

Worksheet 1:

Quantum Mechanical Approaches: Hückel Approximation and Ab-initio Methods

Bibek Adhikari

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Institute for Computational Physics, University of Stuttgart

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General Remarks

- Deadline for the report is **Monday, 25th of April 2016, 12:00 noon**
- In this worksheet, you can achieve a maximum of 20 points.
- The report should be written as though it would be read by a fellow student who attends the lecture, but doesn't do the tutorials.
- To hand in your report, send it to your tutor via email.
 - Frank (fuhlig@icp.uni-stuttgart.de) (Thursday 14:00-15:30)

- Please attach the report to the email. For the report itself, please use the PDF format (we will *not* accept MS Word doc/docx files!). Include graphs and images into the report.
- The report should be 5–10 pages long. We recommend using L^AT_EX. A good template for a report is available online.
- The worksheets are to be solved in **groups of two or three** people.

1 Introduction

In this worksheet, you will first work on several theoretical tasks about the method of linear combination of atomic orbitals (LCAO). In the remainder of the worksheet, you will perform quantum mechanical simulations of a single water molecule using the software package GAMESS.

All files required for this tutorial can be found in the directory `/group/sm/2016/tutorial_01` accessible from the ICP CIP pool machines.

2 Short Questions - Short Answers (4 points)

Task	(4 points)
Answer the following questions:	
<ul style="list-style-type: none"> • What is the Born-Oppenheimer approximation? • What are the simplifications of the Hartree-Fock approach? • What do the Kohn-Sham equations describe? • When is it useful to use DFT compared to Hartree-Fock? Give reasons for your choice. 	

3 Hückel approximation for Benzene (6 points)

Benzene is a cyclic hydrocarbon with the chemical formula C₆H₆. The structure is planar due to six sp² 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.

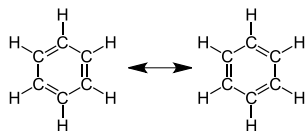


Figure 1: Chemical structure of benzene with mesomeric conformations.

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
- 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)
- Orthonormal basis set, i.e., overlap integrals $S_{kl} = \delta_{kl}$

Schrödinger Equation and Atomic Orbitals

Task Denote the atomic orbitals, expand Ψ into relevant atomic orbitals and write down the corresponding Schrödinger equation.	(1 point)
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Matrix Equation

Task Write an explicit matrix representation for the Schrödinger equation with the following characteristics and orbitals: <ul style="list-style-type: none">• Diagonal elements of the Hamilton matrix are given by α, and coupling terms between neighboring elements (<i>only</i>) by β Solve the equation for the energy eigenvalues and compare the total energy of benzene to that of ethylene.	(3 points)
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Energy Eigenvalues (HOMO and LUMO representation)

Task <ul style="list-style-type: none">• 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.	(2 points)
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4 Electronic Structure Calculations of a Water Molecule with GAMESS (10 points)

In this exercise, you will simulate a single water molecule. You will be using GAMESS (General Atomic and Molecular Electronics Structure System) as an ab-initio code. Further information about the code can be found on the GAMESS homepage (<http://www.msg.ameslab.gov>).

Note that the program is already compiled and the executable and the PDF manual can be found on the ICP CIP pool machines under `/group/sm/2016/tutorial_01/gamess`.

The sample input files for the different tasks are located in corresponding subdirectories under `/group/sm/2016/tutorial_01/tasks`.

Please copy the `/group/sm/2016/tutorial_01` folder to your home directory to proceed with the worksheet. Keep in mind that everytime you perform a simulation run in a different directory you need to copy `auxdata`, `rungms`, `ddikick.x`, `gamess.01.x`, and `gms-files.csh` to that directory.

Setting up a Simulation

1. A standard GAMESS input file `test.inp` can be found in the `gamess` directory. You will see several lines in the input file starting with a space and a dollar sign (`$`). These dollar groups, their key words and values provide the information required for the computations. Lines starting with less or more initial spaces, or starting with different symbols will be ignored.
2. The `$CONTRL` group contains the chemical control data and the type of wavefunction we want to use, the `$BASIS` group contains the basis set specifications and the `$DATA` group provides the molecule information. For description of these groups, please refer to the manual provided. It is important that there are no tab symbols in the file. It is also important that the group lines aren't too long. If you have many keywords for a particular group it is good to simply start a second line.
3. You can execute GAMESS by issuing the command

```
$> ./rungms test &> test.log
```

in your work directory. The files `test.log` and `test.dat` contain all the output information required for further analysis. You can edit the `rungms` script as per your convenience if you want to dump the output and temporary files to any other work directory.

