C7800 Introduction to molecular modelling - seminar
TSM Modeling of molecular structures

Projects
Project A - Water Dimer

Petr Kulhanek

kulhanek@chemi.muni.cz

National Center for Biomolecular Research, Faculty of Science
Masaryk University, Kotlářská 2, CZ-61137 Brno

Water molecule
Water molecule dimer

Quantum-chemical calculations

Water molecule

- structure and energy
  - basis set effect
- properties

Water molecule dimer

- structure and energy
- interaction energy
  - basis set effect
- properties


To think about

- What effect does the basis set size have on the value of the absolute energy of a water molecule?
- What effect does the basis set size have on the value of the absolute energy of the water molecule dimer?
- What effect does the basis set size have on the value of the interaction energy of the water molecule dimer?

How to process results

I recommend to summarize the results in the form of a brief protocol, which should have the following requirements:

- Name and surname, name of the project and date
- For each thematic area:
  - Brief summary of the topic, including a reaction scheme, if appropriate
    - Software used, including versions
    - Results (tables)
      - Tables
        - numbers aligned to the right
        - energies with 6 decimal points (au) or 2 decimal points (kcal/mol)
        - lengths with 4 decimal points (A)
        - angles with 1 decimal points (deg)
        - charges with 3 decimal points (au)
  - Discussion of results in context of the course
  - References (e.g., for experimental values)

Water molecule

(Almost) individual project

- **Reference manuals**
  - Gaussian (QM calculations)
  - Nemesis (preparation, visualization)
  - CBS - Extrapolation to a complete basis set
  - VMD (volumetric data visualization)
  - Infinity (submitting jobs)

Tasks

1) Create a model of water molecule and optimize its geometry using molecular mechanics.
2) Optimize the geometry of the water molecule using the HF/cc-pVDZ
3) Measure significant geometric parameters of the optimized geometry and compare them with the initial model.
4) Employing vibrational analysis, verify that the found geometry corresponds to the local minimum on the PES.
5) Perform energy and property calculation at the HF/cc-pVDZ level of theory and extract:
   - total energy
   - dipole moment
   - Mulliken and MK (Merz-Singh-Kollman) atomic charges
6) Repeat the calculation described in the point 5 on the same geometry for the following basis sets:
   - cc-pVTZ
   - cc-pVQZ
   - cc-pV5Z

Solution

Data organization

- 00.input
- 01.opt
- 02.freq
- 03.props
  - 01.cc-pVDZ
  - 02.cc-pVTZ
  - 03.cc-pVQZ
  - 04.cc-pV5Z

1) Create an initial **geometry of water molecule** in Nemesis (Project: **Build Structure**). Pre-optimize model geometry using molecular mechanics. Select such a force field (Geometry->Optimizer Setup), which in your opinion best describes its geometry.
2) Save pre-optimized model geometry in the **xyz** format under the name **water.xyz** to a folder **00.input** (File->Export Structure as…->OpenBabel). Next, save the input file for the program Gaussian (HF/cc-pVDZ, Geometry Optimization) with name **opt.com** to a folder **01.opt** (File->Export Structure as…->Gaussian).
3) Run the calculation in the program Gaussian in the directory **01.opt** using the Infinity environment.

Solution, cont.

4) In the directory **01.opt**, open the file **opt.log** in the Nemesis program (Project: **Trajectory**, File->Import Trajectory from…-> Gaussian-> Geometry Optimization File). Analyze the course of optimization and the geometry of the optimized model.
5) Save the optimized geometry as an input file for Gaussian (HF/cc-pVDZ, Frequencies) with name **freq.com** to a folder **02.freq** (File->Export Structure as…->Gaussian). In the directory, run the calculation in the program Gaussian using the Infinity environment.
6) In the directory **02.freq**, open the file **opt.log** in the Nemesis program (Project: **Trajectory**, File->Import Trajectory from…-> Gaussian->Vibrations File). Does the geometry correspond to a local minima?
7) If so, successively save the optimized geometry in the directories 03.props/01.cc-pVDZ,… When creating the input file **props.com** for Gaussian select "MK Charges" and the correct basis set. Run the calculations in Gaussian using the Infinity environment (All jobs can be submitted at once).
8) Analyze the calculated data and put them in the following tables.

Results I

Geometry of water molecule

fill in the used force field

Method	MM	HF/cc-pVDZ	Difference
d(HO) [Å]			
Θ(HOH) [˚]			

Results II

Water molecule

Basis set	Cardinal number	E	Er
		[au]	[kcal/mol]
cc-pVDZ	2		0.0
cc-pVTZ	3		
cc-pVQZ	4		
cc-pV5Z	5		
CBS			

result of the calculation absolute energy (E(RHF))

relative energy with respect to cc-pVDZ basis

Results III

Water molecule

Basis set	Cardinal number	Mulliken		ESP		μ
		q(H)	q(O)	q(H)	q(O)	[D]
cc-pVDZ	2					
cc-pVTZ	3					
cc-pVQZ	4					
cc-pV5Z	5					
CBS						

Water molecule dimer

Individual project

- **Reference manuals**
  - Gaussian (QM calculations)
  - Nemesis (preparation, visualization)
  - CBS - Extrapolation to a complete basis
  - VMD (volumetric data visualization)
  - Infinity (submitting jobs)

Tasks

1) Create model of the water molecule dimer and optimize its geometry using molecular mechanics.
2) Optimize the geometry of the water molecule dimer using the HF/cc-pVDZ.
3) Measure significant geometric parameters of the optimized geometry and compare them with the initial model. Try to justify the observed differences.
4) Verify that the found geometry corresponds to the local minimum on the PES, using vibrational analysis.
5) With optimized geometry, perform the energy calculation for the bases:
   - cc-pVDZ
   - cc-pVTZ
   - cc-pVQZ
   - cc-pV5Z
6) For each base, determine the interaction energy between water molecules.
7) Determine the interaction energy extrapolated to CBS.
8) Display the electrostatic potential mapped to electron density calculated by the HF/cc-pVDZ. Compare the potential with a water molecule.

Solution

Data organization

- 00.input
- 01.opt
- 02.freq
- 03.props
  - 01.cc-pVDZ
  - 02.cc-pVTZ
  - 03.cc-pVQZ
  - 04.cc-pV5Z

The procedure is analogous to that of water monomer.

Results I

Geometry of water molecule dimer

fill in the used force field

Method	MM	HF/cc-pVDZ	Difference
d(HO) [Å]			
Θ(HOH) [˚]			
d(H...O) [Å]			

hydrogen bond

At your discretion, list other geometric parameters that best capture the difference between the two geometries.

Results II

Water molecule dimer

Basis set	Cardinal number	E	E_r	E_i
		[au]	[kcal/mol]	[kcal/mol]
cc-pVDZ	2		0.0	
cc-pVTZ	3			
cc-pVQZ	4			
cc-pV5Z	5			
CBS				

result of the calculation

relative energy with respect to cc-pVDZ basis

interaction energy between two water molecules

$$E_i = E_{\mathrm{dim}er} - 2 * E_{monomer}$$