

# Worksheet 1

## Quantum mechanical approaches: Hückel approximation and ab-initio methods

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### Important remarks

- Due date: **Tuesday, May 5<sup>th</sup>, 2015, 12:00**
- You can either send a PDF file to Bibek Adhikari (adbibek@icp.uni-stuttgart.de) or submit a hand-written copy.
- Hints for the solution and an introduction to GAMESS will be given on Thursday, 23<sup>rd</sup>, 2015, 14:00 (CIP-Pool)
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart.de) or Bibek Adhikari (adbibek@icp.uni-stuttgart.de)

### Short Questions (4 points)

- Q1: What is the Born-Oppenheimer approximation?
- Q2: What are the simplifications of the Hartree-Fock approach? Short answer in your own words.
- Q3: What does the Kohn-Sham equation describe?

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- Q4: When is it useful to use DFT compared to Hartree-Fock? Give reasons for your choice.

## 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  $\pi$ -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:

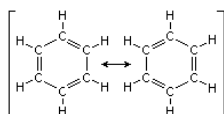


Figure 1: Chemical structure of Benzene with mesomeric conformations. Taken from [www.chemgapedia.de](http://www.chemgapedia.de).

- Applicable for conjugated hydrocarbons
- Only  $\pi$ -electrons are considered,  $\sigma$ -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  $\Psi$  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  $\alpha$  whereas resonance orbitals between neighboring carbon atoms are denoted by  $\beta$
- 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 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: Quantum Simulations of a Water ( $H_2O$ ) molecule. [10 points]

In this exercise, we will simulate a single molecule of water. We will be using GAMESS (General Atomic and Molecular Electronics Structure System) as an ab-initio code. Further information about the code can be found in GAMESS homepage [http : //www.msg.ameslab.gov/](http://www.msg.ameslab.gov/). Note that the program is already compiled and the executable, sample input files etc can be found in the following directories in the ICP pool machines.

<code>/group/allatom/gamess/task</code>	<code>--install directory</code>
<code>/group/allatom/gamess/task/gamess.01.x</code>	<code>--path to the executable</code>
<code>/group/allatom/gamess/task/rungms</code>	<code>--executable script</code>
<code>/group/allatom/gamess/task/test.inp</code>	<code>--sample input file</code>
<code>/group/allatom/gamess/task/gamess_manual.pdf</code>	<code>--GAMESS manual</code>

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

### Setting up a calculation

1. A standard input file for GAMESS `test.inp` can be found in the "task" folder. You could see some keywords in the input file. These dollar groups and key words are the ones used to pass the information regarding the calculation.
2. The `$CONTRL` group contains the chemical control data and the type of wavefunction we may use, the `$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 entries. It is also important that the \$ groups lines aren't too long. If you have many keywords for a particular \$ group it is good to just start a second line.
3. You can execute GAMESS by typing `./rungms test >& test.log` in your work directory. The file `test.log` and `test.dat` contains all the output information you

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

### **T1.1: Basis set study of Water (3 points)**

We will perform a basis set study to determine at what basis set the results converge, their accuracy and computational time using default Hartree-Fock method implemented in GAMESS. All the input files for this task can be found inside directory `Task1.1`

- 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 file and prepare a table with three columns illustrating 1) Basis type, 2) Number of basis functions and 3) CPU time and compare the results.
- Prepare a table with four columns illustrating 1) Basis type, 2) Final Energy, 3) OH bond length 4) Bond angle and 5) Dipole moment and compare the results.
- Visualize orbitals in VMD by typing `vmd filename.log`. Use two representations, one for the atoms (Drawing Method = CPK) and one for the orbital, 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).

### **T1.2: Partial charges (2 points)**

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

- Use the basis type best for your system and calculate the partial charges. Input file *h2o\_partial\_charge.inp* is already provided inside directory `Task1.2`.
- `$ ELPOT IEPOT=1 WHERE=PDC OUTPUT=PUNCH $END` is added to the input for electrostatic potential
- Use `makeresp` utility as such: `./makeresp h2o_partial_charge.dat`. Two files *h2o\_partial\_charge.esp* and *h2o\_partial\_charge.in* will be produced
- These will have to be fed to `RESP` as: `./resp -i h2o_partial_charge.in -e h2o_partial_charge.esp -o h2o_partial_charge.res`
- Take a look at the `qout`, `punch` and *h2o\_partial\_charge.res* produced as output and write down the partial charges.

### **T1.3: Structure as a function of wavefunction type (3 points)**

We will be running optimization of water molecule with different methods implemented in GAMESS)

- Input files for this task is already present inside directory `Task1.3` with different methods listed below:
  - a) PBE (DFT)
  - b) BLYP (DFT)
  - c) B3LYP (DFT)
  - d) MP2 (2nd order many body perturbation theory)
  - e) HF (Hartree Fock)
- Once you have run the optimization calculations, take the optimized geometries and run Hessians for each wavefunction type. (i.e. make a second copy of the respective inputs, paste the optimized geometry into the second input, and change `runtyp` to `HESSIAN`)
- List the data with respect to different type of methods into various columns as 1) Method 2) Final energy (upto 8 decimal places) 3) OH Bond lengths (upto 4 decimal places) 4) Dipole (upto 2 decimal places) 5) Bond angle (upto 4 decimal places).
- Use all the basis sets from task T1.1 and all the methods from task T1.3 and produce a table for the comparison of the final energy. Which method with what basis do you think is the best?

### **T1.4: Continuum solvation methods (2 points)**

We will investigate two water models namely a) water in a dielectric and b) a water molecule in water.

- Run an optimization of water in vacuum with the input *h2o\_vacuum.inp* present inside directory Task1 . 4, and note the O-H bond distance, the dipole, and the final energy
- Take the optimized co-ordinates from the previous run and add this additional line to your input, choose a radius keeping in mind the size of your molecule.  
\$ SCRF RADIUS= XX DIELEC= 80.0
- Run the calculation and note the O-H bond distance, the dipole, and the final solvated energy.
- Calculate the solvation energy:  $[E(\text{vacuum phase}) - E(\text{solution phase})] * 627.517$  (kcal/mol)
- Run the same calculation using cavity radii that is a) smaller than the size of the molecule, and b) much larger than the size of the cavity. Calculate the solvation energies. Is there any difference?
- Take the input *h2o\_vacuum.inp* and replace the line \$SCRF RADIUS=XX DIELEC= 80.0 with \$PCM SOLVNT=WATER \$end
- Run the calculation and record the O-H bond distance, the dipole, and the final solvated energy.
- Calculate the solvation energy:  $[E(\text{vacuum phase}) - E(\text{solution phase})] * 627.517$  (kcal/mol) . Compare your results to the experimental solvation energy value of 6.29.