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## Density Functional Theory Calculations

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This lab session involves calculations using density functional theory (DFT). This approach is an alternative to the Hartree-Fock and post-Hartree-Fock approach. The advantage is that the computational effort is smaller than for post-Hartree-Fock calculations but the disadvantage is that there is not a clear path to the exact results. Several different approximations of the energy functional have been proposed and you will compare a few different examples. The B3LYP functional is one of the most commonly used functionals in computational chemistry today.

### A. Dissociation curve of $H_2$ and $H_2^+$

Calculate the binding curve of  $H_2$  once again using the parameter-scan ('paras') functionality where the energy is calculated using various DFT functionals, such as LDA, BLYP, TPSS and the B3LYP functionals. This is only a small subset of the plethora of available functionals (see e.g., <http://www.tddft.org/programs/libxc/functionals/>).

- a local density approximation, LDA (! UKS LDA)
- a gradient corrected semi-local approximation, BLYP (! UKS BLYP)
- a meta generalized gradient approximation, TPSS (! UKS TPSS)
- a hybrid functional, B3LYP(! UKS B3LYP)
- a hybrid meta generalized gradient approximation, TPSSh (! UKS TPSSh)

(Note: UKS stands for unrestricted Kohn-Sham DFT calculation)

Calculate the  $H_2$  binding curve using the four functionals listed above and the **6-311++G(3df,3pd)** basis set. Remember to specify an unrestricted calculation and use broken-symmetry (see input below for a BLYP calculation). Also, calculate the energy of a single hydrogen atom using each one of the functionals in order to calculate the binding energy of  $H_2$  with respect to two isolated H atoms.

```
!UKS BLYP 6-311++G(3df,3pd)
```

```
%scf BrokenSym 1,1 end
```

```
%paras
```

```
R = 4.00,0.40,40
```

```
end
```

```
*xyz 0 1
```

```
H      0.0   0.0   0.0
```

```
H      {R}   0.0   0.0
```

```
*
```

**Q1:** For what properties are DFT calculations known to give accurate predictions and for what are DFT calculations known to be inaccurate?

**Q2:** Give a concise description of the different types of exchange-correlation functionals mentioned above and explain qualitatively the difference between them.

**Q3:** Make a table of the energy of a single hydrogen atom obtained with the various functional approximations and compare with the energy obtained using HF.

**Q4:** Does any of the calculations give total energy for the H atom that is lower than the exact energy? If so, is this in contradiction with the variational principle? Explain.

**Q5:** Make two graphs showing the binding curves for the various functionals as well as the exact results obtained by Kolos and Wobniewicz. In the first graph, show the binding energy of the molecule as a function of the distance between the atoms. In the second graph, focus on the distance between 0.5 and 1.1 Å. How do the results obtained using the various functionals compare with the exact results? Explain why some functionals work better than others.

Now calculate the binding curve of  $H_2^+$  using BLYP and B3LYP and the 6-311++G(3df,3pd) basis set. For comparison, calculate the binding curve with Hartree-Fock using the same basis set. For these calculations, make the parameter-scan run from 0.2 to 4.0 Å in 40 steps.

**Q6:** What value should the energy approach as the  $H_2^+$  bond breaks?

**Q7:** Make a graph showing the three binding curves (BLYP, B3LYP and HF). How do the results obtained by BLYP and B3LYP compare with the HF results (i) in the bonding region and (ii) when the bond has been stretched (i.e.  $r_{HH} > 3.0$  Å)? Explain possible discrepancies between DFT and HF results. Also, explain the difference in behavior between BLYP and B3LYP.

## B. Bond angle and singlet-triplet splitting in $CH_2$

Calculate the ground-state energy and geometry of the singlet and triplet  $CH_2$  using **B3LYP** and the **6-311++G\*\*** basis set.

**Q8:** How does the geometry and singlet-triplet splitting obtained using B3LYP compare with the Hartree-Fock, CI and MP2 results (from lab 4, 5 and 6) and with the experimental values of  $134^\circ$  (triplet)/ $102^\circ$  (singlet) and a splitting of 9.05 kcal/mol?

