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## Coupled Cluster Method

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In this exercise, you will use the another post Hartree-Fock method, the so-called Coupled Cluster (CC) method.

### A: Dissociation Curve of H<sub>2</sub>

Calculate the energy curve of H<sub>2</sub> using both the **CCSD** method and the **6-311++G\*\*** Pople basis set. As you did previously, use the 'paras' function of ORCA. Below is an example of an ORCA input file for the parameter-scan utilising CCSD.

```
!UHF 6-311++G** CCSD
```

```
%paras  
R = 0.40,2.00,34  
end
```

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

The values of the energy obtained for the various values of the parameter (here bond length) are listed in a table in the output file. Search for the section **The Calculated Surface using the 'Actual Energy'** and **The Calculated Surface using the SCF energy** close to the end of the output file. The **'Actual Energy'** is the CCSD energy you are interested in. The **SCF Energy** is the single Slater determinant approximation on which the post HF calculation is based.

**Q1:** *Why is it not necessary to go beyond the CCSD expansion?*

**Q2:** *Show the binding curve calculated using CCSD with the QCISD result with the 6-311++G\*\* basis set obtained in Lab. 6 and the result of Kolos and Wolniewicz. How do they compare?*

**Q3:** *Explain the difference between CCSD and QCISD. Which kinds of excitation are included in each expansion in Slater determinant space?*

**Q4:** *Is the obtained trend between QCISD and CCSD unique for the H<sub>2</sub> molecule or universal? If you think it is universal for every system, explain why. If you think it is unique for H<sub>2</sub>, give an example in which you expect a difference and explain why.*

### B: Geometrical Parameters of Methylene CH<sub>2</sub>

Optimize the geometry of methylene using CCSD(T)/6-311++G\*\*. As is the case with QCI, analytical gradients are not available with CC in ORCA. Therefore, numerical gradients have to be used in the optimization.

**Q5:** *How does the geometry and singlet-triplet splitting obtained using CCSD(T) compare with the Hartree-Fock and QCISD(T) results (from a previous assignment) and with the experimental values of the bond angle (134° (triplet) and 102° (singlet)) and a singlet-triplet splitting of 9.05 kcal/mol?*

## D: Ozone O<sub>3</sub>

Ozone plays a key role in atmospheric chemistry as it absorbs dangerous components of ultraviolet light. In the 1970s it was recognized that HCFC can damage the ozone layer. It is therefore of vital importance to be able to study the interaction of ozone with the other components present in the atmosphere. However, while ozone is a seemingly simple system, quantum chemical calculation on it are not straightforward.

**Q6:** Draw the most relevant Lewis structures of ozone.

**Q7:** Define static and dynamic correlation. How is static correlation linked to multireference problems?

Create an ozone molecule with ChemCraft and optimize it with UHF/6-311++G\*\*. Make sure that your initial guess for the geometry is bent ( $\angle(\text{O-O-O}) \approx 110^\circ$ ). Check whether the optimization has converged. If not, you can use the output xyz-file ("orca.xyz") as the input file for another optimization and increase the maximum number of geometrical steps by using the command

```
%geom  
MaxIter 300  
end
```

directly after the simple input line (!) in your input file. Use the output xyz-file as the input xyz-file for a UMP2/6-311++G\*\* optimization. In this way you use the result of the UHF geometry optimization as your initial guess for the UMP2 calculation, which accelerates the latter. After your UMP2 optimization has converged, use its result as your initial guess for a UCCSD(T)/6-311++G\*\* optimization. Note that this calculation may take roughly 20 minutes. The experimental results for the bond distance and the bond angle in ozone are  $r_e = 1.272 \text{ \AA}$  and  $\angle(\text{O-O-O}) = 116.8^\circ$ . The molecule shows C<sub>2v</sub> symmetry.

**Q8:** Make a table comparing geometrical parameters of ozone obtained with HF, MP2 and CCSD(T) and the experimental values.

**Q9:** How well do the calculated parameters with CCSD(T) compare with the experimental values? Is there a systematic difference? If so, explain why.

## Proposition for C in the future

Calculation of hydrogen bonded HF or LiH oligomers. The structures up to decamers are optimized with UHF, MP2, QCISD(T) and CCSD(T). The binding energies are calculated for each oligomer and plotted against the number of monomers. The aim of this exercise is to show the size-inconsistency of the quadratic expansion in Slater determinant space used in QCI, if more than two monomers are present in the system. Test calculations have shown that the QCISD(T) and CCSD(T) calculations take too long on a single core on Jötunn at the moment for oligomers containing more than three monomers.