  GUESS=HUCKEL $END
$DATA
Water...RHF/3-21G...exp.geom...R(OH)=0.95781,A(HOH)=104.4776
Cnv      2

OXYGEN      8.0
HYDROGEN    1.0    0.0    0.7572157    0.5865358
$END
```

The first line is just a comment line. The second line tells the program to perform a Restricted Hartree Fock calculation and Optimize the geometry of the molecule. The third line sets memory (in Words = 8 Bytes) and time limits (in minutes) for the calculation. In the fourth line, we define the basis set (more about this later). The fourth line tells the program to obtain the initial charge density for the calculation from a Huckel calculation.

Next, the molecule is defined. First again a comment line, followed by the symmetry label of the molecule in the next line. After the symmetry label, you need to have an empty line unless the molecule has no symmetry, i.e. a symmetry label C1. Following the symmetry information are the coordinates of the symmetry-inequivalent atoms. The symmetry tells the program that there are actually two hydrogen atoms, one at +y and one at -y.

To run the PCGameSS calculation, you need to type

```
pcgameSS -i H2O.inp -o H2O.out
```

Next, let's look at the output. The output file is rather lengthy and we need to find the necessary information. Search for the following terms

- TOTAL ENERGY
- EQUILIBRIUM GEOMETRY
- MOLECULAR ORBITALS

What is the total energy of the molecule?

How does the bond length and bond angle compare to the experimental values of water? What could be the cause of the differences?

How many orbitals are occupied for H₂O? Can you find the energy difference between the HOMO and LUMO?

A good reference for quantum chemistry calculations and experimental data of small molecules is the NIST database

<http://cccbdb.nist.gov/>

Problem 2. Basis set convergence

For any quantum chemistry calculation, one has to ensure that the results are converged to sufficient accuracy with the parameters of the method. Quantum chemistry calculations using Gaussian basis sets need to be checked for basis set convergence. Unfortunately, for Gaussian basis sets there is not a simple single parameter to converge the basis. Instead we need to improve the basis by adding more Gaussian functions. You can find a pretty complete set of Gaussian basis sets for the elements at the Basis Set Exchange: <https://bse.pnl.gov/bse/portal>. To understand the quantum chemistry notation of basis sets, you should read the wikipedia article [http://en.wikipedia.org/wiki/Basis_set_\(chemistry\)](http://en.wikipedia.org/wiki/Basis_set_(chemistry)).

Change the basis of the H₂O molecule to one of the following choices and repeat the Hartree-Fock calculation, skip the optimization by changing the word `optimize` to `energy`:

- 3-21G, 6-31G, 6-311G, 6-311G*, 6-311G**

Report the energy of the H₂O molecule for the different basis sets and note the time to complete the calculation. What do you observe? Can you find convergence for the total energy?

Problem 3. Beyond Hartree-Fock

The Hartree-Fock method does not describe electronic correlation effects. To include these in the calculation we need to go to post Hartree-Fock methods such as density functional theory or correlated wave function methods.

Look at the following two input files

H2O-DFT.inp

H2O-CISD.inp

The first one, is for a DFT calculation using the PBE exchange-correlation functional while the second input file uses correlated wave function methods (Moller-Plesset perturbation theory and coupled-cluster expansions).

Run both calculations and report the following results:

- Relaxed atom positions

- Energy of the input structure
- Final energy of the relaxed structure
- HOMO-LUMO gap

Summary of results for water

How does the energy of the water molecule change in the following methods?

- Hartree-Fock
- Density functional theory with the PBE functional
- Moller-Plesset 2nd order perturbation theory
- Coupled-cluster expansion with single and double excitations

Problem 4. HOMO/LUMO gaps of the Acenes

Generate the structures of the acenes naphthalene to pentacene using the Avogadro program. Avogadro can directly generate input for PCGAmess. Save the input files for PCGAmess. Optimize the geometries and calculate the HOMO/LUMO gap using RHF and the density functional method B3LYP.

Divide up the work between the groups such that every group is doing a different acene molecule and a different quantum chemistry method. Use the 3-21G basis set.

Assemble the results for the HOMO/LUMO gap into a table. Is there a trend in the gap with the size of the acene molecule? How do the gaps in Hartree-Fock and density-functional theory compare with the experimental values?

Acene	Experiment	Hartree-Fock	DFT-B3LYP
Naphthalene	4.3 eV		
Anthracene	3.3 eV		
Tetracene	2.6 eV		
Pentacene	2.1 eV		

4. How Defects Control the HOMO/LUMO Gap

We will again use quantum mechanical tools to study how defect can change the HOMO/LUMO gap in the acenes.

We already determined the structure and formation energies of possible defects for the acene from molecular mechanics calculations using Tinker. Now we will study how the defects affect the HOMO/LUMO gap.

Using the same methods (RHF and DFT-B3LYP) and basis set (3-21G) as for the perfect acene molecules, calculate the HOMO/LUMO gap for the dihydroacene and oxygen defects

Again, divide up the work between the groups and assemble the results in the table.

Acene	Hartree-Fock	DFT-B3LYP
Dihydroacene defect		
Napthalene		
Anthracene		
Tetracene		
Pentacene		
Oxygen defect		
Napthalene		
Anthracene		
Tetracene		
Pentacene		