

Worksheet 1

Quantum mechanical approaches: Hückel approximation and DFT methods

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Important remarks

- Due date: **Thursday, May 2nd, 2013, 12:00**
- You can either send a PDF file to Jens Smiatek (smiatek@icp.uni-stuttgart) or submit a hand-written copy.
- Hints for the solution and an introduction to SIESTA will be given on Tuesday, 23rd, 2013, 8:00 (CIP-Pool)
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart) or Ganesh Sivaraman (ganesh@icp.uni-stuttgart.de)

Theoretical Task: Hückel approximation for Benzene

Benzene (Figure 1) is a cyclic hydrocarbon with the chemical formula C_6H_6 . The structure is planar due to six sp^2 hybridized carbon atoms which means that the electrons in the π -orbitals are largely delocalized. This results in two stable mesomeric conformations as shown in Fig. 1. An analytical approach for the calculation of the energy eigenvalues is given by the Hückel approximation. The Hückel approximation has the following characteristics:

- Applicable for conjugated hydrocarbons

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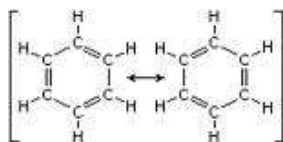


Figure 1: Chemical structure of Benzene with mesomeric conformations. Taken from www.chemgapedia.de.

- Only π -electrons are considered, σ -electrons are ignored
- Usage of Linear combination of atomic orbitals for the determination of the molecular orbitals (LCAO-MO)

Task T1: Schrödinger equation and atomic orbitals (2 points)

Denote the atomic orbitals, write the wave equation for Ψ and the corresponding Schrödinger equation.

Task T2: Matrix equation (1 points)

Write an explicit matrix representation for the Schrödinger equation with the following characteristics and orbitals:

- The orbitals for carbon atoms are given by α whereas resonance orbitals between neighboring carbon atoms are denoted by β
- Only neighboring carbon atoms have resonance orbitals (denoted by $\beta_{ii\pm 1} \neq 0$) while they are otherwise $\beta_{ii} = 0$ with $i = 1, 2, 3, 4$
- Overlap integrals S are only nonvanishing for $S_{ij} = \delta_{ij}$

Task T3: Solve the matrix equation for the energy eigenvalues (4 points)

Solve the matrix equation for the energy eigenvalues with the help of the secular determinant and calculate the values.

Task T4: Energy eigenvalues (HOMO and LUMO representation) (3 points)

Draw the energy eigenvalues in an energy plot and distribute the electrons. Determine the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Draw the wave function schematically and denote the orbitals by \pm notation.

Computational Task: DFT calculations with Siesta

Siesta is the electronic structure theory code that we will use for our exercises. The latest stable release version is 3.2 and the code can be accessed from the following directories in the CIP pool machines . Note that the program is compiled for a multiprocessor run.

```
/usr/local/siesta/siesta-3.2/           -- Install directory
/usr/local/siesta/siesta-3.2/Obj/siesta  -- Path to Siesta Executable
/usr/local/siesta/siesta-3.2/Docs/siesta.pdf -- Siesta Manual
/usr/local/siesta/siesta-3.2/Util/       -- Postprocessing utilities .
```

If you are interested in installing (in serial mode) the code in your laptops, then you may find the following links useful.

```
http://icmab.cat/leem/siesta/CodeAccess/Code/downloads.html
http://www.pa.msu.edu/people/tomanek/SIESTA-installation.html
```

Setting up a calculation

Siesta requires the following input files to invoke a calculation run.

1. An input file specifying all parameters of our chosen system (Eg: chemical species, coordinates, basis set, xc functional etc.). This file is of extension “*fdf*”. (Refer to page 11 of the Siesta manual)
2. A pseudopotential file (*.psf*) for each chemical species. This can be downloaded from <http://icmab.cat/leem/siesta/Databases/Pseudopotentials/periodictable-intro.html>

Once we have prepared all the inputs, start the calculation:

```
> mkdir some_name           ##Make some folder
> cp filename.fdf chemical_species.psf some_name/  ##copy input
files to this folder
> cd some_name              ##change current directory
> mpirun -np 4 /usr/local/siesta/siesta-3.2/Obj/siesta < filename.fdf
|tee some_name.out         ##Start calculations and
write all output to a file.
```

Task C1: Geometry optimization of adenine (5 points)

DNA plays the central role as the information storage device (for protein production) in all biological systems. In this exercise we will try to do a theoretical prediction of stable geometry of an isolated DNA bases name *adenine* using the Kohn-Sham Density functional theory. For general instruction on siesta, refer to the cover sheet.

- Copy the *Adenine.fdf* file. The initial coordinate along with some basic parameters has been already supplied in this file.
 - The theoretical prediction has to be done for two flavors of xc functional namely:
 1. LDA (CA)
 2. GGA (PBE)
 - Modify the .fdf file with suitable parameters for XC and the geometry optimization parameters.
 - Download the pseudopotential files for each flavors of XC functional.
 - Perform the siesta calculation.
 - At the end of calculation there will be systemlabel.xyz file generated and visualize this file in VMD.
 - Now open the Attachment1a.pdf. In the *Figure 1a* and *TABLE I*, where the naming convention of the atoms in Adenine has been defined.
1. Tabulate the bond length and Bond angle predicted by siesta using LDA and GGA calculations following the convention defined in TABLE I.
 2. Make a comparison for GGA vs LDA.
 3. Make a comparison with the experimental results shown in TABLE I and give some observation on the quality of result for each of the two cases.

Note: Express the bond length to an accuracy of three decimal places and the unit should be in Å. Express the bond angle with in two decimal place accuracy.

Task 2: Theoretical Prediction of Watson-Crick Hydrogen-bond length in adenine-thymine base pair (5 points)

The hydrogen bond plays a central role in formation of the double stranded DNA (W-C). In this exercise we will try to see the effectiveness of DFT in predicting the h-bond length for the adenine-thymine base pair.

- Download the Adenine_thymine.fdf file and modify similar to Task C1.
- The theoretical prediction has to be done for two flavours of XC.
 1. LDA (CA)
 2. GGA (PBE)
- Follow the nomenclature defined in TABLE II of Attachment 1a.pdf.

1. Tabulate the bond lengths and bond angle for two cases.
2. Make a comparison for LDA vs GGA.
3. Make a comparison with experimental results from Table 3 of Attachment1b.pdf and give some observation on the quality of results for two cases.