## C. Partial charges of F when the C–F bond of fluoromethane is stretched

In this section, you will calculate the partial charge on the fluorine atom as the C-F bond in fluoromethane ( $CH_3F$ ) is stretched (3.0 Å) and dissociated (4.5 Å) and compared to the partial charge of the equilibrium structure.

To model the fluoromethane molecule, open Chemcraft, go to **Edit**→**Add fragment**→**Molecules** select methane ( $CH_4$ ) and left-click the main window. Then replace one of the H atoms with F, by going to **Edit**→**Add atom** and select F from the interactive periodic table. Click on one of the H atoms.

**Q9:** What would you expect the charge on the F atom to be as the C–F bond is stretched and eventually breaks? What type of molecular geometry would you expect the  $CH_3$  moiety to assume?

Set up an equilibrium structure search using unrestricted Hartree-Fock and copy paste the coordinates from Chemcraft to the input file. In this calculation, use the correlation-consistent Dunning basis set called aug-cc-pVTZ. The correlation-consistent basis sets are being used more and more while the Pople basis sets are being used less. Carry out the calculation and then record the partial charge on the F atom by searching for the last occurrence of "MULLIKEN ATOMIC CHARGES" in the output file.

Open the equilibrium configuration of fluoromethane in Chemcraft, stretch and dissociate the C–F bond. To do this, select both the C and F atom and assign a bond-length of 3.0 Å and later to 4.5 Å in the geometrical editor. Prepare a new ORCA input file and copy-paste the coordinates of the dissociated fluoromethane in the input file. Use the same level of theory as for the previous equilibrium structure search. Perform a

constrained equilibrium structure search where the C–F bond-length is fixed during the optimization. To achieve this add the following 'geometry block' to the input file:

```
%geom
Constraints
{B 0 4 C}
end
end
```

where 'B' stands for bond and 'C' stands for constrained. The numbers 0 and 4 indicate for what atoms the bond should be fixed. Here, the C atom is number 0 and fluorine atom is 4. Note that this could be different in your case, depending on which H atom you selected to be replaced by F.

**Q10:** Find online material/published articles and read about the Dunning basis set. Write a brief summary about this class of basis sets and also explain the (aug)-cc-pVnZ notation.

**Q11:** Read about and explain Mulliken population analysis. Explain how the charge on a particular atom in a molecule is computed in the Mulliken approach.

**Q12:** While Mulliken population analysis is good enough when atoms are well separated as is the case here, there is a mathematical problem with this approach. Explain why.

**Q13:** Why does a bond-constraint need to be applied in the constrained equilibrium structure search calculation of the dissociated fluoromethane?

Repeat the calculations described above using both the BLYP and B3LYP functionals. Note, however, that you do not need to perform the calculation where the C-F bond is dissociated, i.e.  $R(\text{C-F}) = 4.5 \text{ \AA}$ , for the BLYP functional, it is near-impossible to converge that calculation using standard settings. In general, the electronic structure of 'highly stretched molecules / dissociated molecules' is challenging in DFT and problems often arise in the SCF algorithm. If you encounter convergence problems in your calculations, increase the number of steps allowed in the SCF loop by adding the following 'scf' block to the input file:

```
%scf
maxiter 300
end
```

or employ a damping scheme by adding the keywords 'slowconv' or 'veryslowconv' to the simple-input line (i.e. the line that starts with an exclamation mark) of the input file.

**Q14:** Make a table in your report with the results from the Hartree-Fock, BLYP and B3LYP calculations for the partial charge on the F atom at the equilibrium position, stretched C-F bond ( $3.0 \text{ \AA}$ ) and the dissociated molecule ( $4.5 \text{ \AA}$ ).

**Q15:** Compare and contrast the charge on the F atom obtained at Hartree-Fock and B3LYP level of theory. Which is more correct and why?