Many-body perturbation: MP2

This lab, the perturbation approach to post-HF calculations is used. The methodology is often referred to as Møller-Plesset perturbation theory and when carried out to order n, the method is designated as MPn. The calculations here will involve MP2, i.e. the second order perturbation method.

A. Dissociation curve of H_2

Calculate the binding curve of H_2 again, now using the **MP2** method. Use the same settings for the parameter scan ('paras') as in lab 5, see input below. Use the **6-311++G(3df,3pd)** basis set.

```
!UHF MP2 6-311G

%scf BrokenSym 1,1 end

%paras
R = 2.00,0.40,33
end

*xyz 0 1
 H     0.0   0.0   0.0
 H     {R}   0.0   0.0
*
```

Notice that the scan is reversed compared to lab 5, as it now starts with $r_{HH} = 2.0$ Å and then sequentially decreases the bond-length to $r_{HH} = 0.4$ Å. This makes it easier for the broken symmetry method to converge to the correct SCF solution from the start (since the broken symmetry is more important in the asymptotic region where the atoms are far apart).

Carry out the calculation. The table listing the energy for the various values of the bond length is close to the end of the output file. Record the MP2 energy (**'Actual Energy'**) and the HF energy (**SCF energy**) for your report.

In order to carry out a spin-unrestricted MP2 calculation, replace **MP2** by **UHF MP2** in the input file and activate the 'BrokenSym' command in the input (see above).

> **Q1:** *Make a graph showing the calculated binding curves for the restricted and unrestricted MP2 calculation, the corresponding HF values and the exact results by Kolos and Wolniewicz.*

When spin-unrestricted Slater determinants are used, the electronic wave function can become a mix of different spin states. Instead of pure singlet state, the higher energy triplet state can get included. This is called 'spin contamination'. Its effect is largest for half broken bonds.

> **Q2:** *Describe and explain the difference between the restricted and unrestricted MP2 calculation. Identify the region of the unrestricted MP2 binding curve where the effect of spin contamination is significant. Is the effect of spin contamination still present at the dissociation limit? Why/why not?*

> **Q3:** *How do the MP2 results compare with the QCISD(T) results obtained in the previous exercise?*

B. Bond angle and singlet-triplet splitting in CH_2

Calculate the ground-state energy and geometry of the singlet and triplet states of CH_2 using **MP2** and the **6-311++G**** basis set.

Q4: *How does the geometry and singlet-triplet energy splitting obtained using MP2 compare with the Hartree-Fock and QCISD(T) results (from labs 5 and 6) and with the experimental values of $134°$ for the triplet, $102°$ for the singlet and a singlet/triplet energy splitting of 9.05 kcal/mol?*

C. Hydrogen bonded clusters

Calculate the strength of the hydrogen bond in a methanol dimer ($2 \times CH_3OH$) and in a methylamine dimer ($2 \times CH_3NH_2$). MPn methods are a good choice for such calculations of the binding energy in a molecular cluster.

Q5: *Why is the MP2 approximation often a good choice for calculations of the binding energy in a molecular cluster?*

Q6: *What is meant by 'size consistency'? Explain why MP2 is size consistent while QCISD is not.*

Create a dimer of methanol molecules in Chemcraft. Try to have the two molecules in a similar orientation as shown in the figure below so that a hydrogen bond is formed.
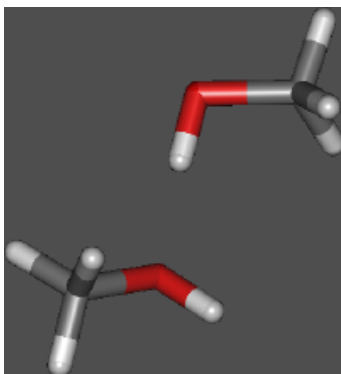
A good general strategy in quantum chemistry calculations is to get a first estimate with a computationally less demanding approximation and then gradually increase the basis set and level of theory. This can be done by sequentially setting up new calculations based on the results of previous, lower level calculations. Create an input file for a geometry optimization (i.e. equilibrium structure search) of the methanol dimer using **HF** and the **3-21G** basis set, and carry out the calculation. Make sure the calculation is converged (i.e. the energy minimum has been located). If the initial guess configuration you created is too far from the energy minimum and the calculation is unable to converge with the given number optimization steps, you can add the following lines to your input file:

```
%geom
maxiter 300
end
```

This increases the allowed number of iterations in the calculation.

When the calculation has finished, use the optimized geometry to start a new **HF** equilibrium structure search using the **6-311G** basis set. Then perform a final optimization with the **MP2** method and the **6-311G** basis set. If the **MP2/6-311G** geometry optimization calculation is started from the initial structure created by hand, the calculation would most probably take significantly longer.

Open the final structure in Chemcraft and delete one of the two molecules (i.e. include only one molecule). Carry out geometry optimization of the single molecule using the same level of theory as the final calculation of the dimer, **MP2/6-311G**. This gives the reference energy for calculating the binding energy of the dimer. Also, set up an equilibrium structure search on the **HF/6-311G** level for comparison.

Create a dimer of methylamine molecules using Chemcraft and perform the same types of calculations as for the methanol dimer above. Remember, to also calculate the **MP2/6-311G** and **HF/6-311G** energy at the equilibrium geometry of the methylamine monomer for comparison.

Q7: *What is the binding energy of the methanol and methylamine dimers at the MP2/6-311G and HF/6-311G level of theory?*

Q8: *How does the binding energy of the dimers correlate with the boiling point of the two fluids (find values on the internet)?*