4. Execute

```
$> grep "NORMALLY" test.log
```

to check whether your job terminated without errors.

5. Use `vmd` or `molden` to visualize the final geometry, orbitals and charge density of your system.

4.1 Basis Set Study of Water

You will perform a basis set study to determine at what basis set the results converge, their accuracy and computational time using the default Hartree-Fock method implemented in GAMESS.

All input files required for this task can be found in the directory `tasks/task_1`.

Task

(3 points)

- Edit the input files by replacing the \$BASIS group with the following:
 - a) STO-3G
 - b) 6-31G
 - c) 6-311+G(d,p)
 - d) DZV(2d,p)
- Take a look at the output files and prepare a table with three columns illustrating basis type, number of basis functions, and CPU time and compare the results.
- Prepare a table with five columns illustrating basis type, final energy, OH bond length, bond angle, and dipole moment and compare the results.
- Visualize the orbitals in VMD by executing

```
vmd <filename>.log
```

Use two representations, one for the atoms (drawing method CPK) and one for the orbitals, then browse through the orbitals. Use the buttons *OrbList* and the drop-down list *Orbital* and play with the isovalue.

- Typing

```
> molinfo top get orboccupancies
```

and

```
> molinfo top get numelectrons
```

in the VMD console will give you the occupied orbitals and the number of electrons. How many orbitals are occupied? Visualize the HOMO (Highest Occupied Molecular Orbital).

4.2 Partial Charges

In this task, you will calculate the partial charges of the individual atoms in a water molecule using RESP. Visit <http://q4md-forcefieldtools.org/RED/overview.php> for further information on the RESP package.

Task

(2 points)

- Use the basis type suited best for your system and calculate the partial charges. The input file `h2o_partial_charge.inp` is already provided in the directory `tasks/task_2`.

In the input file,

```
$ELPOT IEPOT=1 WHERE=PDC OUTPUT=PUNCH $END
```

has to be added for the electrostatic potential.

- After the simulation, use the `makeresp` tool as such:

```
$> ./makeresp h2o_partial_charge.dat
```

This will create two files `h2o_partial_charge.esp` and `h2o_partial_charge.in`.

- These files will have to be fed to `RESP`:

```
$> ./resp -i h2o_partial_charge.in \  
-e h2o_partial_charge.esp \  
-o h2o_partial_charge.res
```

- Take a look at the output files `qout`, `punch` and `h2o_partial_charge.res` and write down the partial charges.

4.3 Structure as a Function of Wavefunction Type

In this task, you will be running optimizations of a water molecule with different methods implemented in GAMESS. All input files for this task are already present in the directory `tasks/task_3`.

Task**(3 points)**

- Perform simulations with the different methods
 - a) PBE (DFT)
 - b) BLYP (DFT)
 - c) B3LYP (DFT)
 - d) MP2 (2nd order many body perturbation theory)
 - e) HF (Hartree Fock)
- From the output data, create a table with the columns method, final energy (8 decimal places), OH bond length (4 decimal places), dipole moment (2 decimal places), and bond angle (4 decimal places).
- Use all the basis sets from task 4.1 and all the methods from this task and provide a table comparing the values of the final energy. Which method with which basis set do you think works best?

4.4 Continuum Solvation Methods

In this task, you will investigate two water models namely a) water in a dielectric medium, and b) a water molecule in water. All input files for this task are already present in the directory `tasks/task_4`.

Task

(2 points)

- Run an optimization of water in vacuum with the input `h2o_vacuum.inp` and note the OH bond length, the dipole moment, and the final energy.
- Take the optimized coordinates from the previous run and add this additional line to your input:
`$SCRF RADIUS=<your_radius> DIELEC=80.0`
Choose a radius keeping in mind the size of your molecule.
- Run the calculation and note the OH bond length, the dipole moment, and the final solvated energy.

- Calculate the solvation energy:

$$E_{\text{solvation}} = (E_{\text{vacuum}} - E_{\text{solution}}) \cdot 627.517 \text{ [kcal/mol]} \quad (1)$$

- Run the same calculation using cavity radii which are a) smaller than the size of the molecule, and b) much larger than the size of the cavity. Calculate the corresponding solvation energies. Is there any difference?
- In the input file `h2o_vacuum.inp`, replace the line
`$SCRF RADIUS=<your_radius> DIELEC=80.0`
with
`$PCM SOLVNT=WATER $end`
- Run the calculation and record the OH bond length, the dipole moment, and the final solvated energy.
- Calculate the solvation energy according to equation (1). Compare your results to the experimental solvation energy of 6.29 kcal/mol.