

Lab #3
Density functional theory simulations of molecules
9/11/2015

1. Aim of the experiment

The aim of this experiment is to apply Density Functional Theory (DFT) simulations to the study of a pair of molecules (1: diazene (N_2H_2); 2: $\text{P}(\text{OH})_5$), and how changing the number of electrons surrounding these molecules changes the structure of the molecules. As we have discussed in lecture, density functional theory is an approach that allows us to understand the quantum mechanical effect of electrons on materials. So in these simulations we will be using the code CPMD [1], which is a plane wave/pseudopotential implementation of DFT that has been designed for *ab initio* molecular dynamics simulations.

2. Background

So unlike the other labs, here we are studying two discretely different systems, and in doing so we will see examples of some of the things that DFT calculations allow us to study that are inaccessible with classical simulation methodologies. Below, I will give you a brief background on the two different root molecules we will be studying. I will leave it up to you to read about the background of the CPMD code at the references that I have provided in Ref. [1].

2.1. Diazene

The first molecule we will be studying is diazene (N_2H_2). It exists as two geometric isomers, cis and trans. Additionally, it is occasionally used as a reagent in organic synthesis. It hydrogenates alkenes and alkynes with selective delivery of hydrogen from one face of the substrate resulting in the same stereoselectivity as a certain class of metal-catalysed addition of H_2 . The only byproduct that is released is nitrogen gas. The use of diazene avoids the high pressures, which can result in potentially explosive hydrogen gas and metal catalysts which can be expensive. An example of its use as a reagent can be seen in Ref. [2].

2.2. $\text{P}(\text{OH})_5$

Pentacoordinated phosphorous is often encountered in reactions that are centered at phosphorus. This species may occur as a transition state species, an intermediate or a stable molecule. As a result it has been found to be an important species for which to understand its chemical nature, as it is important in a variety of chemical and biochemical reactions [3-9]. In the underlying chemical mechanism that governs the hydrolysis reaction of RNA, there is experimental evidence that suggests the first step (the so-called cleavage transesterification) follows one of two possible reaction pathways involving a monoanionic phosphorane transition state and a dianionic phosphorane intermediate. In this lab, we will be carrying out an investigation of both the neutral $\text{P}(\text{OH})_5$ and the monoanionic phosphorane (PO_5H_4^-).

3. Simulation information

As stated previously, you will be using the CPMD software package for this project. In order to use CPMD in the lab, you will need to type:

module load environments/applications/MPI/cpmd 3.17.1

cpmd.x {input file} > {output file}

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Alternatively if you want to run the simulations in parallel, then you would type (after loading the module):

```
mpirun -np 2 cpmd.x {input file} > {output file}.
```

In both cases, *{input file}* and *{output file}* are the names of the input script and output that is written to the screen, respectively.

As usual, you will find a tar ball on KEATS called lab3.tar.gz. Once you have downloaded and unpacked this tar ball. You will have created a directory called lab3/. Inside of that directory, will be subdirectories called: n2h2 and poh5. Within the n2h2 subdirectory, there are four more directories: i) cis, ii) trans, iii) cis+2, iv) trans+2. Subdirectories i) and ii) contain the files for the optimizing the geometry of the cis and trans isomers of the N₂H₂ molecule, respectively. In subdirectories iii) and iv), there are the files to carry out the geometry optimization of the cis and trans N₂H₂ molecule after it has had two electrons removed from it such that it has a net charge of +2. In each of these files, you will find a file that ends with '.inp' and then files that have names '*_BLYP.' The '*.inp' files are the input scripts that you will use in the CPMD execution commands written above. The *_BLYP files are information about the pseudo-potentials.

Within the poh5 directory, there will be two sub directories: i) opt and ii) deprot. In the opt subdirectory, similar files are found as in the n2h2 subdirectories. These are used to carry out the geometry optimization. In the deprot subdirectory, there is the *.inp and *_BLYP files, and also there is a *.vmd file. The files in this directory are meant to carry out the *ab initio* molecular dynamics simulation of a deprotonated P(OH)₅ [PO₅H₄⁻] molecule in vacuum. However, as this is quite a lengthy simulation, the .vmd file is the trajectory from the course of the simulation, which I will allow you to use (as if you had carried out the simulation) in order to answer the related questions.

4. Lab assignment

Below are the questions I would like to have you answer for the two different molecular species. Note that unless otherwise specified in the input file, the default units are as follows:

Time: 1 a.u. = 0.0241888428 fs

Length: 1 a.u. = 1 bohr = 0.5917721092 Angstrom

Energy: 1 a.u. = 1 Hartree = 27.211396641 eV

Plane wave cutoff in Rydberg: 1 Ry = 1 Hartree/2.0

In the xyz files, the units should be Angstroms.

4.1. Diazene

First I would like you to carry out geometry optimization of the cis and trans configurations of the neutral form of diazene (cis/ and trans/ subdirectories). When you carry out these simulations you will generate xyz files (GEO_OPT & GEOMETRY) and then the output to the screen. The GEO_OPT will show the trajectory of the molecule during the course of the optimization. The energy of the system can be found in the output to the screen (or output file if you direct it to a file). I would like you to use these files along with VMD to answer the following questions:

1) Please read the CPMD manual and the provided input scripts for these two simulations and describe what the simulations are doing in your own words. (NOTE: if

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the two simulations are identical except for the molecular structure then there is no need to describe both).

2) Compare the final energies of the optimized cis and trans configurations. Which structure is the more energetically favourable structure?

3) Determine the lengths of the bonds (N-H, N-N), the measure of the N-N-H angle and the H-N-N-H dihedral of the optimized structures.

4) Compare the values you found in 3) to the equilibrium values found within the OPLS forcefield: $r_0(\text{N-N}) = 0.1445$ nm, $r_0(\text{N-H}) = 0.101$ nm, & $\theta_0(\text{H-N-N}) = 118.4^\circ$.

5) The functional form for the OPLS dihedral (see [10]) is a series of cosine terms and for the H-N-N-H dihedral the values of the prefactors are $V_1 = 0.0$ kcal/mol, $V_2 = 0.0$ kcal/mol, $V_3 = 0.3$ kcal/mol and $V_4 = 0.0$ kcal/mol. At what angles does this dihedral potential have a minimum energy? How does the energy in the OPLS forcefield compare for the cis and trans configurations? Does this agree with the results from your geometry optimization calculations? Does the OPLS classical forcefield capture the behavior of the molecules observed in the CPMD calculations?

6) As you will remember from the description of classical forcefields, the bond and bond angle terms also have force constants that are part of the force field. In the case of the OPLS forcefield, the values for these force constants are $k_b(\text{N-N}) = 350$ kcal/mol, $k_b(\text{N-H}) = 434$ kcal/mol, $k_\theta(\text{N-N-H}) = 56.0$ kcal/mol. Also we discussed that one way of determining these values is from the results of quantum mechanical simulations. Please discuss what you would need to do in order to obtain the data that would allow you to determine these values.

Now carry out the geometry optimization calculations of the cis and trans configurations of the $\text{N}_2\text{H}_2^{2+}$, which have had two electrons removed (cis+2/ & trans+2/). Again similar files will be produced as above, and please use those files to answer the following questions.

7) Explain the trajectory that the cis and trans species undergo during the course of the geometry optimization.

8) Compare the energies of the optimized structures of the cis- and trans- molecules.

9) Compare the bond lengths (N-N & N-H), bond angles (N-N-H) and dihedral angle (H-N-N-H) in the two optimized structures. Compare them to the same quantities of the neutral configurations.

10) Compare the measured quantities from 9) to the values defined in the OPLS classical forcefield that are described in 4) and 5) above. Does the OPLS forcefield capture the behavior of the charged structures?

4.2. $\text{P}(\text{OH})_5$

First I would like you to carry out a geometry optimization of the $\text{P}(\text{OH})_5$ molecule (opt/subdirectory). Similar files will be generated as a result of this simulation as those you carried out to study diazene. Again I would like to have you use these files to answer the following questions:

11) Describe the optimized structure. What is the average length of the P-O and O-H bonds? What is the average measure of the P-O-H and O-P-O bond angles? What is the average measure of the O-P-O-H torsion angle? Is there any evidence of hydrogen bonding occurring within the molecule?

12) Describe any trends you may observe with the evolution of the bond lengths, bond angles and torsions in comparison to the evolution of the system energy during the optimization.

13) Compare the values you find in 13) to the values from the OPLS classical forcefield listed here: $r_0(\text{P-O}) = 0.161$ nm, $r_0(\text{O-H}) = 0.0945$ nm, $\theta_0(\text{O-P-O}) = 102.6^\circ$ & $\theta_0(\text{P-O-H}) = 108.5^\circ$.

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Finally, due to the amount of time necessary to carry out molecular dynamics simulations of an interesting system with *ab initio* MD simulations, I have taken the liberty to carry out the MD simulation in advance and I have provided you with the input script, and resulting trajectory and energy output for the simulations. I would like you to use these three files to answer the following questions regarding the molecular dynamics simulation of $\text{P}(\text{O}_5\text{H}_4)^-$ anion.

14) Describe the simulation that was carried out in order to produce the output files that I have provided.

15) Describe what you observe occurring in the trajectory (poh5-dep.vmd, the command to load this file is 'vmd -e poh5-dep.vmd') and then you can play the movie of the trajectory. For any bond breaking forming that may occur, please describe the conditions at which the bonds break and/or form (i.e. bond lengths, and any other measured quantities of the system that you find interesting/important).

16) Using the file which contains all of the thermodynamic information regarding the simulation (poh5dep-energies.dat), please plot and comment on the system energy (5th column) and system temperature (3rd column) as a function of step number (1st column). In doing so, relate it to the included trajectory (i.e. any changes observed in the temperature and energy, please correlate with any observed interesting behavior in the trajectory).

5. Report submission deadlines

Please answer the above questions. The due date for the report is **Wednesday 18/11/2015 at 11.55PM**. As usual, you will be expected to submit via KEATS and in a pdf format.

[1] <http://cpmd.org/the-code> ; <http://cpmd.org/documentation/cpmd-html-manual>

[2] <http://en.wikipedia.org/wiki/Diazene>

[3] K. C. Kumara Swamy & N. Satish Kumar, *Acc. Chem. Res.* (2006) **39**, 324.

[4] N. L. Doltsinis & M. Sprik, *PCCP* (2003) **5**, 2612.

[5] F. H. Westheimer, *Acc. Chem. Res.* (1968) **1**, 70.

[6] M. Oivanen, S. Kuusela & H. Lonnberg, *Chem. Rev.* (1998) **98**, 961.

[7] D. M. Perreault & E. V. Anslyn, *Angew. Chem. Int. Ed. Engl.* (1997) **36**, 432.

[8] X. Lopez, M. Schneider, A. Dejaegere & M. Karplus, *J. Am. Chem. Soc.* (2002) **124**, 5010.

[9] J. E. Davies, N. L. Doltsinis, A. J. Kirby, C. D. Roussev & M. Sprik, *J. Am. Chem. Soc.* (2002) **124**, 6594.

[10] http://lammps.sandia.gov/doc/dihedral_opls.html